Journal Article

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Publication Date:
2009

Permanent Link:
https://doi.org/10.3929/ethz-a-006104740

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ADSORPTION AND DESORPTION MEASUREMENTS ON SELECTED EXOTIC WOOD SPECIES. ANALYSIS WITH THE HAILWOOD-HORROBIN MODEL TO DESCRIBE THE SORPTION HYSTERESIS

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ABSTRACT

Our preceding investigations showed that the Hailwood Horrobin model is suitable for the description of water vapour sorption of wood. The goal of the submitted study at select exotic wood species is to describe the phenomenon sorption hysteresis with help of this model. Additionally it was tried the wood species due to the hysteresis loop to differentiate from each other.

KEY WORDS: wood, water vapour, adsorption, desorption, sorption hysteresis

INTRODUCTION

The wood is due to the microscopical, the submicroscopical and the chemical structure very complex. Many scientists in the past and also nowadays have tried the phenomenon sorption hysteresis to describe and the physical causes to explain (Everett 1954, 1955, Peralta and Bangi, 1998, Time 2002, Frandsen, et al. 2007, Frandsen and Svensson 2007). At Institute for Building Materials (ETH Zurich) accomplished water vapour adsorption and desorption measurements on selected exotic wood species were analysed by the Hailwood-Horrobin model with the aim to differentiate them due to different sorption hysteresis loops.
WOOD RESEARCH

MATERIAL AND METHODS

Wood species used in this study are summarized in Tab. 1.

Tab. 1: The material tested

<table>
<thead>
<tr>
<th>Wood species</th>
<th>Latin name</th>
<th>Plant family</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilinga</td>
<td>Nauclea diderrichii Merill</td>
<td>Rubiaceae</td>
</tr>
<tr>
<td>Bongossi</td>
<td>Lophira alata Banks ex Gaertn. f.</td>
<td>Ochnaceae</td>
</tr>
<tr>
<td>Canalete (Cordia)</td>
<td>Cordia sp.</td>
<td>Boraginaceae</td>
</tr>
<tr>
<td>Danta</td>
<td>Nesogordonia papaverifera (A. Chev.) R. Capuron</td>
<td>Sterculiaceae</td>
</tr>
<tr>
<td>Doussié</td>
<td>Afzelia sp.</td>
<td>Caesalpiniaceae</td>
</tr>
<tr>
<td>Makassar</td>
<td>Diospyros celebica Bakh.</td>
<td>Ebenaceae</td>
</tr>
<tr>
<td>Mansonia</td>
<td>Mansonia altissima A. Chev.</td>
<td>Sterculiaceae</td>
</tr>
<tr>
<td>Merbau; Hintsy</td>
<td>Intsia sp.</td>
<td>Caesalpiniaceae</td>
</tr>
<tr>
<td>Okouné</td>
<td>Aucoumema klaineana Pierre</td>
<td>Burseraceae</td>
</tr>
<tr>
<td>Ramin</td>
<td>Gonystylus bancanus (Miq.) Kurz</td>
<td>Gonystylaceae</td>
</tr>
<tr>
<td>White Lauan</td>
<td>Shorea sp</td>
<td>Dipterocarpaceae</td>
</tr>
<tr>
<td>Wengé</td>
<td>Miletta laurentii De Wild.</td>
<td>Papilionaceae</td>
</tr>
<tr>
<td>Zebrano</td>
<td>Microberlinia sp.</td>
<td>Caesalpiniaceae</td>
</tr>
</tbody>
</table>

Spruce was selected as reference wood.

Test conditions

The attempt samples were conditioned in a climate chamber (KPK 200, Feutron) at constant temperature of 20±0.2°C and with relative humidity RH from 35%, 50%, 85% to 93% (ΔRHs ±3%). The equilibrium moisture content EMC of the attempt samples was determined according to DIN 52 183 (1977).

