

## Alteration of the Unsteady Sorption Behaviour of Spruce and Maple due to Thermal Treatment

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### ABSTRACT

The aim of the investigations was to evaluate the influence of a thermal modification on the unsteady sorption behaviour of spruce (*Picea abies* (L.) Karst.) and maple (*Acer pseudoplatanus* L.). It was examined in untreated and thermally modified samples in tangential and, for the first time, in longitudinal sorption direction and for the adsorption and desorption process. The unsteady-state sorption process between two equilibria of humidity was modelled as a diffusion process using Fick's second law. After recording the rate of sorption of wood samples by the gravimetric method a water vapour diffusion coefficient of the material could be determined through numerical methods with finite differences and inverse parameter identification. The diffusion coefficient in tangential sorption direction is smaller than in longitudinal direction. With increasing levels of humidity, diffusion coefficients in tangential sorption direction increase. In contrast, the diffusion coefficients in longitudinal direction decrease. Furthermore the diffusion coefficients are decreasing when the thickness of the specimens decreases.

### INTRODUCTION

The thermal modification of wood has long been recognized as a potentially useful method to improve dimensional stabilization of wood and increase its decay resistance (e.g. Kamdem *et al.* 2002). The cause of this is mainly the degradation of hemicelluloses. This leads to the reduction of hydroxyl groups, and the number of intra- and intermolecular hydrogen bonds (e.g. Boonstra and Tjeerdsma 2006, Windeisen *et al.* 2007). For this reason, thermally modified wood has lower equilibrium wood moisture than native wood (e.g. Popper *et al.* 2005). The rate of the moisture transport is related to parameters like relative humidity, temperature, kind of wood, velocity of atmosphere surrounding the sample, and the presence of gradients of moisture within the wood. By the simultaneous examination of modified and unmodified twin samples the influence of the thermal modification to the unsteady water absorption can be determined (Pfriem and Wagenführ 2007). In terms of the changed kinetics of the water vapour sorption at the Technische Universität Dresden investigations were carried out.

### MATERIALS AND METHODS

#### *Materials and Experimental*

The investigations were carried out on unmodified and thermally modified wood twin samples (Pfriem *et al.* 2007) of spruce (*Picea abies* (L.) Karst.) and maple (*Acer pseudoplatanus* L.).

The heat treatment was performed in a single stage dry process at 180 °C and at 200 °C for 4 h in a commercial plant at Mitteramskogler GmbH in Gaflenz (Austria). The unsteady sorption behaviour was examined in untreated and thermally modified samples in tangential and, for the first time, in longitudinal sorption direction. The process of absorption and desorption by wood contacted with various atmospheres was tested. Each test series consisted of four pairs of twin samples of modified (180 °C and 200 °C) and unmodified wood collected from the same annual rings with variation in 3 different thicknesses of the specimens. The thicknesses of the specimens with tangential sorption directions were 2 mm, 4 mm, and 6 mm and with longitudinal sorption directions were 4 mm, 6 mm, and 8 mm. A total of 144 samples were tested. For the investigations of unsteady water absorption an experimental rig following Wadsö (1992) and Viiri and Tyrväinen (1999) was used, which permits the simultaneous gravimetric analysis of the sorption behaviour of 72 samples with identical test conditions. The full experimental details are given elsewhere (Pfriem and Wagenführ 2007). The sorption measurements were performed by sudden changes of always 10 % relative humidity under isothermal conditions (27 °C). The range of relative humidity was 33 % to 93 % (adsorption) and 93 % to 33 % (desorption) respectively. During the experiments the weight gain or loss was registered in short intervals. After reaching a state of mass equilibrium the next sudden changes of relative humidity was performed. Depending on the time the unsteady-state sorption process between two equilibria of humidity (and equilibrium of mass) can be recorded.

