

SORPTION PROPERTIES OF MATURE AND JUVENILE LIME WOOD (*TILIA* SP.)

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SYNOPSIS. The sorption isotherms of mature and juvenile lime wood were determined for the successive phases of the process. The Hailwood-Horrobin model was used to examine and explain changes in the equilibrium moisture content. The reduction of the dissolved water content was found. The accessibility of water vapour to the sorption sites as well as the hydrated water content was practically the same for mature and juvenile wood. The Fiber Saturation Point was determined with the method of the extrapolation of sorption isotherms. The diversified values of the Fiber Saturation Point were found for juvenile wood as compared to mature wood. The influence of sorption phases on values of the Fiber Saturation Point was determined. The hysteresis of the sorption was quantified.

KEY WORDS: equilibrium moisture content, sorption isotherm, Hailwood-Horrobin model

INTRODUCTION

Wood products are usually manufactured from timber which was dried to the target moisture content. The products in their normal use are exposed to the environment of moist air, which is characterized by the natural variation of its parameters. The changes of the air relative humidity and temperature are responsible for gaining and losing water by wood. In turn of that changes of water content in wood induce dimensional variation of the products as well as stress development. These factors are responsible for possible damage of the products. The problem is specially significant when wooden cultural objects are exposed to the variation of the air parameters.

The problem of wooden cultural objects deterioration is specially important when heating systems of the indoor environment are installed in churches or other buildings in which wooden historical objects are exposed. The importance of the proper use of the interior heating became aware as early as in the 18th and 19th century. DOBROWOLSKA and BEHAL (2006) reported recommendations of the proper microclimate in houses and churches, while OSIPIUK and BEHAL (2007)

discussed the influence of too low air relative humidity on undesirable decrease of moisture content of objects made of hygroscopic materials. Also the modern heating systems may cause new threats. SAMEK et AL. (2007) pointed out the importance of the proper selection and design of electric overhead heating systems in historic churches in the context of possible damage of paintings or sculptures.

The effects of the air parameters variation on moisture content changes in wooden historical objects were already studied with the methods of water transport modelling in hygroscopic and porous materials. JAKIEŁA et AL. (2008) predicted moisture content changes in a lime wood cylinder modelling a sculpture for a step variation of air relative humidity. PERRÉ et AL. (2006) modelled water transfer in the poplar panel base of the Mona Lisa for the typical conditions of the museum display of the painting. They used the TransPore code based on the concept of a hybrid scheme of the control volumes and finite elements (PERRÉ and TURNER 1999). All studies concerning the moisture content prediction required credible data on the relation between equilibrium moisture content of wood and air relative humidity. The equilibrium moisture content values are usually introduced in modelling through the convective boundary condition. Unfortunately, the predictions are often made with the use of the equilibrium moisture content data representing “average” values for a group of wood species as well as for adsorption and desorption processes, e.g. data obtained in the Forest Products Laboratory (Wood handbook... 1999) and generalized by SIMPSON (1973).

Wooden historical objects such as wooden altars, sculpted statues of saints, putti etc. were usually made of lime wood. Some of the objects had relatively high dimensions and therefore, might include both mature and juvenile wood. Therefore, the objective of the present study was to determine sorption isotherms for the both zones of the transverse cross-section of lime wood. Additionally, the influence of the sorption hysteresis was studied.

MATERIAL AND METHODS

The sorption isotherms were determined for lime wood (*Tilia* sp.). The material was obtained from an 80-year old tree freshly cut in November 2007. The test tree was selected from a fresh mixed coniferous forest located in the Forest District Babki (West Poland). Wooden discs were cut from the tree at the height of ca. 1.5 m from the root collar. The discs were used to obtain strips containing mature or juvenile wood only (Fig. 1). Immediately after the strips were obtained the rectangular prisms were cut from the central part of each strip. The prisms were used for cutting samples of the following dimensions $1.5 \times 35 \times 45$ mm. The dimensions corresponded to tangential, radial and longitudinal directions, respectively. The two groups of samples were obtained, i.e. containing mature or juvenile wood. The dimensions of the samples were selected in order to ensure obtaining the equilibrium with moist air within 48 hours. The maximum value of the relative error of moisture content determination was the additional criterion of the dimen-

sion selection of the samples. The minimum mass of a sample was determined using the approach proposed by JAROS et AL. (1994).

