Supplementary Material for

Effect of acetylation on wood-water interactions studied by sorption calorimetry

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This document details previous experimental data on the thermodynamics of water in modified wood as well as additional information about the experiments conducted for this study.

Fig. S1 shows the differential enthalpy of mixing of various types of wood modifications derived from sorption isotherm data or solution calorimetry and compared with relevant sorption calorimetric data where available.

Fig. S2 illustrates the entropy of mixing of various types of wood modifications derived from sorption isotherm data.

Fig. S3 depicts the correlation between the equilibrium moisture content obtained with an automated sorption balance and the moisture content in the sorption calorimetric measurements in this study. The parameters describing the linear correlations for the various wood materials are shown in Table S1.

Fig. S4 presents the differential enthalpy of mixing as function of relative humidity (a-e) and moisture content (f-j) from the sorption calorimetric measurements. Fig. S3f-j are similar to Fig. 1f-j.

Fig. S5 shows the gravimetrically determined absorption isotherms at two temperatures for derivation of the differential enthalpy of mixing from the Clausius-Clapeyron equation.

Fig. S6 illustrates moisture content at 90% RH and the hydroxyl accessibility in early- and latewood of Norway spruce, all quantities are shown relative to the values obtained for untreated wood. These data are also shown in Tables S2 and S3.

Fig. S7 depicts the entropy of mixing derived from sorption calorimetric data and the ABC fits of Fig. S5 for determining the equilibrium RH value at specific moisture contents.

Fig. S8-S10 present the rate of sorption in the automated sorption balance measurements that produced the absorption isotherms of Fig. S4.