### **Numerical modeling**

During a sudden change of humidity water vapour is taken up to the wood and to the pore system by diffusion procedures. The movement of moisture in wood at moisture content below the fibre saturation point is described by transient diffusion. The sorption process can be described by Fick's second law in one-dimension (Eqn. 1). Fick's second law predicts how diffusion causes the concentration field to change with time.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \cdot \left( D \cdot \frac{\partial C}{\partial x} \right) \quad (1)$$

Eqn. 2 describes the change of relative moisture content.

$$E = \frac{C - C_0}{C_\infty - C_0} = \frac{\omega - \omega_0}{\omega_\infty - \omega_0} \quad (2)$$

For Wood, the diffusion coefficient D is a function of concentration C (moisture-dependence). Normally an exponential relationship is assumed as shown in Eqn. 3 (Droin-Josserand *et al.* 1988).

$$D(E) = D_1 \cdot \exp(D_2 \cdot E) \quad (3)$$

To solve the partial differential equation, numerical methods must be applied (Crank 1979). Therefore a computing routine based on the program Matlab was developed. These model based on numerical methods with finite differences. The full details on these numerical methods are given elsewhere (Droin-Josserand *et al.* 1988).

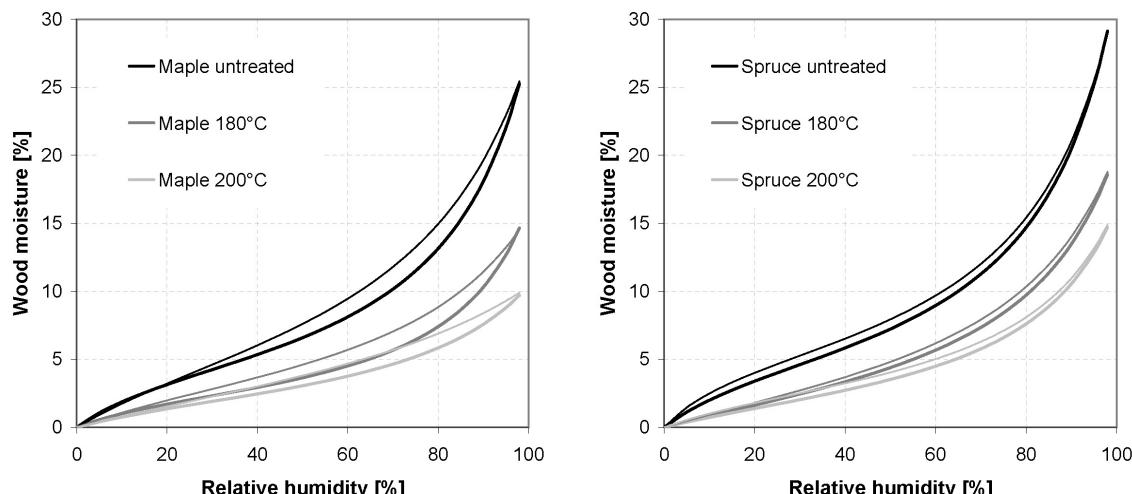
## Evaluation

For each test of sudden changes of relative humidity and for each sample (a total of 1728 tests) the determination of the diffusion coefficient between two equilibrium of humidity was analysed. The diffusion coefficient has been averaged for every series consisting of four samples. The state of equilibrium of mass at the different levels of humidity can be used for calculated sorption isotherms for unmodified and thermally modified woods. Therefore the Dent sorption theory was used (Pfriem 2006). Hence the diffusion coefficient of modified and unmodified woods can be plotted as a function of the wood moisture.

## RESULTS AND DISCUSSION

### Dent-Sorption isotherms

Figure 1 presents the calculated adsorption and desorption isotherms for unmodified and thermally modified maple and spruce samples. These data were used for the calculation of the dependence of diffusion coefficient from wood moisture presented further down.



**Figure 1:** Dent-Sorption isotherms (adsorption and desorption) for unmodified and modified maple (left) and spruce (right)

The calculated sorption curves clearly show the well-known hysteresis between adsorption (bold lines) and desorption (fine lines). As expected, the equilibrium wood moistures of spruce are higher than these of maple. As well known to, thermally modified wood has lower equilibrium wood moistures than unmodified wood.

### Diffusion coefficients in tangential sorption direction

In Figure 2 (maple) and 3 (spruce) the diffusion coefficients determined in desorption experiments are presented. For each sudden changes of humidity the resulting wood moistures were determined. The diffusion coefficients were plotted in dependency on the wood moisture, the degree of modification, and the sample thickness. With increasing level of humidity and with increasing moisture content the diffusion coefficients in tangential sorption direction increase as shown in Figure 2 for maple and in Figure 3 for spruce. The reduced moisture content due to thermal treatment influences the diffusion coefficient in tangential sorption direction. But the trends of the diffusion coefficients (closed lines in Figure 2 and 3) include all three levels of modification.

