Internal and external moisture transport resistance during non-stationary adsorption of moisture into wood

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Abstract

The assumption that non-stationary sorption processes associated with wood can be evaluated by analysis of their transient system response to the disturbance developed is undoubtedly correct. In general it is, in fact, possible to obtain by time analysis of the transient phenomenon - involving the transition into an arbitrary new state of equilibrium - all data required for a credible evaluation of the observed system. Evaluation of moisture movement during drying or moistening requires determination of external moisture transfer resistance from or to wood surfaces, as well as internal resistance. Time-dependent changes in the moisture content of the spruce (*Picea abies* Karst.) samples of different thickness were monitored gravimetrically, during which the frequency of weighing was in accord with the speed of moistening. It was assumed that quasi-isothermal sorption processes associated with wood could be evaluated as first order systems. The characteristic time constant τ determines, wholly and uniformly, the time dependence of the sorption process for the relevant sorption range of wood tissue. The connection between the time constant and the thickness of the sample measured in the direction of the material flux is potential, with the power depending solely on the relationship between the external mass transfer convection and internal diffusion resistance. To determine the said resistances or coefficients of mass transfer convection and diffusivity, the experiment must be carried out on samples of varying thickness. It is only in this way that the external mass transfer convection and internal diffusion resistance can be correctly distinguished.

Key words: wood sorption, first order system, time constant, mass transfer, diffusivity

Notranji in zunanji transportni upor v procesu nestacionarne adsorbcije vlage v les

Izvleček

*Predpostavka, da je možno nestacionarne sorptivne procese, povezane z lesom, ovrednotiti z analizo njihovega časovnega prehodnega sistemskega odziva na nastalo motnjo, je nedvomno pravilna. V splošnem je namreč s časovno analizo prehodnega pojava, gre za prehod v poljubno novo ravnovesno stanje, možno pridobiti vse potrebne podatke za verodostojno vrednotenje opazovanega sistema. Vsak prehod v novo ravnovesno stanje je ne glede na lastnosti opazovanega sistema nestacionaren in kot tak primeren za analizo nestacionarnih pojavov, kot so na primer sorptivni procesi, povezani z lesom. Za analizo sorpcijskih transportnih značilnosti je treba poznati tako notranji difuzijski kakor tudi zunanji masni prestopni upor. Časovno odvisne spremembe vlažnosti v smrekovih vzorcih (*Picea abies *Karst.) različnih debelin smo spremljali gravimetrično, pri čemer je bila pogostnost tehtanja skladna hitrosti navlaževanja, se pravi v začetku največja, z naraščajočo maso vzorcev pa se je zmanjševala. Predpostavljeno je bilo, da lahko sorbcijske procese, povezane z lesom, vrednotimo kot sisteme prvega reda. Značilna časovna konstanta τ določa časovno odvisnost sorbcijskega procesa za relevantno sorptivno območje lesnega tkiva v celoti in enolično. Zveza med časovno konstanto in debelino vzorca, merjeno v smeri snovnega toka, je potenčna, pri čemer je vrednost potence odvisna zgolj od razmerja med zunanjim prestopnostnim in notranjim difuzijskim uporom. Za določitev omenjenih uporov oziroma koeficientov snovne prestopnosti in difuzivnosti je treba napraviti eksperiment na vzorcih različnih debelin. Samo tako je mogoče korektno ločiti zunanji prestopnostni in notranji difuzijski upor.*

Ključne besede: *sorpcija lesa, sistem prvega reda, časovna konstanta, masna prestopnost, difuzivnost*

1 Introduction

1 Uvod

The migration of moisture between the ambient air and wood depends on the potential difference, which is the driving force of any migration, and on the resistances that the migration flow must overcome. For transport of moisture in wood and for its exchange on the boundary surface between wood and the surrounding medium, the moisture content of wood is essential. From the technological aspect and from the aspect of physical properties of wood, the hygroscopic range is more important, i.e. the range when the saturation of wood structure has not yet been reached. Since available sorption sites in wood structure have not yet been occupied, only bound water, in addition to water vapours, is present in the wood. The direction of migration