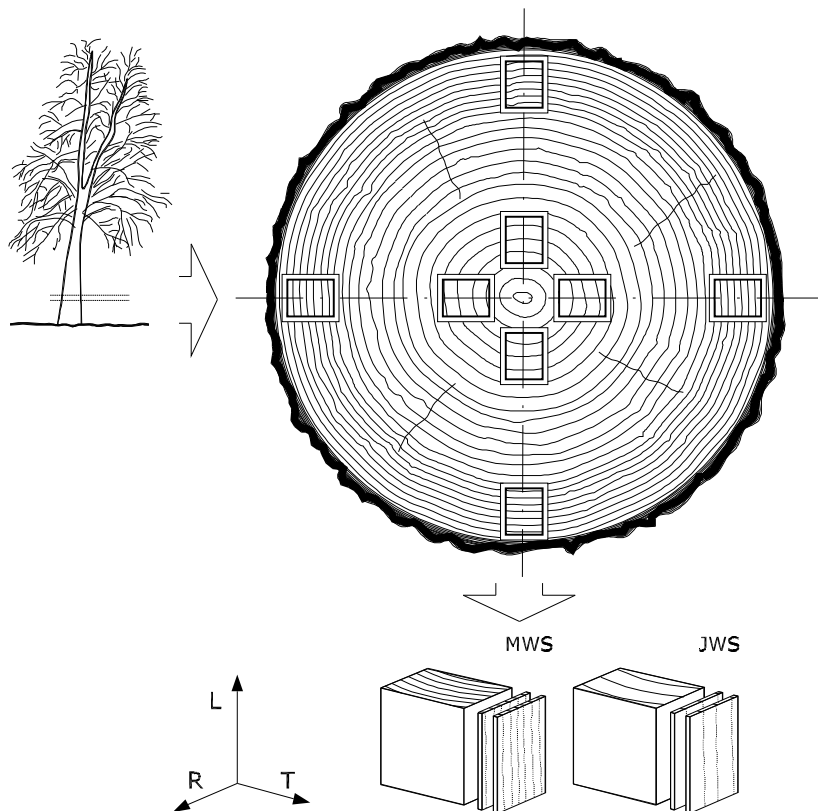


Fig. 1. Scheme of obtaining lime wood samples for sorption experiments: MWS – mature wood samples, JWS – juvenile wood samples

The sorption experiments were performed in the set-up already used in our previous study (MAJKA and OLEK 2007). The samples containing mature or juvenile wood were placed in the inner chamber of the set-up. Air circulation in the inner chamber was forced by the fan, while the relative humidity was controlled by salt solutions, which were successively changed in order to obtain different levels of air relative humidity. In the present study the actual values of air temperature and relative humidity were measured with a thermohygrometer type LB 706 made by LAB-EL. The measured values of the air parameters were stored in the data acquisition system.

Air temperature in the inner chamber of the experimental set-up was equal to $25 \pm 1^\circ\text{C}$. The use of salt solutions, phosphorus pentoxide and distilled water let to obtain nine levels of the relative humidity inside the inner chamber of the set-up. The approximated mean values of the relative humidity obtained for the first desorption, first adsorption and second desorption are listed in Table 1. The

samples were weighed at least twice at each humidity level. After finishing the sorption experiments the samples were placed in a laboratory drier and their oven-dry mass was determined. Each group of samples, i.e. obtained from mature or juvenile wood, consisted of 16 pieces. Therefore, each value of equilibrium moisture content was the average of 16 measurements. The detailed procedure of the sorption experiments was described in MAJKA and OLEK (2007).