These curves follow an exponential trend as described by Droin-Josserand *et al.* (1988). Beyond the reduced moisture content no other influence of thermal treatment on diffusion coefficients in tangential sorption direction can be assumed. But in considering identical test conditions (that means that identical temperature and air humidity result in different moisture content of unmodified and modified samples) the diffusion coefficient of thermally modified wood is lower than for unmodified samples. That means that under identical test conditions thermally modified wood compared to unmodified wood show a reduced reaction to climatic variability (Pfriem and Wagenführ 2007).

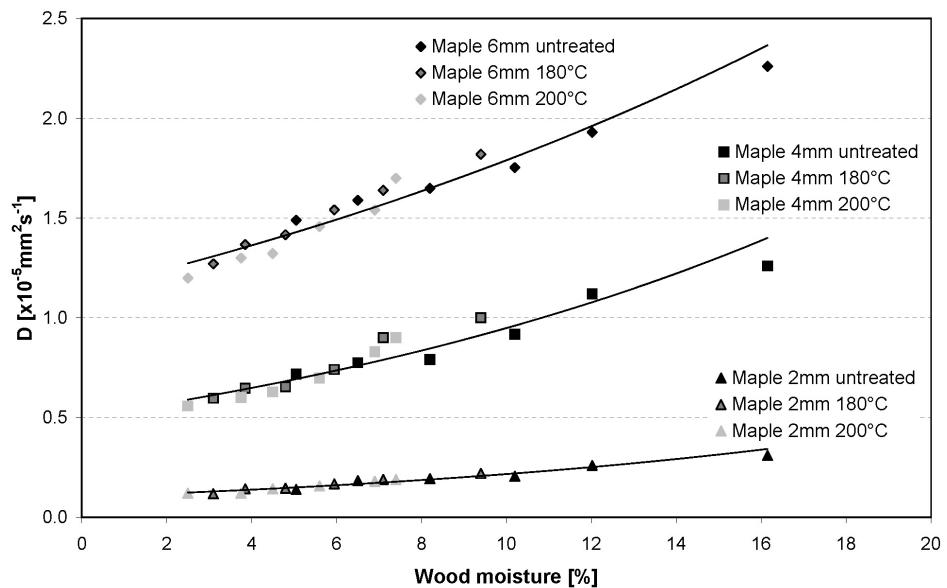


Figure 2: Diffusion coefficient D in tangential sorption direction of unmodified and modified maple – Dependence of the thickness of the samples

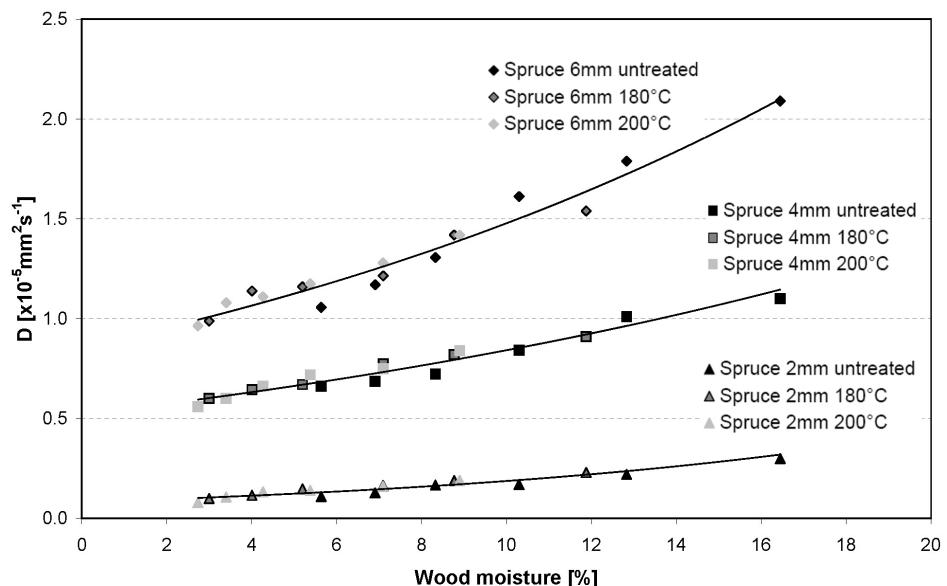


Figure 3: Diffusion coefficient D in tangential sorption direction of unmodified and modified spruce – Dependence of the thickness of the samples