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or transport is determined by the sign of the difference between the actual and equilibrium moisture content of the wood, while the moisture flow itself is controlled by two resistances, namely the external and internal resistance. The external resistance is the resistance of the boundary layer of the surrounding medium, and the internal resistance is usually assessed as the diffusion resistance. Since here two series-connected resistances are concerned, the total resistance, which the moisture flow must overcome, depends on their sum. The transport phenomena which accompany the migration of moisture in the wood and between the wood and the surrounding medium have been dealt with in the past by numerous authors (CHOONG / SKAAR 1969, 1972, ROSEN 1978, AVRAMIDIS / SIAU 1987, EL KOUALI / VERGNAUD 1991, SÖDERSTRÖM / SALIN 1993, WADSÖ 1993ab, 1994, DINCER / DOST 1996, PANG 1996, ROSENKILDE / ARFVIDSSON 1997, SIMPSON / LIU 1997, HUKKA 1999, LIU / SIMPSON 1999). The basis for the analysis of isothermal moisture transport phenomena associated with wood is the diffusion equation or II. Fick's law. Assuming that the diffusion coefficient is constant, and selecting the suitable initial and boundary conditions, the solution of the diffusion equation for the time-dependent dimensionless moisture potential E can be written in the following form (CRANK 1975):

$$E = \sum_{n=1}^{\infty} \frac{2Bi_m^2}{\beta_n^2 \left(\beta_n^2 + Bi_m^2 + Bi_m\right)} \exp\left(-\frac{\beta_n^2 D}{L^2}t\right) \quad (1)$$

where Bi_m is Biot's number of mass transfer, and β_n is the positive n-root of the equation

$$\beta_n \tan \beta_n = Bi_m ,$$

while L is the dimension of the sample measured in the direction of diffusion flow. Biot's number of mass transfer Bi_m gives the connection between mass transfer convection S between a solid substance and the surrounding medium, and the diffusivity of the solid substance D. It is expressed in the following form:

$$Bi_m = \frac{S \cdot L}{D}$$

The present paper has not been drawn up with the objective of confirming or refuting in any way whatsoever the validity of Fick's law. This remains undoubtedly valid; however, the application of the said law to a universal interpretation of sorptive processes associated with wood may become problematic, above all from the aspect of boundary conditions. The basic aim of the paper is to present the analysis of non-stationary sorption processes associated with wood as the analysis of transient system response to the disturbance developed. In general it is, in

fact, possible to obtain by time analysis of the transient phenomenon - involving the transition into an arbitrary new state of equilibrium - all data required for a credible evaluation of the observed system. Each transition into a new state of equilibrium is - irrespective of the properties of the observed system - non-stationary, and is as such suitable for analysis of non-stationary phenomena, such as sorption processes associated with wood.

2 Materials and methods
2 *Material in metode*

Samples were made of spruce (*Picea abies* Karst.). The thickness of the samples varied, namely 5, 10, 15, and 20 mm, while the remaining two dimensions were the same in all samples, namely 100 by 20 mm. The spruce samples were conditioned at a temperature of 22 °C to a moisture content of 6.3% at a variability of 0.2%. The changes in the moisture content of the samples were monitored gravimetrically with an accuracy of ±0.005 g. After conditioning, the spruce samples were partly applied with a two-component epoxyde coat EPOLOR HB with a very high proportion of dry substance (82±2%). On each sample, one radial longitudinal (RL) surface was left untreated, while on the five remaining surfaces, epoxyde coating was applied in three layers, each layer being applied in intervals of 10 hours. In this way, mass transfer was limited to only one surface and the conditions for one-dimensional diffusion of bound water in the interior of the samples were fulfilled in the continuation of the experiment. The coated samples were then returned into the climate chamber and subjected for further 10 days to the same climate conditions as before coating. After ten days, the samples were put into a ventilated vessel with a saturated salt solution $ZnSO_4 x7H_2O$. Air movement along the untreated surfaces of the samples was not controlled. The time-dependent changes in the moisture content of the samples were monitored gravimetrically, with the frequency of weighing being consistent with the speed of moistening, i.e. the largest at the beginning, and decreasing with the increasing mass.