Table 1. Salt solutions applied in sorption experiments and approximated relative humidity values at temperature of $25 \pm 1^\circ\text{C}$

Salt solution	Relative humidity [%]		
	1st desorption	1st adsorption	2nd desorption
Water (H ₂ O)	92.2	95.0	95.0
Potassium chloride (KCl)	85.1	83.0	85.7
Sodium chloride (NaCl)	76.5	75.3	76.7
Sodium bromide (NaBr)	59.2	62.2	60.3
Potassium carbonate (K ₂ CO ₃)	46.2	44.3	46.4
Calcium chloride (CaCl ₂ · 6H ₂ O)	35.2	32.6	32.7
Potassium acetate (CH ₃ COOK)	24.3	23.2	26.5
Lithium chloride (LiCl)	13.9	13.4	13.7
Phosphorus pentoxide (P ₂ O ₅)	1.4	1.4	2.6

RESULTS OF SORPTION ISOTHERMS DETERMINATION

The obtained experimental data of equilibrium moisture content for mature and juvenile wood as well as for the successive sorption phases were statistically processed. The detailed information on averaged values of equilibrium moisture content and results of the statistical analysis are presented in the Appendix.

The obtained results of the sorption isotherms determination were generalized with the Hailwood-Horrobin model (SKAAR 1988). The one hydrate form of the model was selected as it was in our previous study (MAJKA and OLEK 2007):

$$M = M_h + M_d = \frac{m_{\text{water}}}{m_{\text{wood}}} \cdot \frac{100K_1K_2H}{100 + K_1K_2H} + \frac{m_{\text{water}}}{m_{\text{wood}}} \cdot \frac{100K_2H}{100 - K_2H}$$

- where: M – equilibrium moisture content of wood [%],
 M_h – monolayer (hydrated) water content [%],
 M_d – polymolecularly sorbed (dissolved) water content [%],
 m_{water} – molecular mass of water (here 18 kg/kmol) [kg/kmol],
 m_{wood} – molecular mass of the dry wood in kg per kmol of sorption sites (i.e. molecular mass of a polymer unit which forms a hydrate) [kg/kmol],
 H – air relative humidity [%],
 K_1 – equilibrium constant between dissolved water and hydrates,
 K_2 – equilibrium constant between dissolved water and water vapor in moist air.

The Hailwood-Horrobin model was separately fitted to each of the six sets of results as obtained for the combination of wood zones in the transverse cross-section (i.e. juvenile and mature wood) and sorption phases (i.e. the first desorption, first adsorption and second desorption). The obtained values of K_1 , K_2 and m_{wood} are presented in Table 2. The results were supplemented by values of the coefficient of determination (R^2). The obtained high values of R^2 showed that the Hailwood-Horrobin model adequately described the desorption and adsorption for juvenile and mature lime wood.

The applied Hailwood-Horrobin model also enabled to determine the fraction of wood which was inaccessible for water. The fraction was calculated as $(m_{\text{wood}} - m_{\text{AGU}})/m_{\text{wood}}$, where m_{wood} was the polymer unit which contains one characteristic sorption site and m_{AGU} was molecular mass of the anhydrous glucose unit (AGU) and equal to 162 kg/kmol (HARTLEY and SCHNEIDER 1993). The obtained values of the fraction are also presented in Table 2. There was no observed significant difference in the fraction for juvenile and mature wood. However, the parameter was significantly differing for successive sorption phases. The fraction increased for adsorption indicating the reduction the accessibility of water vapour to the sorption sites in wood. The more profound changes were observed for the second desorption where the fraction was decreasing to 0.376 and 0.343 for juvenile and mature wood, respectively. It showed that the water accessibility was much higher for desorption as compared to adsorption.