Furthermore the diffusion coefficients are decreasing when the thickness of the specimens decreases. Unmodified and thermally modified spruce and maple show so-called non-Fickian diffusion behaviour (Crank 1979). Very thin samples (2 mm) show

only a low dependence of the diffusion coefficients on wood moisture. These samples outweigh the influence of the surface coefficients. If the sudden changes of humidity were carried out in adsorption or desorption direction, the resulting diffusion coefficients differ. The diffusion coefficients of desorption experiments are higher than the coefficients of adsorption experiments (Figure 4 for maple and Figure 5 for spruce). There may be a hysteresis, similar to the known hysteresis of wood moisture (Figure 1).

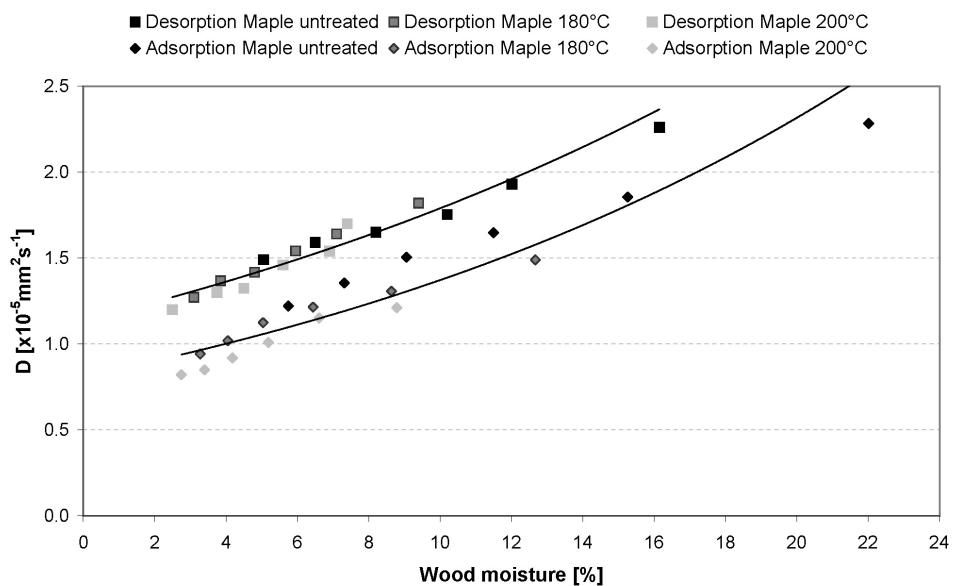


Figure 4: Diffusion coefficient  $D$  in tangential sorption direction of unmodified and modified samples of maple (6 mm thickness) in dependency on adsorption (below) and desorption (above)

