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INTERRELATION BETWEEN STEAM SORPTION BY WOOD AND TEMPERATURE

The applicability of two water sorption models (GDW and GAB) to description of selected multi-temperature data of water sorption on wood is presented. From the obtained best fit parameters the plots of isosteric sorption enthalpy are generated. According to our knowledge this is the first report showing the enthalpy of water sorption on wood. The obtained results lead to a general mechanism of water sorption on studied materials. Finally, we show that Hailwood and Horrobin equation, which is widely applied in wood science, is a special case of the GDW model.

Keywords: water sorption, GAB model, GDW model, Hailwood and Horrobin equation, enthalpy of sorption.

Introduction and aim of the study

Water sorption by wood is the subject of interest to many researchers [Ball et al. 2001; Chauhan et al. 2001; Fan et al. 1999; Jannot et al. 2006; Militz et al. 2003; Nakano 2006; Pakowski et al. 2007; Papadopoulos, Hill 2003; Papadopoulos 2005; Papadopoulos, Avramidis 2005; Popper et al. 2005]. This is so because of the influence of moisture content on different properties of wood. As it was mentioned by Fan and co-workers [1999], understanding the relationship between relative humidity, temperature and equilibrium moisture of wood is important to most phases of wood processing and to its end use in order to optimize processing and minimize the problems associated with shrinking and swelling of wood, respectively.

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The aim of this study is to attempt a theoretical description of multi-temperature (i.e. determined for different temperatures) water sorption data measured on different types of wood. This attempt will be limited to two models with strong theoretical basis. First of them is called Generalised D'Arcy and Watt (GDW). It has been proposed recently for description of water sorption on carbonaceous adsorbents [Furmaniak et al. 2005, 2008]; however, it was also found applicable to description of water sorption data measured (also for different temperatures) on different foodstuffs [Furmaniak et al. 2007a, 2007b, 2007c]. The second considered model is called GAB. It was successfully applied to description of data on water sorption on wood (for example [Jannot et al. 2006]); however, it is better known in the field of food engineering science [Furmaniak et al. 2007b, 2007c]. Moreover, as it was shown previously the GAB model is a simplified version of the GDW.

The values of the best fit parameters obtained from the fitting of experimental data of water sorption on wood can be applied to calculation of the isosteric enthalpy of sorption, which gives the insight into the energetics of sorption and, what is more important, into the mechanism of this process.

Applied theoretical models

As mentioned above two models will be applied to description of water sorption data on wood. The GDW can be written in the following form [Furmaniak et al. 2007a, 2007b, 2007c]:

$$M = \frac{mKh_r}{1 + Kh_r} \cdot \frac{1 - k(1 - w)h_r}{1 - kh_r}, \quad (1)$$

where: M [%] – is moisture content in wood, h_r – is relative humidity, m [%] – is the maximum sorption value on the primary sorption centres. K and k are kinetic constants related to sorption on primary and secondary centres, and w is the parameter determining what part of water molecules sorbed on primary sorption sites convert into the secondary sorption sites.

The GAB is usually presented as [Furmaniak et al. 2007b, 2007c]:

$$M = \frac{mCKh_r}{(1 - Kh_r)(1 - Kh_r + CKh_r)}, \quad (2)$$

where: m [%] is monolayer capacity, C is the kinetic constant related to the sorption in the first layer, K is the kinetic constant related to multilayer sorption.

To perform a simultaneous description of multi-temperature sorption data it is necessary to apply the relations which take into account temperature dependence of the parameters of the both models. Therefore, for both models applied

in this study we assumed (as previously) that m and w are temperature independent ($m, w \neq f(T)$) [Furmaniak et al. 2007a, 2007b, 2007c]. Contrary, the remaining kinetic/equilibrium constants (K and k (GDW model); C and K (GAB model)) depend on temperature according to the general relation [Furmaniak et al. 2007a, b, c]:

$$X = X_0 \exp\left(\frac{q_X}{RT}\right), \quad (3)$$

where: X is the considered constant, X_0 is the almost temperature independent entropic term, q_X [kJ mol^{-1}] is the enthalpy related to this parameter, T [K] is temperature, and R is the gas constant. For the constants occurring in eqs. (1) and (2) the following notation is applied in eq. (3) for the GDW model:

$$K = K_0 \exp\left(\frac{Q}{RT}\right), \quad (4)$$

$$k = k_0 \exp\left(\frac{q}{RT}\right) \quad (5)$$

and for the GAB:

$$C = C_0 \exp\left(\frac{q_C}{RT}\right), \quad (6)$$

$$K = K_0 \exp\left(\frac{q_K}{RT}\right). \quad (7)$$

Isosteric enthalpy of sorption

For models with strong thermodynamic basis the application of Clausius – Clapeyron equation [Furmaniak et al. 2005, 2008] makes it possible to derive an equation describing the isosteric sorption enthalpy:

$$q^{st} - L = RT^2 \left(\frac{\partial \ln h_r}{\partial T} \right)_M, \quad (8)$$

where: L [kJ mol^{-1}] is the enthalpy of water condensation.

These formulas were derived earlier for both models applied in this study and have the following forms:

for the GDW model [Furmaniak et al. 2005, 2007a, 2007b, 2007c, 2008]:

$$q^{st} - L = \frac{\frac{K}{(1+Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1-kh_r}\right) \cdot Q + \frac{Kh_r}{1+Kh_r} \cdot \frac{wk}{(1-kh_r)^2} \cdot q}{\frac{K}{(1+Kh_r)^2} \cdot \left(1 + \frac{wkh_r}{1-kh_r}\right) + \frac{Kh_r}{1+Kh_r} \cdot \frac{wk}{(1-kh_r)^2}} \quad (9)$$

and for the GAB model [Furmaniak et al. 2007b, c]:

$$q^{st} - L = \frac{(1-Kh_r)^2 q_C + q_K + (C-1)K^2 h_r^2 q_K}{1 + (C-1)K^2 h_r^2} \quad (10)$$

Experimental data

In this study we applied five sets of sorption data available in the literature and determined for different types of wood. First set of data is standard data for wood (recommended by the US Department of Agriculture) at temperatures: 21.1, 43.3, 65.6 and 87.8 °C [Nakano 2006]. Next there are four sets of data taken from [Fan et al. 1999] and measured for: sitka spruce, western hemlock, western red cedar and lodge pole pine (all data measured for: 30, 45 and 60 °C).

Description of experimental data

Theoretical models were fitted to experimental data by applying the minimization procedure using the differential evolution (DE) algorithm proposed by Storn and Price [1996, 1997]. This procedure was successfully applied to description of multi-temperature water sorption data in the field of food engineering science [Furmaniak et al. 2007a, b, c]. The details thereof can be found elsewhere [Furmaniak et al. 2007c].

In particular the measure of the fit of theoretical models to experimental data can be measured by the value of the determination coefficient:

$$DC_T = 1 - \eta_T, \quad (11)$$

where:

$$\eta_T = \frac{\sum_i (M_i^o - M_i^t)^2}{\sum_i (M_i^o - \overline{M}^o)^2} \quad (12)$$

and M_i^o is observed moisture content for i -th experimental point, M_i^t is theoretical value of moisture content calculated based on theory, and \overline{M}^o is the average observed moisture content.

The global parameter describing the goodness of the fit of theory to the set of experimental data determined for different temperatures is defined by:

$$DC = 1 - \sqrt{\frac{\sum \eta_T^2}{N}} \quad (13)$$

where: η_T denotes the normalised sum of squares of deviation of theoretical curve from experimental points determined at the chosen temperature (defined by eq. (12)), and N is number of considered temperatures.

Results and discussion

Tables 1 and 2 collect the values of the best-fit parameters, and figs. 1–3 show the graphical representation. The fit of both models to experimental data is satisfactory (DC is equal to 0.99 or more). The GDW model leads to slightly better fit (the average DC values are equal to 0.9941 for the GDW model and 0.9925 for the GAB model). However, this model has one best-fit parameter more than the GAB model. Moreover, as we showed previously, the GDW can be simplified to the GAB model [Furmaniak et al. 2007b].