3 Results and discussion
3 *Rezultati in diskusija*

Assuming that for the processes of adsorption and desorption there apply the principles of a first order system, their behaviour can be described by means of a differential equation:

$$\tau \cdot \frac{dm}{dt} + m = G\Phi(t) \qquad (2)$$

where τ is the time constant of the system, G is the gain, and $\Phi(t)$ is the time change of the ambient conditions. For the observed system, the mentioned change represents a disturbance, which forces it to change to a new state of equilibrium. The transition into a new state of equilibrium,

which is also called system response, is characteristic of the observed system.

If a continuously distributed system is lumped, with the time changes of moisture content in the sample representing actually the changes in the average moisture contents along the relevant dimension, the sorption time constant, which is characteristic of the first order system under observation, can be expressed in the form:

$$\tau = R_S C_u \quad , \tag{3}$$

where R_S is the total sorption resistance, and C_u is the lumped moisture capacitance of the system or test specimen. The time change in the moisture content of the sample is assessed as a change in the average moisture content. The total sorption resistance consists undoubtedly of two resistances, i.e. of the mass transfer convection and diffusion resistance. Due to the interphase material transport, the relevant resistances cannot be simply added up. If, however, the relevant resistances are multiplied by the appertaining coefficients, the total resistance can be expressed in the form:

$$R_S = c_1 \frac{L}{D} + c_2 \frac{1}{S} \quad , \tag{4}$$

where c_1 and c_2 are the coefficients that depend on Biot's number. If the moisture capacitance C_u is expressed simply by a linear dimension of the test specimen L, measured in the direction of the diffusion flow - this can be done in the case when the cross-sectional area of the test specimen is constant over its entire thickness - the time constant τ, which can also be written as $t_{0.63}$, can be expressed, taking into account the expression for the total diffusion resistance, in the form:

$$\tau \equiv t_{0.63} = c_1 \frac{L^2}{D} + c_2 \frac{L}{S} \quad . \tag{5}$$

Equation 5 is very similar to the simplified Newman's equation given by Choong and Skaar, 1969. The first term of the right side of the equation represents the contribution of the internal diffusion resistance, while the second term is the contribution of the external mass transfer convection resistance. Newman's equation is valid for half time of the sorption process, i.e. for the time when the dimensionless potential reaches the value 0.5. Accordingly, the values of coefficients 0.2 at the internal diffusion and 0.7 at the external mass transfer convection resistance are determined. The two mentioned coefficients can be determined by developing the Fourier number for mass transfer - expressed as

$$Fo_m = \frac{D \cdot t}{L^2}$$

and located in equation 1 in the exponent at the positive root β_n- into the MacLaurin series (SÖDERSTRÖM and SALIN, 1993).

If a new variable a - expressed as

$$a = \frac{1}{Bi_m}$$

- is introduced, the series can be written as:

$$Fo_m = Fo_{m0} + \left(\frac{\partial Fo_m}{\partial a}\right)_0 a + \frac{1}{2!}\left(\frac{\partial^2 Fo_m}{\partial a^2}\right)_0 a^2 + \frac{1}{3!}\left(\frac{\partial^3 Fo_m}{\partial a^3}\right)_0 a^3 + o\left(a^4\right)$$

For example, when $E = 0.63$ and $t = \tau$, the series is written as:

$$\frac{\tau D}{L^2} = 0.318659 + 1.04306\left(\frac{1}{Bi_m}\right) - 0.0962643\left(\frac{1}{Bi_m}\right)^2 +$$
$$+ 0.0259785\left(\frac{1}{Bi_m}\right)^3 + O\left(\frac{1}{Bi_m}\right)^4$$

If only the first two terms of the series are taken into account, the series is equal to equation 5, with the rounded values of the coefficients c_1 and c_1 being 0.32 and 1, respectively.