Table 2. Estimated coefficients of the Hailwood-Horrobin model for different sorption phases and lime wood zones in the transverse cross-section and fraction of wood inaccessible for water

Wood zone in the transverse cross-section	Sorption phase	Coefficients of the Hailwood-Horrobin model and calculated fraction of wood inaccessible for water				
		K_1	K_2	m_{wood}	R^2	$\frac{(m_{\text{wood}} - m_{\text{AGU}})}{m_{\text{wood}}}$
Juvenile wood	1st desorption	8.861	0.908	328.17	0.999	0.506
	adsorption	9.230	0.878	385.73	0.999	0.580
	2nd desorption	4.612	0.802	259.45	0.999	0.376
Mature wood	1st desorption	7.142	0.882	314.31	0.999	0.485
	adsorption	8.166	0.860	380.02	0.999	0.574
	2nd desorption	3.767	0.772	246.69	0.999	0.343

Figure 2 presents the equilibrium moisture content (M) as obtained in the successive phases of the sorption experiments as well as the values obtained from the fitted Hailwood-Horrobin model for the juvenile and mature wood, respectively. The direct comparison of the desorption and adsorption isotherms confirmed the earlier observation on the water accessibility obtained after calculating the fraction $(m_{\text{wood}} - m_{\text{AGU}})/m_{\text{wood}}$.

The Hailwood-Horrobin model assumes that the total absorbed water at a given level of air relative humidity is the sum of hydrated water and dissolved water. In the case of wood the two water subsystems may be associated with the monolayer and polymolecularly sorbed water, respectively (SIMPSON 1980). The contents of the two subsystems were determined for juvenile and mature wood as well

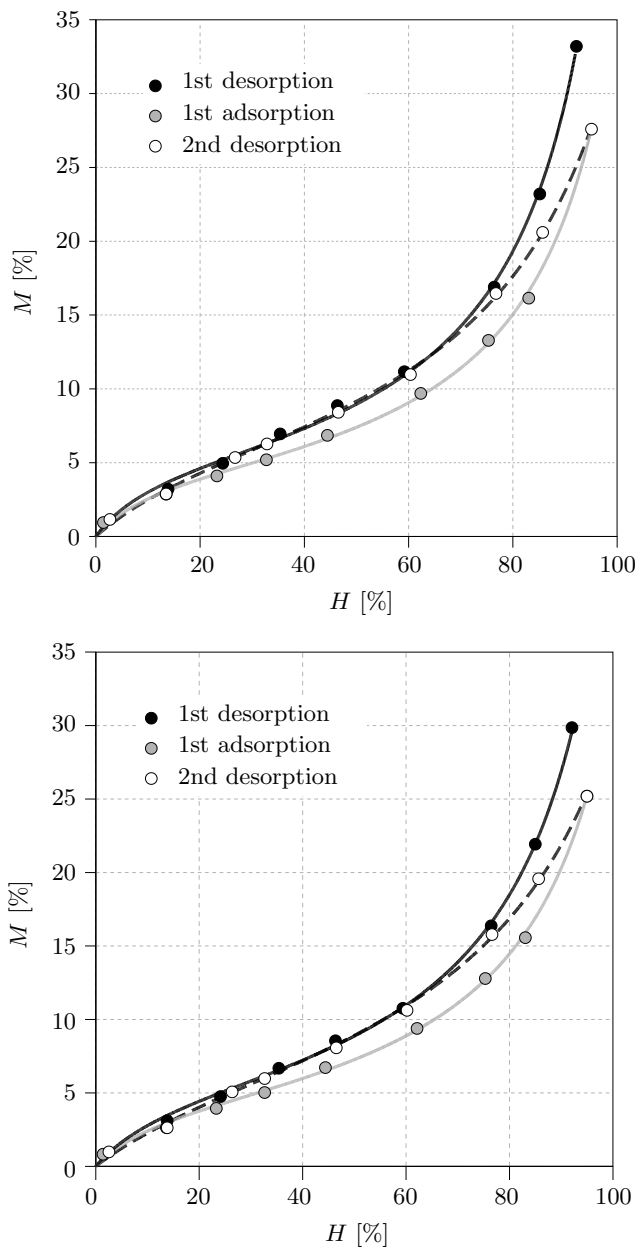


Fig. 2. Sorption isotherms for the successive phases of the process as obtained for (a) juvenile and (b) mature lime wood (the Hailwood-Horrobin model – 1st desorption solid black curve, 1st adsorption solid dark gray curve, 2nd desorption dashed black curve, experimental data – 1st desorption black dots, 1st adsorption dark gray dots, 2nd desorption white dots)

as for all sorption phases. An example of the sorption isotherm separation into the contents of the monolayer and polymolecularly sorbed water was presented in Figure 3. The maximum values of the obtained contents are shown in Table 3. The maximum values of the monolayer water contents were practically the same for juvenile and mature wood. However, the differences were found for the different sorption phases, i.e. significantly smaller values of M_h were found for adsorption as compared to the first and second desorption. The maximum values of the poly-

