

Research Article

Moisture Sorption and Thermodynamic Properties of Wood under Dynamic Condition

Tiantian Yang and Erni Ma

College of Materials Science and Technology, Beijing Forestry University, Beijing 100083, China

Correspondence should be addressed to Erni Ma; maerni@bjfu.edu.cn

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Thermodynamic approach is a useful method to study interactions between water and wood at molecular level. This work investigated the dynamic moisture sorption and thermodynamic properties for two thick poplar woods (*Populus euramericana* Cv.) subjected to sinusoidal relative humidity (RH) changes between 45% and 75% for cyclic period of 1, 6, and 24 h, at two temperatures of 25°C and 40°C. Moisture changes of the specimens were measured during the successive adsorption and desorption processes, giving the following results: (1) moisture content changed sinusoidally with the imposed RH and was inversely related to specimen thickness as well as temperature, but in a positive correlation with cyclic periods; (2) all of Q_L , ΔG , and $T\Delta S$ of the adsorbed water during dynamic sorption decreased with increasing moisture content or specimen thickness and decreasing cyclic period. However, temperature had opposite effects on ΔG and $T\Delta S$. (3) Both moisture sorption hysteresis and thermodynamic sorption hysteresis could be found. The former became weak with rising temperature or thicker specimens, while the latter got clear when temperature or specimen thickness increased.

1. Introduction

Interaction between wood and water has always been the focus in the field of wood science, which has significant influences not only on the physical and mechanical properties of wood, but also on the application of wood products in service. Although moisture sorption behaviors of wood have been discussed systematically from every respect in the literature [1–6], knowledge from these studies is usually macroscopic and limited. Because the moisture change in wood is inevitably accompanied by an exchange of heat, namely, heat generated during adsorption (exothermic) or consumed during desorption (endothermic) [7], thermodynamic approach provides a new alternative to explore wood-water relations in terms of energy since the method is actually an indicator for the state of the water adsorbed by wood substrate at molecular level [8].

The thermodynamic properties associated with moisture sorption by wood mainly include three parameters of differential heat of sorption (or net isosteric heat of sorption) Q_L , free energy change ΔG , and differential entropy $T\Delta S$, which can be obtained from both experimental measurement

and theoretical calculation [9]. The Q_L indicates the bonding energy between water molecules and wood substance, that is, the total energy changes, including the ΔG and $T\Delta S$. The ΔG refers to the work that water molecules swell wood and cut hydrogen bonds among wood structure to expose sorption sites. The $T\Delta S$ represents arrangement regularity of water molecules adsorbed in wood [10].

Vobehr first measured the wetting heat of wood using Bunsen ice calorimeter, as reported in Cao [11, 12], followed by the measurements of integral sorption heat and differential sorption heat for Klinki pine, conducted by Kelsey and Clarke [13].

On the other hand, Stamm and Loughborough [14] applied the Clausius-Clapeyron equation into sorption isotherms of Sitka spruce to calculate the differential heat of sorption over the temperature range from 20°C to 100°C and the results agreed well with the measured values [15]. Weichert [16] also calculated the Q_L of European spruce and European beech with the same equation and got similar results. Further, many researchers found that the differential heat of sorption decreased as moisture content increased

and Q_L was higher in desorption than in adsorption [17, 18], defined as thermodynamic sorption hysteresis by Cao [11, 12]. This indicated the bonding energy was greater in desorption compared with adsorption, which is probably due to the higher presence of active polar groups on wood surface during desorption [19]. Other studies employed this method to investigate the change in moisture sorption state after heat treatment [20] or the effect of wood age [21].

In 2001, Cao [11] initially introduced the thermodynamic approach into moisture nonequilibrium state through a critical discussion on the validity of Clausius-Clapeyron equation by the Assumption of Local Equilibrium, and the Q_L , ΔG and $T\Delta S$ of adsorbed water during wood adsorption and desorption were worked out.

However, it can be noticed that moisture sorption by wood in these studies was conducted under static condition (i.e., constant temperature and RH). Because atmospheric temperature and RH during wood processing and use are always changing, which may be sinusoidal according to Schniewind [22], it is of great importance to understand this time-dependent moisture state and condition in wood and to shed light on interaction between wood and water in changing environment.