Sorption analysis

Hailwood-Horrobin model

For the characterisation of the interaction between the attempt material (wood) and the water vapour the Hailwood-Horrobin sorption model (1946) was used because the agreement of the measured values with the computed isotherms are usually very good. The Hailwood-Horrobin sorption model (further called HH-model) is based on the assumption that the sorbed water exists as a simple solution and as hydrate of the wood. The HH-model assumes further that the sorbed layer which consists of no hydrated, hydrated wood and of free liquid water forms an ideal solid solution. This sorption model makes possible to separate the monomolecular $U_m$ from the polymolecular water sorbed $U_p$ and the estimation of the fiber saturation point $U_{FS}$. The sorption equation for the HH-model is as follows:

$$ U_{tot} = U_m + U_p $$

$$ U_{tot} = \frac{1800}{M_p} \left( \frac{\alpha \cdot \beta \cdot h}{1 + \alpha \cdot \beta \cdot h} \right) + \frac{1800}{M_p} \left( \frac{\alpha \cdot h}{1 - \alpha \cdot h} \right), $$

Where $U_{tot}$ total water sorbed (%), $U_m$ monomolecular water sorbed (%), $U_p$ polymolecular water sorbed (%), $\beta$ relative vapour pressure, $M_p$ hypothetical molecular weight of the dry wood polymer, $\alpha$ equilibrium constant of the hydrated wood, $\beta$ equilibrium constant of the no hydrated wood.
Further allows the HH-model to calculate following values:
- The specific surface of the sorbent $\Sigma$
- and the inaccessibility of the sorbent to the sorbate $Z$.

**Sorption hysteresis**

At the water vapour sorption are the pathways for the water uptake and release different. The relative vapour pressure on adsorption of a porous material (wood) is greater than on desorption. This phenomenon is called sorption hysteresis. Possible explanation for the true hysteresis (the irreversible sorption) is the formation of metastable states of adsorbate in fixed pores (capillary condensation hysteresis) (Sing et al. 1985; Burgess et al. 1989, Liu et al. 1993, Neimark et al. 2000, Aharoni 2002, Sander et al. 2005). It is assumed that the reason for hysteresis is the difference in the sorbate filling and sorbate emptying of the pores. This can be described with the fundamental Kelvin equation.

The equation for adsorption on a cylindrically concave surface is as follows:

$$\frac{P_{AD}}{P_0} = \exp \left[ -\left( \frac{\gamma \cdot V_M}{r \cdot R \cdot T} \right) \cdot \cos \Theta \right]$$  \hspace{1cm} (3)

The equation for desorption on a spherically concave surface can be written in the following manner:

$$\frac{P_{DES}}{P_0} = \exp \left[ -\left( \frac{2 \cdot \gamma \cdot V_M}{r \cdot R \cdot T} \right) \cdot \cos \Theta \right]$$ \hspace{1cm} (4)

From equation 3 and 4 follows:

$$P_{AD} > P_{DES}$$ \hspace{1cm} (5)

Where:
- $P_{AD}$ vapour pressure on adsorption in $Pa$,
- $P_{DES}$ vapour pressure on desorption in $Pa$,
- $P_0$ saturation vapour pressure in $Pa$,
- $\gamma$ surface tension in $J.m^2$,
- $r$ pore radius in $m$,
- $V_M$ molar Volume in $m^3.kmol^{-1}$,
- $R$ gas constant in $J.K^{-1}.kmol^{-1}$,
- $T$ Temperature in $K$,
- $\Theta$ contact angle in $deg$.

The Kelvin equation is for the wood only limited applicable because the shape of the pores is not necessarily cylindrical there. Nevertheless the hysteresis phenomenon in combination with the HH-model is favourable in respect to differentiate the wood species from each other.

The wood/water contact angle parallel to the grain, which is needed for the determination of capillary radius, was taken up with the fast video camera and evaluated with help of image processing software. The measurement of the contact angle happened 20 seconds after the falling water drop the wood surface affected.
The hysteresis loop $H$ is defined as follows:

$$H = \int_{h=0}^{h=ipoint} (U_{des} - U_{ads}) \cdot dh$$

(6)

Where
- $U_{des}$ computed totally adsorbed water content within the hygroscopic range from $h=0$ to $ipoint$,
- $U_{ads}$ computed totally desorbed water content within the hygroscopic range from $h=0$ to $ipoint$,
- $h$ relative vapour pressure,
- $ipoint$ the relative vapour pressure at the intersection point of the adsorption and the desorption curves.