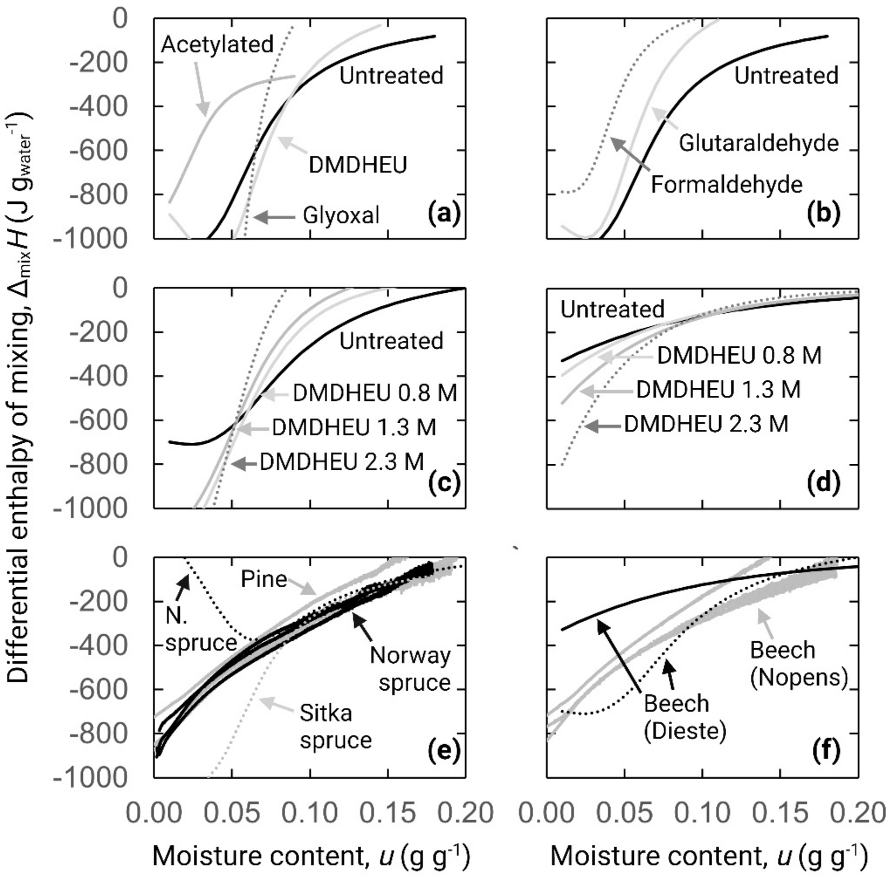

Fig. S1 Literature data on differential enthalpy of mixing for modified wood: (a)-(b) Sitka spruce with various chemical modifications (Yasuda et al. 1995) and differential enthalpy of mixing derived from the Clausius-Clapeyron (C-C) equation, (c)-(d) European beech modified by DMDHEU (Dieste et al. 2008) to various extents and differential enthalpy of mixing derived (c) by the C-C equation or (d) from solution calorimetric measurements. (e) differential enthalpy of mixing of untreated Norway spruce from this study, either measured by sorption calorimetry (black solid line) or derived by the C-C equation (black dotted line), untreated pine measured by sorption calorimetry (Nopens et al. 2019) (grey solid line), and for the untreated Sitka spruce data of (a)-(b). (f) differential enthalpy of mixing of beech measured by sorption calorimetry (Nopens et al. 2019) or derived from solution calorimetric data (solid black line) in (d) or from the C-C equation (black dotted line) in (c). Moisture contents for modified wood materials have been corrected for mass gain from modification (R_{mod})

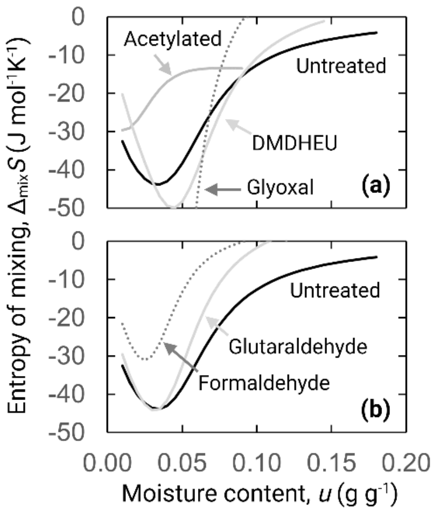

Fig. S2 Entropy of mixing (J mol^{-1} K^{-1}) for the modified Sitka spruce of Fig. S1. The quantity was derived by first calculating the Gibbs energy of mixing at the given moisture content ($RT \ln \varphi$), and then determining the entropy change associated with water sorption by traditional thermodynamic analysis

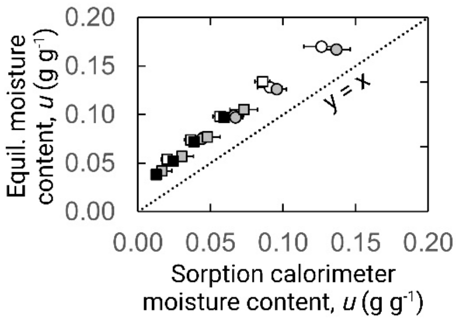

Fig. S3 Equilibrium moisture content determined with an automated sorption balance (Digaitis et al. 2021) plotted against the moisture content during the sorption calorimetric measurements for untreated (white circles), pyridine treated (grey circles), and acetylated wood with a mass gain, R_{mod} of 12.8 g g^{-1} (white squares), 14.2 g g^{-1} (grey squares), and 20.9 g g^{-1} (black squares). Only data <90% RH included. Moisture contents for acetylated wood have been corrected for mass gain from modification (R_{mod})

Table S1 Linear correlation between moisture content in sorption calorimetry measurements and equilibrium moisture content determined gravimetrically in an automated sorption balance. Correlations determined for data shown in Fig. S2

Wood material	**Offset**	**Inclination**	**R^2**
Untreated	0.023	1.157	0.9996
Pyridine treated (R_{mod} = -0.02 g g^{-1})	0.031	0.996	0.9999
Acetylated (R_{mod} = 0.13 g g^{-1})	0.030	1.214	0.9999
Acetylated (R_{mod} = 0.14 g g^{-1})	0.023	1.121	1.0000
Acetylated (R_{mod} = 0.21 g g^{-1})	0.022	1.267	0.9991