The plots of the values of the isosteric enthalpy of sorption generated from both models for studied samples show similar qualitative behaviour (fig. 4). For low M the value of this enthalpy is large and decreases at intermediate values. Finally, it reaches practically constant level (close to the value of the enthalpy of water condensation) for large M values. This confirms the widely accepted mechanism of sorption of water by wood, where strong bonding (even chemisorption) of water molecules occurs in the first stage. In the next stage physical sorption occurs, and finally water molecules condense in the spaces formed by the components of wood (see for example [Popper et al. 2004, 2005]). The discrepancies (observed at low M values) between the plots of enthalpy generated from the both models can be explained in two ways. In the case of standard data for wood the major reason is worse quality of the fit of the GAB to experimental data for low M values, for other samples the most important thing is the lack of experimental data in this range which results in the fact that the plots of enthalpy are in fact extrapolated.

Table 1. The values of the best-fit parameters obtained from the fitting of experimental data by the GDW model (eqs. (1), (4), (5))

Tabela 1. Wartości parametrów najlepszego dopasowania dla modelu GDW (równania (1), (4), (5))

Data Dane	m [%]	K ₀	k ₀	Q	q	w	DC _T ^{*)}	DC
Standard data for wood <i>Standardowe dane dla drewna</i>	10.60	2.485 10 ⁻²	0.8289	12.52	~0	0.5466	0.9980; 0.9979; 0.9987; 0.9984	0.9982
Sitka spruce <i>Świerk sitkajski</i>	8.004	2.656 10 ⁻⁴	0.4975	24.67	1.173	0.7607	0.9884; 0.9933; 0.9945	0.9916
Western hemlock <i>Chojna górską</i>	14.70	6.636 10 ⁻³	0.6142	13.94	0.6849	0.4423	0.9899; 0.9945; 0.9968	0.9931
Western red cedar <i>Żywotnik olbrzymi</i>	2.025	2.208 10 ⁻⁸	0.3779	55.43	1.675	2.932	0.9894; 0.9930; 0.9954	0.9922
Lodgepole pine <i>Sosna wydymowa</i>	11.27	5.966 10 ⁻³	0.6717	15.15	0.5586	0.4539	0.9948; 0.9959; 0.9961	0.9956

^{*)} the values arranged according to the rise in temperature.

^{*)} wartości ułożono zgodnie ze wzrostem temperatury.

Table 2. The values of the best-fit parameters obtained from the fitting of experimental data by the GAB model (eqs. (2), (6), (7))
Tabela 2. Wartości parametrów najlepszego dopasowania dla modelu GAB (równania (2), (6), (7))

Data Dane	m [%]	C ₀	K ₀	q _c	q _k	DC _T ^{*)}	DC
				[kJ mol ⁻¹]			
Standard data for wood <i>Standardowe dane dla drewna</i>	5.945	2.086 10 ⁻³	0.5724	21.66	0.8215	0.9959; 0.9968; 0.9966; 0.9941	0.9957
Sitka spruce <i>Świerk siskajski</i>	5.750	3.676 10 ⁻⁵	0.2357	31.79	3.030	0.9874; 0.9894; 0.9917	0.9893
Western hemlock <i>Choina górską</i>	6.530	2.164 10 ⁻³	0.2599	20.37	2.697	0.9897; 0.9919; 0.9961	0.9921
Western red cedar <i>Żywotnik olbrzymi</i>	4.129	3.759 10 ⁻²	0.3583	12.74	1.997	0.9879; 0.9934; 0.9957	0.9917
Lodgepole pine <i>Sosna wydymowa</i>	5.497	5.117 10 ⁻⁴	0.3201	24.97	2.297	0.9937; 0.9935; 0.9945	0.9939

^{*)} the values arranged according to the rise in temperature.

^{*)} wartości ułożono zgodnie ze wzrostem temperatury.

The additional advantage of the GDW model is its generality, i.e. as it was shown [Furmaniak et al. 2005, 2008] it can be easily reduced to the D'Arcy and Watt model [1970], and the Hailwood and Horrobin equation [1946] can be easily derived from the latter (see Appendix). The latter model is widely applied to description of water sorption by wood (see for example [Ball et al. 2001; Papadopoulos, Avramidis 2005]).