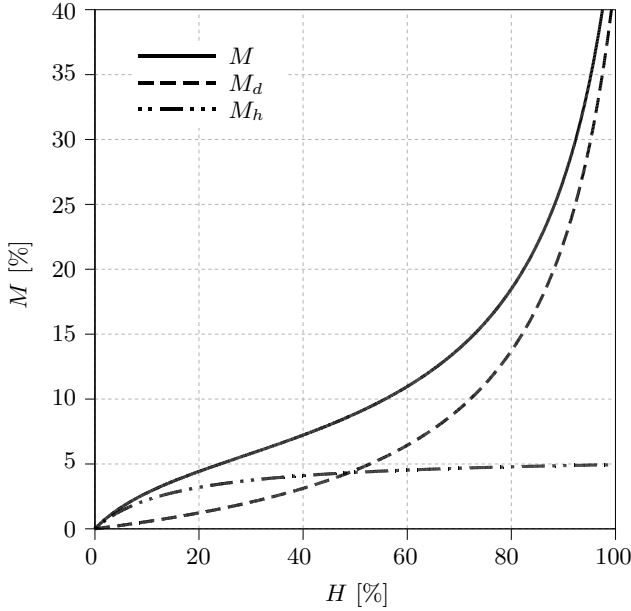


Fig. 3. Equilibrium moisture content (M), monolayer (hydrated) water content (M_h) and polymolecularly sorbed (dissolved) water content (M_d) as functions of air relative humidity for mature lime wood and the first desorption

Table 3. The estimated maximum values of contents of monolayer (hydrated) water (M_h), polymolecularly sorbed (dissolved) water (M_d) and interpolated Fibre Saturation Point (FSP)

Wood zone in the transverse cross-section	Sorption phase	M_h [%]	M_d [%]	FSP [%]
Juvenile wood	1st desorption	4.88	54.19	59.07
	adsorption	4.15	33.44	37.59
	2nd desorption	5.46	28.19	33.65
Mature wood	1st desorption	4.94	42.62	47.56
	adsorption	4.15	29.02	33.16
	2nd desorption	5.43	24.65	30.08

molecularly sorbed water content were smaller for the mature wood of ca. 4% as compared to the juvenile wood during the adsorption and second desorption. Much higher difference in the polymolecularly sorbed water content was found for the first desorption. The clear tendency of the reduction of the polymolecularly sorbed water content with the successive sorption phases was found for both wood zones in the transverse cross-section.

Table 3 also contains values of the Fiber Saturation Point obtained by the extrapolation of sorption isotherms to air relative humidity of 100%. BABIAK and KÚDELA (1995) pointed out that the method may lead to the results of the Fiber Saturation Point determination which are strongly affected by the sorption model. They suggested to use the method primary for the adsorption process. The results obtained in the present study supported the suggestion as the results found for the first desorption were rather unrealistic. However, the application of the method of the Fiber Saturation Point determination clearly showed higher values for the juvenile wood as compared to mature wood. Moreover, the strong tendency for the Fiber Saturation Point reduction was found for the successive sorption phases in both zones of the investigated lime wood.

The obtained results of the equilibrium moisture content let to determine the hysteresis of sorption. In order to quantify the hysteresis the following ratio was defined M_{1stAds}/M_{2ndDes} where M_{1stAds} – equilibrium moisture content during the first adsorption, M_{2ndDes} – equilibrium moisture content during the second desorption. The sorption hysteresis ratio was determined for the typical values of the relative humidity of air being in contact with wood products. The results of the ratio obtained for the juvenile and mature wood are presented in Table 4. The obtained values of the ratio showed that the hysteresis was distinct in the investigated range. The majority of sorption models do not take into account the hysteresis. It also concerns the two hydrate form of the Hailwood-Horrobin model as applied for wood by SIMPSON (1973, 1998). In the case of bound water transfer modelling in wood, which is subjected to varying relative humidity of air, the neglecting the sorption hysteresis must influence the convective boundary condition and lead to false results of the modelling.