Figure 1 shows the effect of the thickness of a sample or test specimen on the time constant of moistening. From equation 5 it is evident that the dependence between the thickness of a sample and the time constant is potential, with the power being in the range between 1 to 2. The power depends above all on the relationship between the internal and external resistance, which the material flux must overcome. If the power is near 1, this means that the material flux almost entirely controls the external mass transfer convection resistance; if, however, the power is near 2, the situation is exactly the opposite, which means that the diffusion resistance is the one that prevails in the control of the material flux.
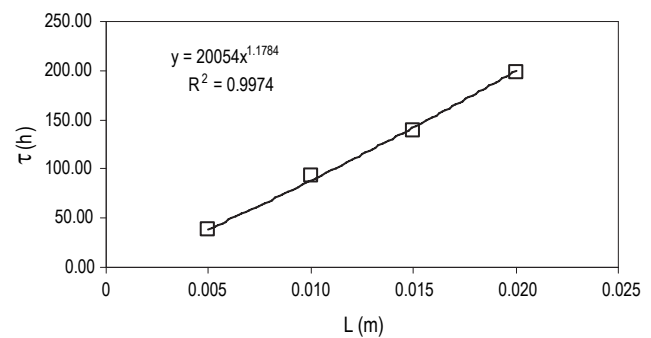

Figure 1: The influence of sample thickness on time constant of moistening

Slika 1: Vpliv debeline vzorca na časovno konstanto procesa adsorpcije

From the dependence shown in Figure 1 it is evident that the case of sorption is involved when the moistening mass flow is almost wholly controlled by the external mass transfer convection resistance.

If equation 5 is written in a slightly changed form:

$$\frac{\tau}{L^2} = 0.32 \frac{1}{D} + \frac{1}{S \cdot L}$$

and the dependence is shown graphically, the diffusion coefficient D and the coefficient of mass transfer convection S (Figure 2) can be easily determined on the basis of a regression line equation. The values of the two mentioned coefficients amounted in our case for spruce to $D = 4.9 \cdot 10^{-10}$ m²/s and $S = 4.07 \cdot 10^{-8}$ m/s. The coefficient of mass transfer convection is rather small, which is the result of insufficient air flow along the surfaces of the samples during the experiment. Owing to that, the formation of a boundary layer with an elevated concentration of moisture occurred, which, however, strongly reduces the coefficient of mass transfer convection, i.e. increases the external mass transfer convection resistance.
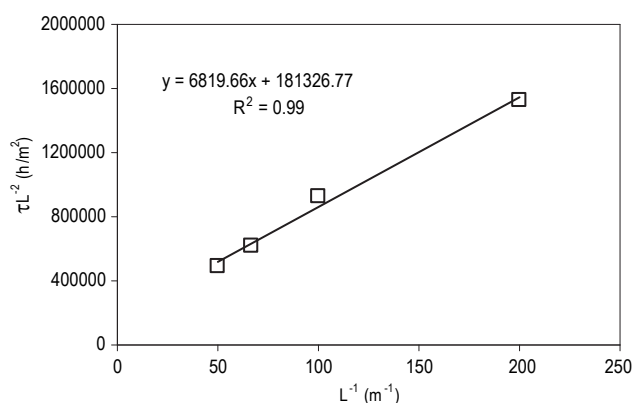

Figure 2: Regression line for determination of diffusivity D and mass convection coefficient S
Slika 2: *Določitev koeficientov difuzivnosti D in masne prestopnosti S*

4   Conclusions
4   *Zaključki*

The assumption that non-stationary sorptive processes associated with wood can be evaluated by analysis of their transient system response to the disturbance developed is undoubtedly correct. In general it is, in fact, possible to obtain by time analysis of the transient phenomenon - involving the transition into an arbitrary new state of equilibrium - all data required for credible evaluation of the observed system. Each transition into a new state of equilibrium, irrespective of the properties of the observed system, is non-stationary and as such suitable for analysis of non-stationary phenomena, such as sorption processes associated with wood.

The results of the analyses performed indicate that isothermal sorption processes associated with wood can be evaluated as first order systems. The characteristic time constant τ determines, wholly and uniformly, the time dependence of the sorption process for the relevant sorption range of wood tissue. The connection between the time constant and the thickness of the sample measured in the direction of the material flux is exponential, with the value of the exponent depending solely on the relationship between the external mass transfer convection and internal diffusion resistance. From the said correlation it may also be concluded that for the determination of the above-mentioned resistance or coefficients of mass transfer convection and diffusivity, the experimental data obtained only on the sample of only one thickness do not suffice, but that the experiment must be carried out on samples of varying thickness. It is only in this way that the external mass transfer convection and internal diffusion resistance can be correctly distinguished.