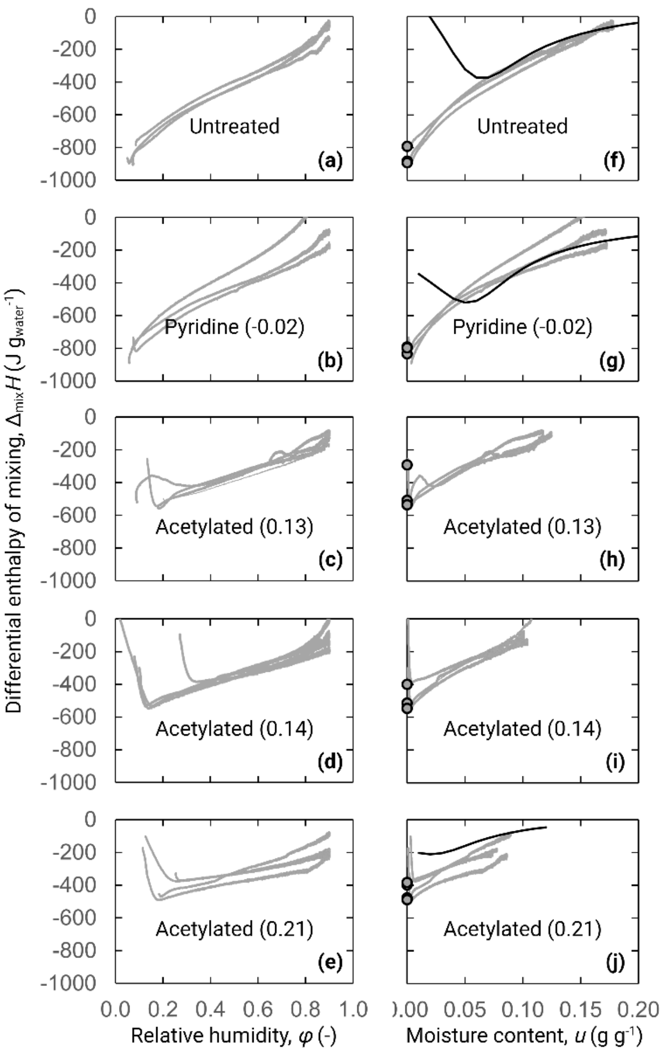

Fig. S4 Differential enthalpy of mixing, $\Delta_{mix}H$, as function of relative humidity (a-e) and moisture content (f-j) for the five different wood materials (grey lines). Numbers in parentheses mark the mass gain from modification, R_{mod} (g g^{-1}). Data have been cut off above 90% RH. Filled circles illustrate the extrapolated $\Delta_{mix}H$ in the dry state, i.e. at 0 g g^{-1} moisture content. The black lines describe the differential enthalpy of mixing derived from the Clausius-Clapeyron equation for gravimetric absorption data for the same materials at 20 °C and 40 °C using an automated sorption balance. Moisture contents for acetylated wood have been corrected for mass gain from modification (R_{mod})

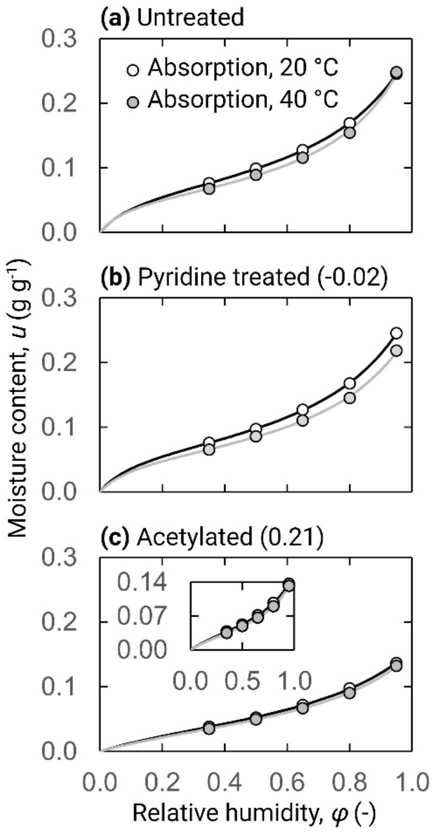

Fig. S5 Absorption isotherms determined with an automated sorption balance at 20 °C (white circles) and 40 °C (grey circles) for untreated, pyridine treated, and acetylated wood with R_{mod} = 0.21 g g^{-1}. Also shown are the fits to absorption data of the ABC isotherm at 20 °C (black lines) and 40 °C (grey lines). Moisture contents for acetylated wood have been corrected for mass gain from modification (R_{mod})