**RESULTS AND DISCUSSION**

Tab. 2 show the average values of the measured equilibrium moistures for the ad- and desorption at 20°C. For each wood species 3 samples were used.

The following Figs. 1 - 13 show the adsorption and desorption isotherms of the tested material computed according to the HH-model. From HH-model derived physical values are summarized in Tab 3. As one can see from Tab. 2 the ad- and desorption measurements were provided up to RH 93%. Desorption measurements did not start at $h=1$ but already at $h=0.93$. This is the reason for lower desorption values compare to the adsorption values above $h=0.93$. The agreement of the measured values with the computed isotherms is in the used measuring range excellent. For computations of hysteresis loops, values up to the intersection point were used. The HH-model is used as a standard method for estimation of the fiber saturation point.

**Tab. 2: Equilibrium moistures of selected exotic wood species and of the spruce**

<table>
<thead>
<tr>
<th>Wood species</th>
<th>Equilibrium moisture $U_a$ in % at relative humidity $RH$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35%</td>
</tr>
<tr>
<td>Bongossi</td>
<td>6.46/9.11</td>
</tr>
<tr>
<td>Canaleté</td>
<td>5.75/7.76</td>
</tr>
<tr>
<td>Danta</td>
<td>6.88/8.89</td>
</tr>
<tr>
<td>Doussié</td>
<td>5.34/7.36</td>
</tr>
<tr>
<td>Merbau</td>
<td>7.58/9.77</td>
</tr>
<tr>
<td>Okouné</td>
<td>6.32/8.05</td>
</tr>
<tr>
<td>Ramin</td>
<td>6.28/7.83</td>
</tr>
<tr>
<td>Wengé</td>
<td>5.93/6.08</td>
</tr>
<tr>
<td>Zebrano</td>
<td>6.08/8.72</td>
</tr>
<tr>
<td>Spruce</td>
<td>6.63/8.26</td>
</tr>
</tbody>
</table>
Where

- $U_a$ measured equilibrium moisture content with adsorption in 
- $U_d$ measured equilibrium moisture content with desorption in 

**Tab. 3: Computed values of the sorption analysis according to the Hailwood-Horrobin model for the attempt wood species at the fiber saturation point**

<table>
<thead>
<tr>
<th>Wood species</th>
<th>$U_{am}/U_{dm}$ (%)</th>
<th>$U_{ap}/U_{dp}$ (%)</th>
<th>$U_{aot}/U_{d_{tot}}$ (%)</th>
<th>$Z_a/Z_d$ (m².g⁻¹)</th>
<th>$Z_a/Z_d$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilinga</td>
<td>5.10/7.30</td>
<td>22.90/18.14</td>
<td>28.00/25.44</td>
<td>180/259</td>
<td>52/28</td>
</tr>
<tr>
<td>Bongossi</td>
<td>5.20/7.81</td>
<td>23.60/19.03</td>
<td>28.80/26.84</td>
<td>185/277</td>
<td>50/23</td>
</tr>
<tr>
<td>Canalete</td>
<td>4.60/6.87</td>
<td>18.20/13.85</td>
<td>22.80/20.72</td>
<td>163/244</td>
<td>56/33</td>
</tr>
<tr>
<td>Danta</td>
<td>5.40/7.54</td>
<td>23.00/19.33</td>
<td>28.40/26.87</td>
<td>192/268</td>
<td>48/26</td>
</tr>
<tr>
<td>Doussié</td>
<td>4.30/6.77</td>
<td>13.50/9.42</td>
<td>17.80/16.19</td>
<td>152/240</td>
<td>59/34</td>
</tr>
<tr>
<td>Mansonia</td>
<td>4.70/6.68</td>
<td>24.30/20.22</td>
<td>29.00/26.90</td>
<td>167/237</td>
<td>55/35</td>
</tr>
<tr>
<td>Merbau</td>
<td>6.00/8.73</td>
<td>20.20/16.48</td>
<td>26.20/25.21</td>
<td>212/310</td>
<td>43/13</td>
</tr>
<tr>
<td>Okoumé</td>
<td>4.90/6.65</td>
<td>26.90/22.94</td>
<td>31.70/29.58</td>
<td>172/236</td>
<td>54/35</td>
</tr>
<tr>
<td>Ramin</td>
<td>4.70/6.37</td>
<td>28.30/23.84</td>
<td>33.00/30.21</td>
<td>168/226</td>
<td>55/38</td>
</tr>
<tr>
<td>White Lauan</td>
<td>5.00/6.69</td>
<td>23.90/21.14</td>
<td>28.90/27.83</td>
<td>176/237</td>
<td>53/35</td>
</tr>
<tr>
<td>Wengé</td>
<td>4.90/7.54</td>
<td>15.40/11.94</td>
<td>20.30/19.48</td>
<td>172/268</td>
<td>54/26</td>
</tr>
<tr>
<td>Zebrano</td>
<td>4.60/6.45</td>
<td>25.60/22.20</td>
<td>30.30/28.65</td>
<td>164/229</td>
<td>56/38</td>
</tr>
<tr>
<td>Spruce</td>
<td>5.04/6.80</td>
<td>27.94/20.90</td>
<td>32.97/27.70</td>
<td>179/241</td>
<td>52/34</td>
</tr>
</tbody>
</table>