Table 4. The sorption hysteresis ratio for juvenile and mature lime wood

Wood zone in the transverse cross-section	Relative humidity [%]	Sorption hysteresis ratio [-]
Juvenile wood	70	0.820
	50	0.804
	30	0.847
Mature wood	70	0.822
	50	0.820
	30	0.875

CONCLUSIONS

1. The significantly higher equilibrium moisture content values were observed for juvenile lime wood as compared to mature wood.
2. The accessibility of water into wood tissue was much higher for the desorption phases as compared to adsorption.
3. The lower values of the equilibrium moisture content in mature wood may be related to the lower polymolecularly sorbed water content as the content of the monolayer water was practically the same.
4. The Fiber Saturation Point was higher for juvenile wood as compared mature one. Moreover, the Fiber Saturation Point was decreasing for the successive sorption phases.
5. The distinct sorption hysteresis was found for both zones of lime wood, which has to be taken into account for accurate modelling of water transfer.

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Appendix. Raw data for the Hailwood-Horrobin model estimation

In order to make an individual comparison of the sorption data for mature and juvenile wood as well as for the successive sorption phases the coefficient of variation was determined and the t-test was performed. The statistical analysis was made for a 95% significance level.

Table. Averaged values of equilibrium moisture content (M) as obtained at temperature of $25 \pm 1^\circ\text{C}$ for juvenile (JW) and mature (MW) lime wood and successive sorption phases

Sorption phase								
1st desorption			adsorption			2nd desorption		
H [%]	M [%]		H [%]	M [%]		H [%]	M [%]	
	MW	JW		MW	JW		MW	JW
92.2	29.83* (2.9)	33.20* (2.0)	95.0	25.26* (4.9)	27.59* (3.8)	95.0	25.26* (4.9)	27.59* (3.8)
85.1	21.94* (1.7)	22.75* (1.4)	83.0	15.61* (1.5)	16.16* (1.0)	85.7	19.64* (1.5)	20.60* (1.1)
76.5	16.38* (1.9)	16.85* (1.2)	75.3	12.80* (0.9)	13.31* (1.4)	76.7	15.84* (1.0)	16.53* (0.9)
59.2	10.81* (1.3)	11.14* (0.8)	62.2	9.38* (1.3)	9.61* (0.9)	60.3	10.68* (1.0)	11.00* (1.0)
46.2	8.62* (1.0)	8.82* (1.1)	44.3	6.69* (1.1)	6.87* (1.4)	46.4	8.12* (1.2)	8.41* (0.9)
35.2	6.68* (1.8)	6.93* (1.5)	32.6	5.06* (1.8)	5.16* (1.8)	32.7	6.02* (0.7)	6.27* (1.7)
24.3	4.85* (1.7)	4.95* (1.8)	23.2	4.00* (2.5)	4.10* (2.0)	26.5	5.10* (1.3)	5.32* (1.8)
13.9	3.17* (2.6)	3.26* (2.4)	13.4	2.79 n.s. (3.2)	2.87 n.s. (3.6)	13.7	2.99* (1.6)	3.16* (2.3)
1.4	0.91 n.s. (6.8)	0.97 n.s. (11.9)	1.4	0.91 n.s. (6.8)	0.97 n.s. (11.9)	2.6	1.04* (6.0)	1.19* (3.5)

The coefficient of variation (COV) is defined as $100 \cdot \text{SD} / M$ where: M – average equilibrium moisture content, SD – standard deviation. The COV values are expressed in % and given in parentheses below the averaged values of equilibrium moisture content. The significant values of M are indicated by *while not significant by n.s. Level of significance $\alpha = 0.05$.

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