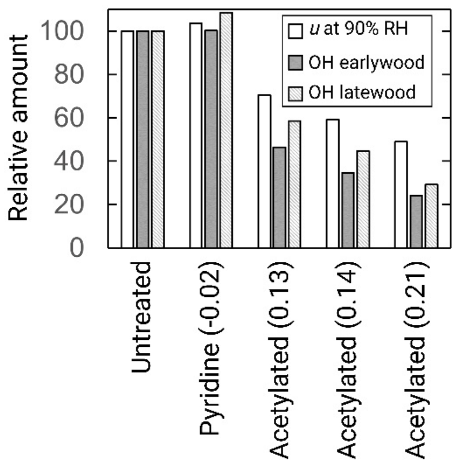

Fig. S6 Amount of water and water-accessible hydroxyls in the various wood materials relative to untreated wood. The relative amount of water is determined from the moisture content (u) at 90% RH in the sorption calorimetric measurements, whereas the relative amount of hydroxyls is determined from the gravimetrically measured hydroxyl accessibilities in isolated earlywood and latewood by Digaitis et al. (2021)

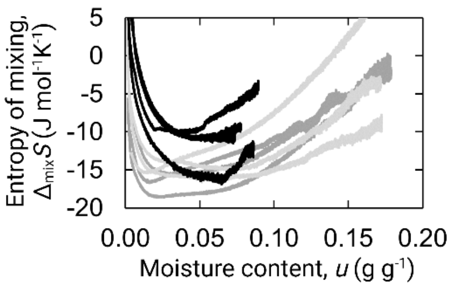

Fig. S7 Entropy of mixing derived from sorption calorimetry data obtained in this study on acetylated wood with R_{mod} = 0.21 g g^{-1} (black), pyridine controls (light grey), and untreated controls (dark grey). The entropy was derived by first determining the Gibbs energy of mixing ($RT \ln \varphi$) at a specific moisture content based on the RH value in equilibrium with this as determined from the ABC fit of Fig. S5. The entropy of mixing is then calculated as the difference between the enthalpy measured with sorption calorimetry and the calculated Gibbs energy divided by the absolute temperature.

Table S2 Hydroxyl accessibility in earlywood and latewood of the five different wood materials as determined by Digaitis et al. (2021) and moisture contents at 90% RH determined by the sorption calorimetric measurements. Both physical quantities are given in mmol per gram wood, corrected for R_{mod}, and % relative to the amount present in untreated wood.

Wood material	**Hydroxyl accessibility**				**Moisture content at 90% RH**	
	Earlywood		Latewood			
	(mmol/g)	(%)	(mmol/g)	(%)	(mmol/g)	(%)
Untreated	8.65 (0.42)	100.0	9.47 (0.09)	100.0	9.27 (0.92)	100.0
Pyridine treated (R_{mod} = -0.02 g g^{-1})	8.67 (0.46)	100.2	10.28 (1.09)	108.6	9.60 (0.07)	103.5
Acetylated (R_{mod} = 0.13 g g^{-1})	4.01 (0.24)	46.4	5.54 (0.63)	58.5	6.53 (0.31)	70.4
Acetylated (R_{mod} = 0.14 g g^{-1})	2.99 (0.25)	34.6	4.23 (0.73)	44.7	5.49 (0.54)	59.2
Acetylated (R_{mod} = 0.21 g g^{-1})	2.08 (0.34)	24.0	2.77 (0.41)	29.3	4.55 (0.35)	49.0

Table S3 Reduction in hydroxyl (OH) accessibility in earlywood and latewood of the five different wood materials as well as reduction in moisture content at 90% RH compared with the untreated wood. Based on the data of Table S2.