Where

- $U_{am}$ Computed adsorbed water content in the monomolecular layer at relative vapour pressure of $b=1$,
- $U_{dm}$ Computed desorbed water content in the monomolecular layer at relative vapour pressure of $b=1$,
- $U_{ap}$ Computed adsorbed water content in the polymolecular layer at relative vapour pressure of $b=1$,
- $U_{dp}$ Computed desorbed water content in the polymolecular layer at relative vapour pressure of $b=1$,
- $U_{aot}$ Computed totally adsorbed water content at relative vapour pressure of $b=1$,
- $U_{d_{tot}}$ Computed totally desorbed water content at relative vapour pressure of $b=1$,
- $Z_a$ Computed specific surface on adsorption (m².g⁻¹),
- $Z_d$ Computed specific surface on desorption (m².g⁻¹),
- $Z_a$ Computed inaccessibility of the sorptive active sites of the sorbent to sorbate on adsorption (%),
- $Z_d$ Computed inaccessibility of the sorptive active sites of the sorbent to sorbate on desorption (%).
Fig.1: Adsorption and desorption isotherm of Bilinga and Spruce as a reference wood at 20°C

Fig.2: Adsorption and desorption isotherm of Bongossi and Spruce as a reference wood at 20°C

Fig.3: Adsorption and desorption isotherm of Canalete and Spruce as a reference wood at 20°C
Fig. 4: Adsorption and desorption isotherm of Danta and Spruce as a reference wood at 20°C

Fig. 5: Adsorption and desorption isotherm of Doussié and Spruce as a reference wood at 20°C

Fig. 6: Adsorption and desorption isotherm of Makassar and Spruce as a reference wood at 20°C
Fig. 7: Ad- and desorption isotherm of Mansonia and Spruce as a reference wood at 20°C

Fig. 8: Ad- and desorption isotherm of Merbau and Spruce as a reference wood at 20°C

Fig. 9: Ad- and desorption isotherm of Okoumé and Spruce as a reference wood at 20°C
Fig. 10: Ad- and desorption isotherm of Ramin and Spruce as a reference wood at 20°C

Fig. 11: Ad- and desorption isotherm of white Lauan and Spruce as a reference wood at 20°C

Fig. 12: Ad- and desorption isotherm of Wengé and Spruce as a reference wood at 20°C
As a measure for hysteresis the differences between the water totally sorbed in the measuring range on desorption and adsorption was selected:

\[
\Delta U_{\text{tot}} = U_{\text{tot,DES}} - U_{\text{tot,ADS}}
\]  

Fig. 14 shows the shape of a hysteresis loop curve by the example of Bongossi, Doussié and Spruce in function of the capillary radius.

Fig. 14: Hysteresis loop of Bongossi, Doussié and Spruce as a function of capillary radius
Tab. 4 lists for all the examined wood species the maximum hysteresis loop value $\Delta U_{tot}$, the appropriate relative humidity $RH$ and the hypothetical capillary radius $r$ computed according to Kelvin equation.