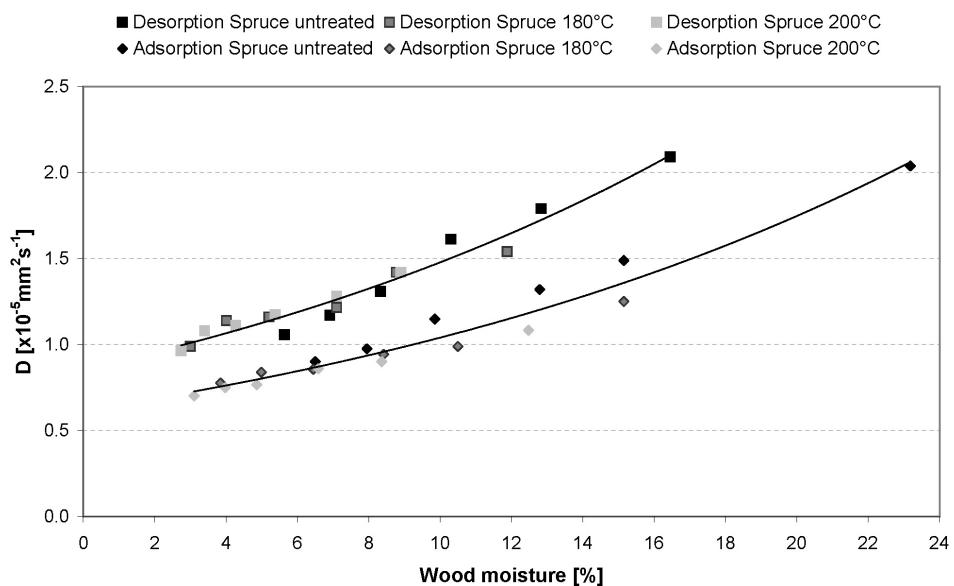
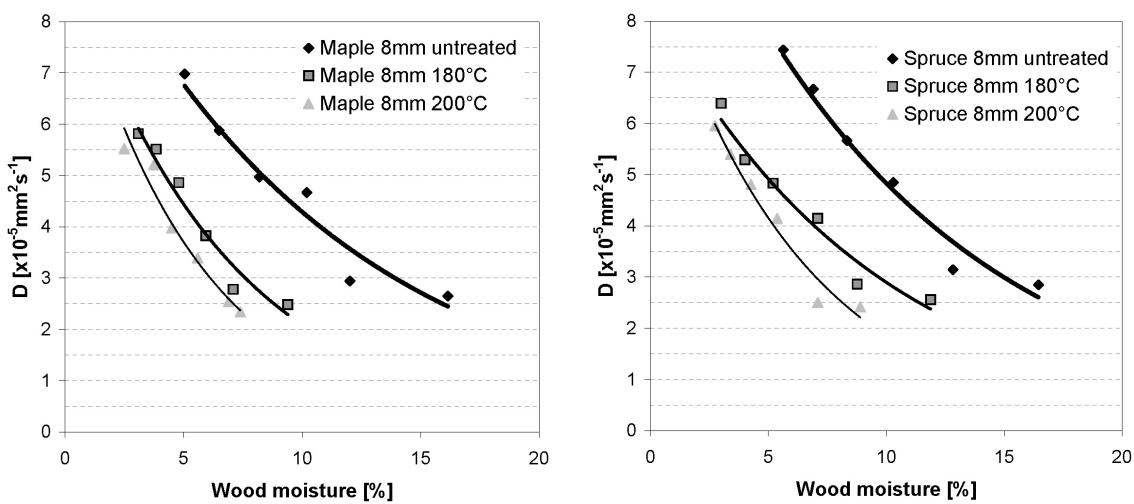


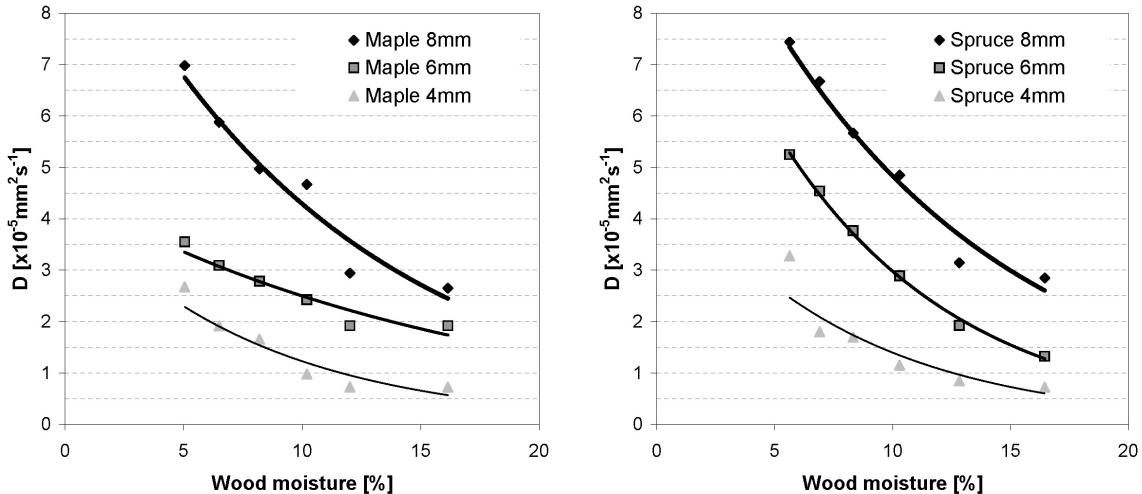
Figure 5: Diffusion coefficient  $D$  in tangential sorption direction of unmodified and modified samples of spruce (6 mm thickness) in dependency on adsorption (below) and desorption (above)