Wood material	**Reductions compared with untreated wood**		
	OH earlywood (mmol/g)	OH latewood (mmol/g)	Moisture (mmol/g)
Untreated	0.00	0.00	0.00
Pyridine treated (R_{mod} = -0.02 g g^{-1})	-0.02	-0.81	-0.33
Acetylated (R_{mod} = 0.13 g g^{-1})	4.64	3.93	2.75
Acetylated (R_{mod} = 0.14 g g^{-1})	5.66	5.24	3.78
Acetylated (R_{mod} = 0.21 g g^{-1})	6.57	6.70	4.73

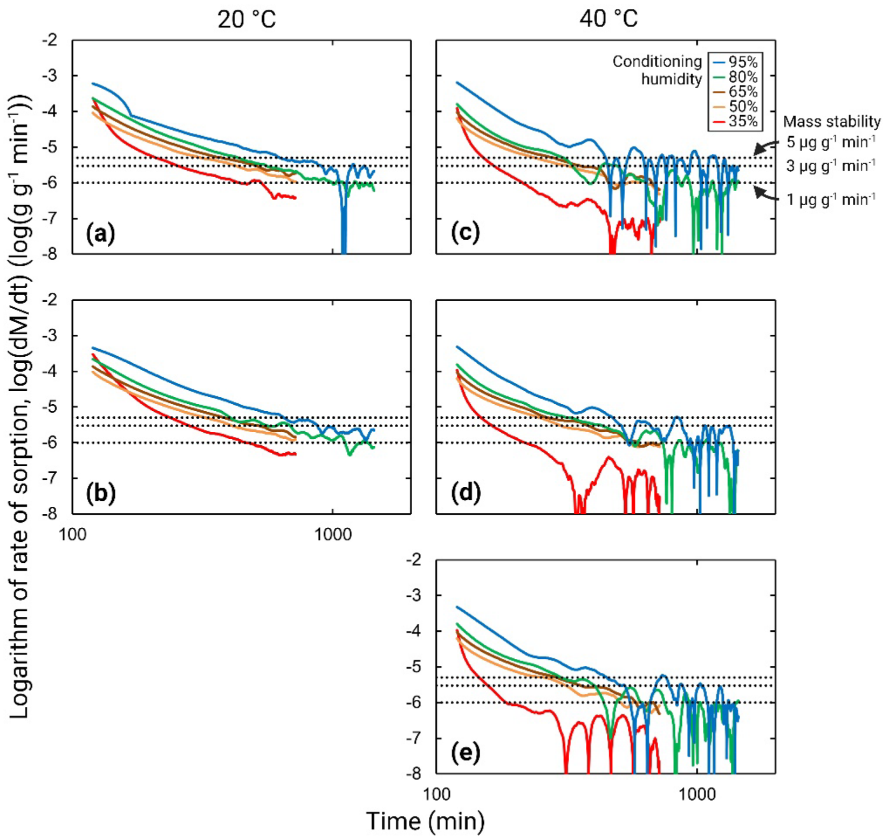

Fig. S8 Rate of sorption calculated over a 2-hour time window observed during experiments carried out on untreated wood. Each row corresponds to one replicate measured during absorption from initial dry state at 20 °C (left) or 40 °C (right). The dotted lines illustrate three levels of mass stability discussed in the manuscript