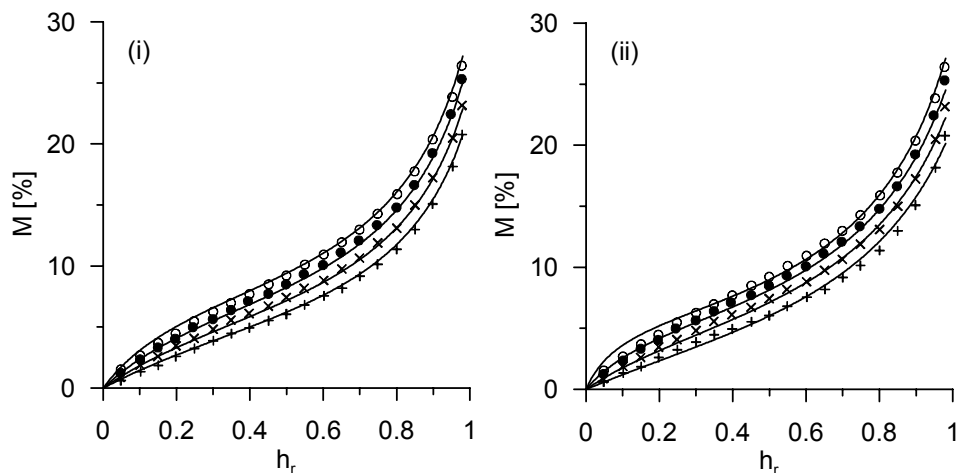


Fig. 1. The results of the fitting of the standard data for wood using the GDW (i) (eqs. (1), (4) and (5)) and the GAB (ii) (eqs. (2), (6) and (7)). Points – experimental data for 21.1 (○), 43.3 (●), 65.6 (×) and 87.8 (+) °C, lines – theory

Rys. 1. Wyniki opisu standardowych danych dla drewna modelami GDW (i) (równania (1), (4) i (5)) oraz GAB (ii) (równania (2), (6) i (7)). Punkty – dane doświadczalne dla 21.1 (○), 43.3 (●), 65.6 (×) i 87.8 (+) °C, linie – przebiegi teoretyczne