Tab. 4: Lists the values of hysteresis loop $H$, the maximum of hysteresis curve $\Delta U_{tot}$ and the hypothetical capillary radius $r$ at appropriate relative humidity $RH$

<table>
<thead>
<tr>
<th>Wood species</th>
<th>$H$</th>
<th>Maximum $\Delta U_{tot}$</th>
<th>at $RH%$</th>
<th>$r \times 10^{-3} cm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bongossi</td>
<td>218</td>
<td>3.198</td>
<td>65</td>
<td>15</td>
</tr>
<tr>
<td>Merbau</td>
<td>207</td>
<td>3.013</td>
<td>63</td>
<td>17</td>
</tr>
<tr>
<td>Makassar</td>
<td>204</td>
<td>2.981</td>
<td>63</td>
<td>17</td>
</tr>
<tr>
<td>Wengé</td>
<td>197</td>
<td>2.799</td>
<td>60</td>
<td>13</td>
</tr>
<tr>
<td>Mansonia</td>
<td>181</td>
<td>2.678</td>
<td>70</td>
<td>18</td>
</tr>
<tr>
<td>Zebrano</td>
<td>179</td>
<td>2.677</td>
<td>72</td>
<td>23</td>
</tr>
<tr>
<td>Danta</td>
<td>181</td>
<td>2.658</td>
<td>65</td>
<td>19</td>
</tr>
<tr>
<td>Bilinga</td>
<td>176</td>
<td>2.627</td>
<td>64</td>
<td>14</td>
</tr>
<tr>
<td>Okoumé</td>
<td>172</td>
<td>2.587</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td>Canalete</td>
<td>172</td>
<td>2.516</td>
<td>60</td>
<td>18</td>
</tr>
<tr>
<td>White Lauan</td>
<td>168</td>
<td>2.471</td>
<td>73</td>
<td>31</td>
</tr>
<tr>
<td>Ramin</td>
<td>158</td>
<td>2.405</td>
<td>72</td>
<td>20</td>
</tr>
<tr>
<td>Doussié</td>
<td>164</td>
<td>2.391</td>
<td>52</td>
<td>12</td>
</tr>
<tr>
<td>Spruce</td>
<td>133</td>
<td>2.074</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

Due to sorption analysis of the tested wood species the following conclusions regarding the water absorption respectively water desorption can be made:

**Adsorption and desorption**

1. The lowest fiber saturation point of all examined wood species show Doussié with $U_{atot}=17.80\%$ resp. $U_{dtot}=16.19\%$ whereby Ramin with $U_{atot}=33.00\%$ resp. $U_{dtot}=30.21$ show the highest fiber saturation point.
2. Generally the higher monomolecular bound water belongs to the desorption and the higher polymolecular bound water to the adsorption.
3. The absolutely highest monomolecular bound water points Merbau followed from Bongossi. These two wood species shows the strongest affinity for the water, which demonstrates also the very low $Z$-value.
4. To the wood species with the strongest portion of monomolecular bound water on entirely adsorbed respective desorbed water belong Doussié (42%), Wengé (39%), Merbau (35%) and Canalete (33%).
5. To the wood species with those the physical and the structural forces are mass-giving for the entire water adsorption and desorption, belongs Ramin (79%), Okoumé (78%), Zebrano (77%), white Lauan (76%) and Mansonia (75%).

**Hysteresis**

1. The maximum of the hysteresis curve show Bongossi at the normal climate (20°C, RH=65%) with the highest value of 3.198.
2. Doussié 2,391 shows the lowest value of the exotic wood species at 20°C and RH=52%. Even lower value of 2.074 (20°C, RH=60%) is by Spruce to find.
Most wood species has the maximum of the hysteresis curve at relative humidity between 60% and 65%, which corresponds to the calculated capillary radius from 13 to 19 $\times 10^{-8}$cm. At relative humidity between 70% and 73% is the maximum of the hysteresis curve of Okoumé, Mansonia, Zebrano, Ramin and white Lauan. The capillary radius these wood species lies between 18 und 31 $\times 10^{-8}$cm. The greatest shift of the maximum of the hysteresis curve to the lower relative humidity shows Doussié (20°C, RH=52%), which corresponds to the calculated capillary radius of 12.10$^{-8}$cm. The magnitude of the $H$ value follows nearly the maxima of the hysteresis curves.

REFERENCES

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