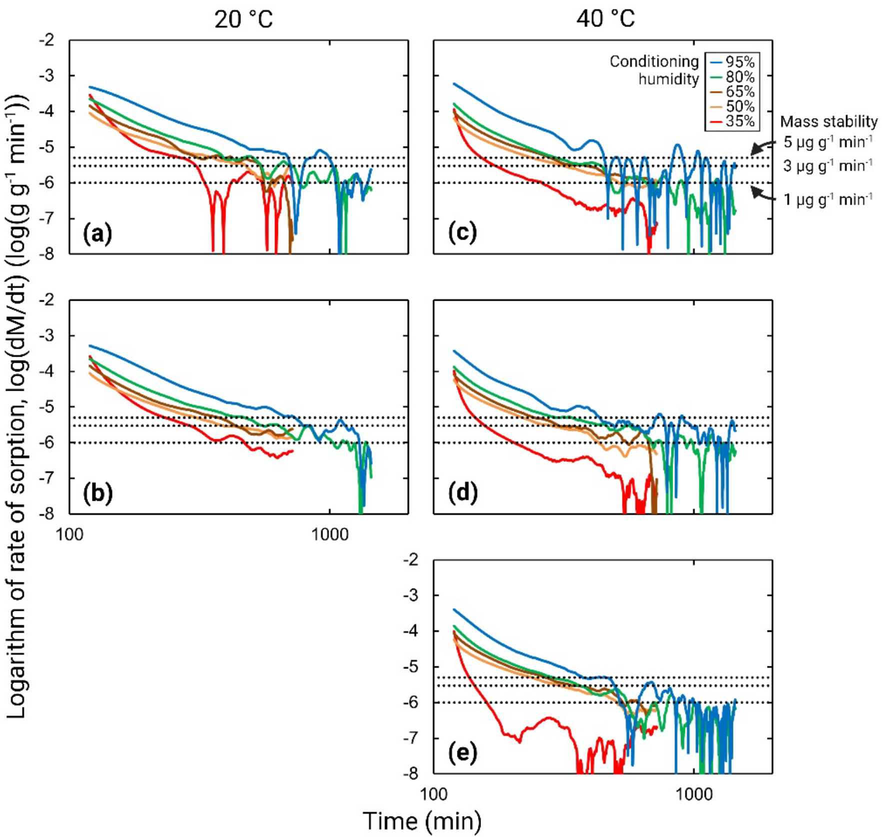

Fig. S9 Rate of sorption calculated over a 2-hour time window observed during experiments carried out on pyridine treated wood. Each row corresponds to one replicate measured during absorption from initial dry state at 20 °C (left) or 40 °C (right). The dotted lines illustrate three levels of mass stability discussed in the manuscript

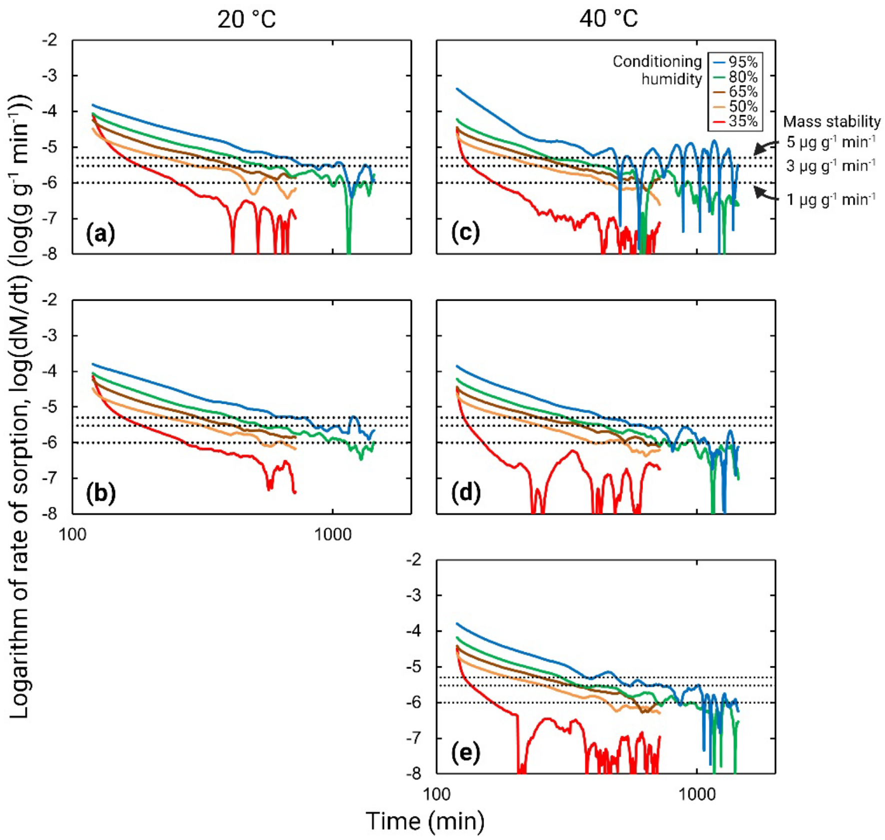

Fig. S10 Rate of sorption calculated over a 2-hour time window observed during experiments carried out on acetylated wood with R_{mod} = 0.21 g g^{-1}. Each row corresponds to one replicate measured during absorption from initial dry state at 20 °C (left) or 40 °C (right). The dotted lines illustrate three levels of mass stability discussed in the manuscript

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