5   Povzetek

Migracija vlage med okoliškim zrakom in lesom je odvisna od potencialne razlike, ki je gonilo kakršne koli migracije ter uporov, ki jih mora migracijski tok premagovati. Za transport vlage v lesu ter izmenjavo le-te na mejni površini med lesom in okoliškim medijem je bistvenega pomena vlažnostno stanje lesa. S tehnološkega vidika ter vidika fizikalnih lastnosti lesa je pomembnejše higroskopno območje, se pravi območje, ko nasičenje strukture lesa še ni doseženo. Ker razpoložljiva sorpcijska mesta v strukturi lesa še niso zasedena, poleg vodnih par v lesu ostane samo še vezana voda. Smer migracije oziroma transporta je določena s predznakom razlike med dejansko in ravnovesno vlažnostjo lesa, sam tok vlage pa nadzorujeta dva upora, in sicer zunanji in notranji. Zunanji upor ponazarja upor mejnega sloja okoliškega medija, notranji upor pa se navadno vrednoti kot difuzijski upor. Ker gre za serijsko vezana upora, je skupni upor, ki ga mora tok vlage premagovati, odvisen od njune vsote.

Pričujoči članek ni nastal z namenom, da bi na kakršen koli način potrdili oziroma ovrgli veljavnost Fickovega zakona. Ta nedvomno velja, problematična pa lahko postane, predvsem z vidika robnih pogojev, uporaba omenjenega zakona za vsesplošno interpretacijo sorptivnih procesov, povezanih z lesom. Osnovni namen članka je prikazati analizo nestacionarnih sorptivnih procesov, povezanih z lesom, kot analizo časovnega prehodnega sistemskega odziva na nastalo motnjo. V splošnem je namreč s časovno analizo prehodnega pojava, gre za prehod v poljubno novo ravnovesno stanje, mogoče pridobiti vse potrebne podatke za verodostojno vrednotenje opazovanega sistema. Vsak prehod v novo ravnovesno stanje je ne glede na lastnosti opazovanega sistema nestacionaren in kot tak primeren za analizo nestacionarnih pojavov, kot so na primer sorptivni procesi, povezani z lesom. Predpostavka,

da je možno nestacionarne sorptivne procese, povezane z lesom, ovrednotiti z analizo njihovega časovnega prehodnega sistemskega odziva na nastalo motnjo, je nedvomno pravilna. V splošnem je namreč s časovno analizo prehodnega pojava, gre za prehod v poljubno novo ravnovesno stanje, možno pridobiti vse potrebne podatke za verodostojno vrednotenje opazovanega sistema. Vsak prehod v novo ravnovesno stanje je ne glede na lastnosti opazovanega sistema nestacionaren in kot tak primeren za analizo nestacionarnih pojavov, kot so na primer sorptivni procesi, povezani z lesom.

Rezultati opravljenih analiz kažejo na to, da lahko izotermne sorbcijske procese, povezane z lesom, vrednotimo kot sisteme prvega reda. Značilna časovna konstanta τ določa časovno odvisnost sorbcijskega procesa za relevantno sorptivno območje lesnega tkiva v celoti in enolično. Zveza med časovno konstanto in debelino vzorca, merjeno v smeri snovnega toka, je eksponentna, pri čemer je vrednost eksponentna odvisna zgolj od razmerja med zunanjim prestopnostnim in notranjim difuzijskim uporom. Iz navedene korelacije lahko tudi zaključimo, da za določitev omenjenih uporov oziroma koeficientov snovne prestopnosti in difuzivnosti ne zadoščajo eksperimentalni podatki, dobljeni zgolj na vzorcih ene same debeline, temveč je treba napraviti eksperiment na vzorcih različnih debelin. Samo tako je mogoče korektno ločiti zunanji prestopnostni in notranji difuzijski upor.

6   References
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