### **Diffusion coefficients in longitudinal sorption direction**

Some results of the experiments to determine the diffusion coefficient in longitudinal sorption direction are shown in Figure 6. Again, the desorption experiments were evaluated as described further up. Generally, the diffusion coefficient in longitudinal direction is greater than in tangential direction. The water vapour transport is faster in longitudinal direction. In contrast to the diffusion in tangential direction a clear dependence of the diffusion coefficient in longitudinal sorption direction on the degree of thermal modification could be proved. Thus, in Figure 6 the presentation of the data of different sample thicknesses is waived. This dependence is exemplified presented in Figure 7 for unmodified samples.



**Figure 6:** Diffusion coefficient  $D$  in longitudinal sorption direction (desorption) of unmodified and modified samples of maple (left) and spruce (right) (8 mm thickness) – Dependence of the degree of modification



**Figure 7:** Diffusion coefficient  $D$  in longitudinal sorption direction (desorption) of unmodified samples of maple (left) and spruce (right) – Dependence of the thickness of the samples

In contrast to diffusion in tangential direction, the diffusion coefficients in longitudinal direction decrease with increasing level of humidity and wood moisture. The reason for this lies in the diminishing accessibility of small pores by increasing wood moisture and swelling effects.

With increasing degree of modification the diffusion coefficients decrease. The cause of this is to seek in the alteration of pore structure. As described by the authors elsewhere (Zauer and Pfriem 2009 in ECWM4 proceedings, and Pfriem *et al.* 2009) a trend of an increasing porosity with a higher degree of thermal treatment can be observed. This alteration of pore structure affects the diffusion behaviour of modified woods in longitudinal sorption direction significantly. As described for diffusion in tangential direction the diffusion coefficients are decreasing when the thickness of the specimens decreases (Figure 7). Furthermore, the diffusion coefficients of desorption experiments are higher than the coefficients of adsorption experiments. This trend has been observed for all degrees of modification.

## CONCLUSIONS

It's clearly evident that the thermal treatment has results in changes of the unsteady sorption behaviour for both wood species. Rising diffusion coefficients result in increased water vapour transport. Generally the diffusion coefficient in tangential sorption direction is smaller than in longitudinal direction. With increasing levels of humidity the diffusion coefficients in tangential sorption direction increase. In contrast, the diffusion coefficients in longitudinal direction decrease. The reduced moisture content due to thermal treatment influences the diffusion coefficient in tangential sorption direction.

Beyond that no other influence of thermal treatment in tangential sorption direction can be assumed! In contrast the alteration of pore structure affects the diffusion behaviour of modified woods in longitudinal sorption direction significantly (see also Zauer and Pfriem (2009) in this proceeding). It could be proven that a thermal modification influences the diffusion coefficients in longitudinal direction.

With increasing degree of modification the coefficient decreases. Furthermore the diffusion coefficients are decreasing when the thickness of the specimens decreases. Summarily the results clearly show, that unmodified and thermally modified spruce and maple have non-Fickian diffusion behaviour. An overview of these results is shown in Table 1.

*Table 1: Dependence of the diffusion coefficients in tangential or longitudinal sorption direction*

<b>Changes in Property</b>	<b>Initiated alteration of diffusion coefficients in</b>	
	<b>Tangential sorption direction</b>	<b>Longitudinal sorption direction</b>
Species of wood	Maple higher than spruce	Spruce higher than maple
Increase of thickness	Increase	Increase
Increase of wood moisture	Increase	Decrease
Adsorption / Desorption	Desorption higher than adsorption	Desorption higher than adsorption
Increasing degree of modification	No influence	Decrease

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