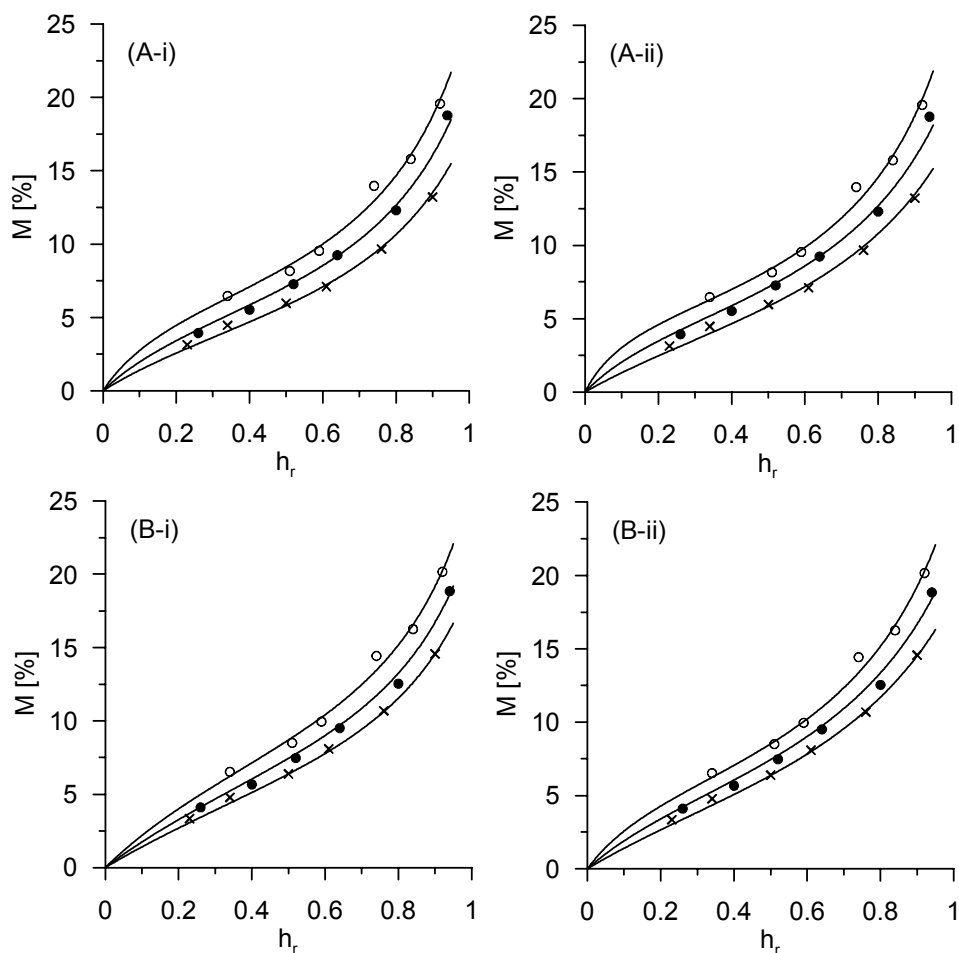


Fig. 2. The results of the fitting of the standard data for sitka spruce (fig. A) and for western hemlock (fig. B) using the GDW (i) (eqs. (1), (4) and (5)) and the GAB (ii) (eqs. (2), (6) and (7)). Points – experimental data for 30 (○), 45 (●) and 60 (×) °C, lines – theory

Rys. 2. Wyniki opisu danych doświadczalnych dla świerka sitkajskiego (rys. A) oraz dla choiny górskiej (rys. B) modelami GDW (i) (równania (1), (4) i (5)) oraz GAB (ii) (równania (2), (6) i (7)). Punkty – dane doświadczalne dla 30 (○), 45 (●) i 60 (×) °C, linie – przebiegi teoretyczne

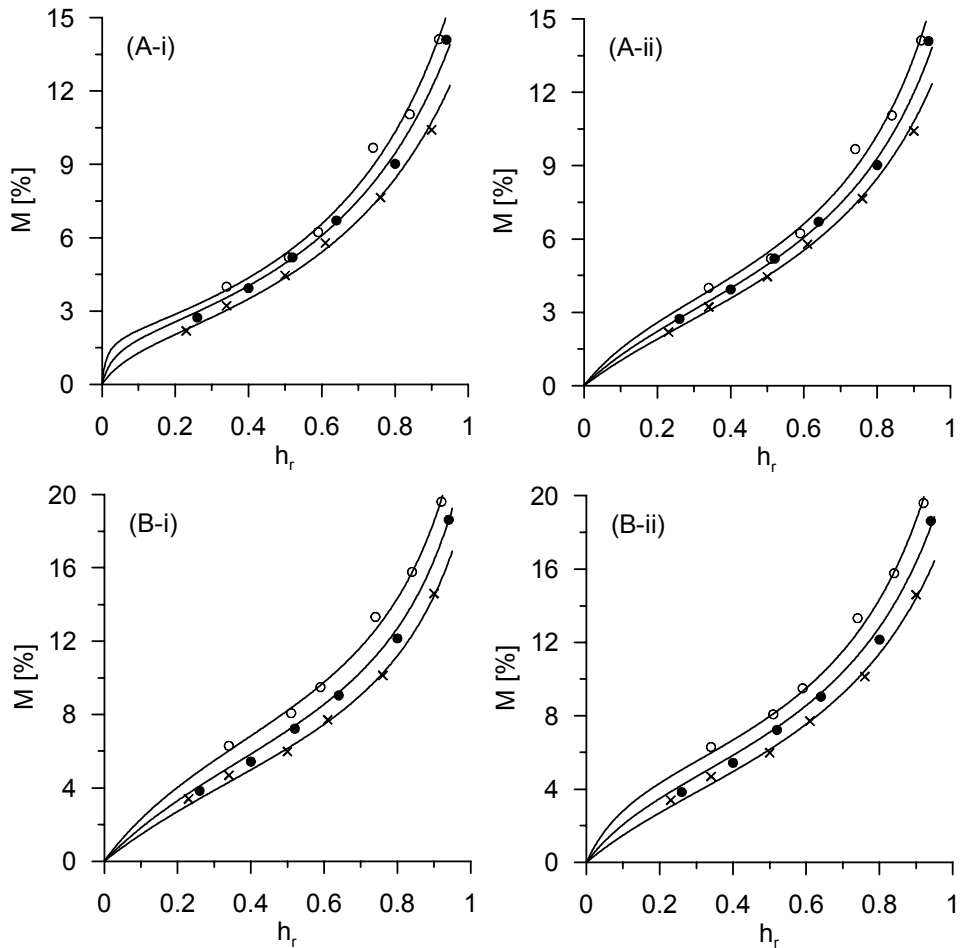


Fig. 3. The same as in fig. 2 but the data concerns western red cedar (A) and lodgepole pine (B). Symbols as in fig. 2

Rys. 3. To samo, co na rys. 2, lecz dla żywotnika olbrzymiego (A) i sosny wydmowej (B). Symbole jak na rys. 2

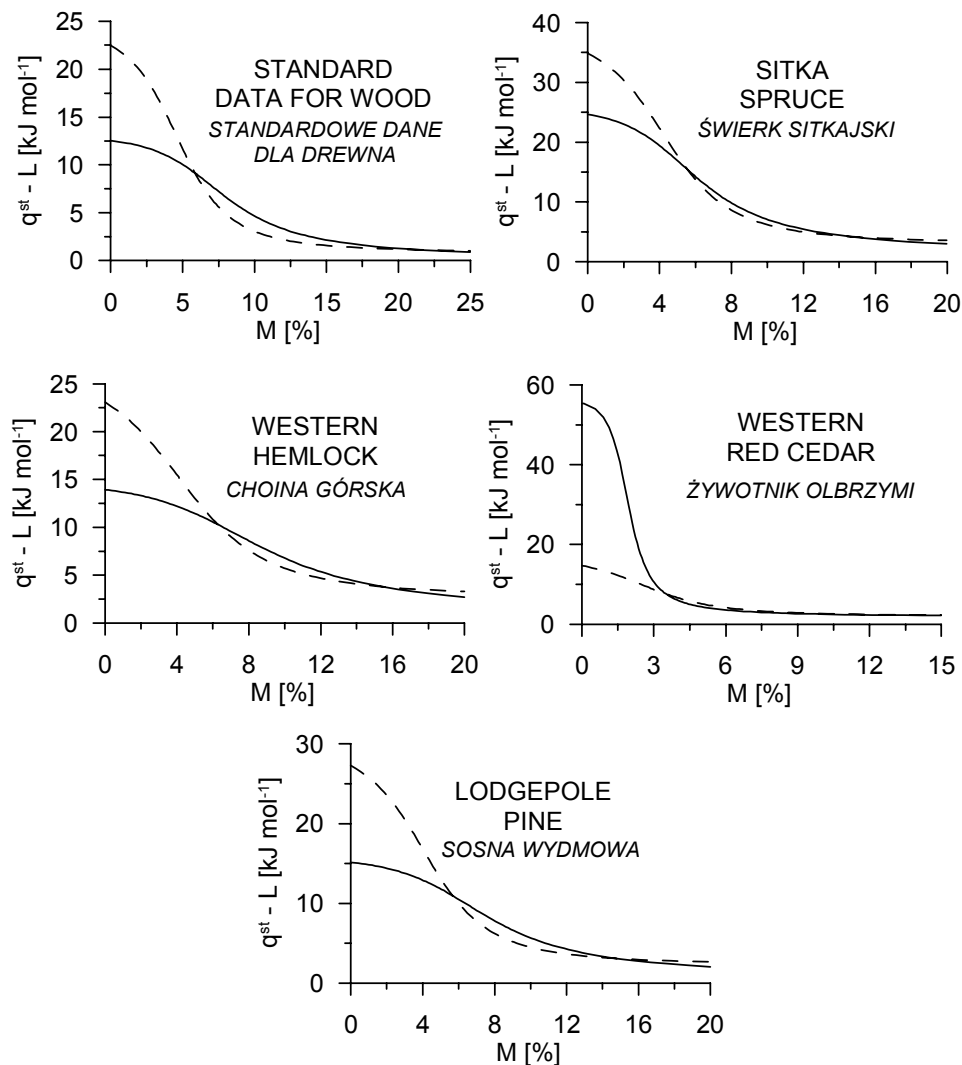


Fig. 4. The plots of the isosteric enthalpy of sorption for the studied sets of data generated from eqs. (9) and (10) and from the parameters shown in tabs. 1 and 2 (all plots are generated for $t = 45$ °C, solid line – the GDW model, dashed line – the GAB model)

Rys. 4. Przebiegi izosterycznej entalpii sorpcji dla rozważanych zestawów danych wygenerowane na podstawie równań (9) i (10) oraz wartości parametrów w tabelach 1 i 2 (wszystkie krzywe wygenerowane dla $t = 45$ °C, linia ciągła – model GDW, linia przerywana – model GAB)

Conclusions

Describing a series of data on water sorption on wood we have shown the applicability of the GDW model. According to our knowledge, this is the first report showing the enthalpy of water sorption on wood. From the results a three-stage mechanism of sorption of water by wood can be proposed where strong bonding (even chemisorption) of water molecules occurs in the first stage. In the next stage physical sorption occurs, and finally water molecules condense in the spaces formed by the components of wood. We have also shown that the GDW model is the most general equation describing water sorption on wood, and that this model can be easily reduced to the D'Arcy and Watt isotherm. The Hailwood and Horrobin equation can then be easily derived from the latter model.

Appendix – The simplification of the GDW model to the D'Arcy and Watt and Hailwood and Horrobin equations

Eq. (1) can be transformed to the following form [Furmaniak et al. 2005]:

$$M = \frac{mKh_r}{1 + Kh_r} + w \cdot \frac{mKh_r}{1 + Kh_r} \cdot \frac{ch}{1 - ch}, \quad (\text{A1})$$

where the first term describes sorption on the primary centres, and the second term on the secondary. Since the primary centres are relatively quick saturated, the concentration of the secondary centres (term $w \cdot mKh_r / (1 + Kh_r)$) reaches a constant value at low relative humidity levels. In this case this term can be replaced by constant value (M_s) and eq. (A1) can be simplified to:

$$M = \frac{mKh_r}{1 + Kh_r} + \frac{M_s ch}{1 - ch} \quad (\text{A2})$$

which is the simplest form of the D'Arcy and Watt [1970] isotherm. Assumption that the concentrations of primary and secondary centres are the same:

$$m = M_s = M_0 \quad (\text{A3})$$

and definition of $K^\#$ as the following combination of constants K and k :

$$K^\# = \frac{K}{k} \quad (\text{A4})$$

lead to the form of eq. (A2):

$$M = M_0 \left(\frac{K^{\#}kh_r}{1 + K^{\#}kh_r} + \frac{kh_r}{1 - kh_r} \right) \quad (\text{A5})$$

which is the Hailwood and Horrobin [1946] isotherm.

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TEMPERATUROWA ZALEŻNOŚĆ SORPCJI PARY WODNEJ PRZEZ DREWNO

Streszczenie

W pracy zaprezentowano zastosowanie dwóch modeli teoretycznych do jednoczesnego opisu danych sorpcji wody przez drewno mierzonych w kilku temperaturach. Stosowano uogólniony model D'Arcy i Watt GDW, będący modelem autorskim, oraz GAB o dobrze ugruntowanej pozycji w naukach sorpcyjnych. Ich stosowalność została pokazana na przykładzie kilku zestawów danych zaczerpniętych z literatury (mierzonych w wielu temperaturach) dla różnych gatunków drewna. Wśród nich znajdują się również standaryzowane dane dla drewna, rekomendowane przez Departament Rolnictwa USA.

Opis danych z zastosowaniem obydwu modeli dał satysfakcjonujące rezultaty (uzyskano wartości współczynnika determinacji przekraczające 0.99). Lepsze wyniki daje, posiadający o jeden parametr najlepszego dopasowanie więcej, model GDW. Nie dziwi to wobec pokazanej we wcześniejszych pracach możliwości uproszczenia modelu GDW do modelu GAB.

Na podstawie uzyskanych wartości parametrów najlepszego dopasowania, wykreślono przebiegi izosterycznej entalpii sorpcji wody dla poszczególnych rodzajów drewna. Wszystkie krzywe wykazują podobne zachowanie – rozpoczynają się od wysokich wartości entalpii

dla niskich zawartości wilgoci, następnie maleją dla pośrednich wartości. W końcu dla wysokich zawartości wilgoci osiągają praktycznie stałą wartość bliską entalpii kondensacji wody. Taki charakter zależności potwierdza powszechnie akceptowany mechanizm sorpcji wody przez drewno – początkowo silne wiązanie cząsteczek wody (nawet chemisorpcję), następnie sorpcję fizyczną i, na koniec, kondensację kapilarną w przestrzeniach między komponentami drewna.

Dodatkowo pokazano, iż model GDW można uprościć do równania Hailwooda i Horrobina, które jest jednym z najczęściej stosowanych modeli opisu sorpcji wody przez drewno.

Słowa kluczowe: sorpcja wody, model GAB, model GDW, równanie Hailwooda i Horrobina, entalpia sorpcji