Therefore, the present work was conducted to clarify dynamic moisture sorption at molecular level by thermodynamic approach for two thicknesses of poplar wood subjected to sinusoidal RH changes.

The results should be helpful in providing a fundamental understanding on the relation between wood and water at nonequilibrium state theoretically, as well as promoting some new wood processing methods practically, such as the plastication technology, large deformation processing, and bending technology.

2. Materials and Methods

2.1. Experimental. Poplar (*Populus euramericana* Cv.) from the Greater Khingan Mountains in China was chosen as the study species. The specimens, 20 mm in radial and tangential directions with two thicknesses of 4 mm and 10 mm along the grain, were first oven-dried at 105°C. After their oven-dried weights were measured, the specimens were conditioned at 45% RH at both 25°C and 40°C controlled by saturated salt solutions of potassium carbonate and magnesium nitrate, respectively [23]. They were then moved into a conditioning oven to conduct cyclic tests where RH changed sinusoidally between 45% and 75% for 1, 6, and 24 h, at two constant temperatures of 25°C and 40°C. The RH in the oven was programmed to vary in discrete steps according to a predetermined schedule, and a thermo recorder was placed near the specimens to ensure the desired RH and temperature inside the oven. During the process, weight changes were measured by an electronic analytical balance (0.1 mg) [4].

In addition, there were three end-matched replicates for each period. And each test was repeated three times and mean values of the three tests for weights of the specimens were taken as the final result.

TABLE 1: Comparison of moisture response for poplar wood between 25°C and 40°C at different periods.

| Thickness/mm | Period/h | Temperature/°C | |
|--------------|----------|----------------|--------------|
| | | 25 | 40 |
| 4 | 1 | 6.92 (0.011) | 6.62 (0.018) |
| | 6 | 9.44 (0.023) | 8.86 (0.013) |
| | 24 | 9.76 (0.017) | 9.13 (0.009) |
| 10 | 1 | 6.83 (0.023) | 6.52 (0.031) |
| | 6 | 8.77 (0.023) | 8.39 (0.008) |
| | 24 | 9.64 (0.023) | 9.10 (0.012) |

Data provided as the average (standard deviation) per cycle from several replicate experiments.

2.2. Theoretical. Experimental results were analyzed by the Clausius-Clapeyron equation [11, 12] to calculate the three thermodynamic parameters as follows:

$$\begin{aligned} Q_L &= Q_V - Q_0 = -0.254 \left[\frac{d \log(p/p_0)}{d(1/T)} \right] \\ &= +0.254 \left[\frac{d \log(1/h)}{d(1/T)} \right], \\ \Delta G &= \left(\frac{RT}{18} \right) \ln \left(\frac{p_0}{p} \right) = \left(\frac{RT}{18} \right) \ln \left(\frac{1}{h} \right), \\ T\Delta S &= Q_L - \Delta G, \end{aligned} \quad (1)$$

where Q_V is the energy required to evaporate one gram of water from the cell wall (cal/g water) and Q_0 is the energy required to evaporate one gram of water from the liquid state (cal/g water). h is the relative vapor pressure. T is absolute or Kelvin temperature (K). R is gas constant.

This method requires at least two isotherms at different temperatures and considers that Q_L is independent of the temperature [24]. In addition, calculation of the parameters for adsorbed water in wood was based on moisture contents from the steady cycles during dynamic sorption and averaged for each analyzation.

3. Results and Discussions

3.1. General Moisture Responses. Moisture response of 10 mm thick poplar wood to sinusoidally varying RH cycled at 24 h, 25°C, is shown in Figure 1 as an example. It is apparent that the moisture content is generally sinusoidal but lags behind the imposed RH. It also seems as if a repetitive “steady state” in the moisture responses is reached from the third cycle.

Table 1 gives a comparison on the moisture response for poplar wood between 25°C and 40°C at each cyclic period where the data was calculated based on the average values from all cycles tested. It is clear that moisture changes are lower at 40°C than those at 25°C, which is in accordance with static studies [25]. This is because the hygroscopicity of wood decreases with increasing temperature as a result of losing sorption sites [26, 27].

TABLE 2: A/D ratio for poplar wood under dynamic condition.

| Thickness/mm | Period/h | 25°C | | 40°C | |
|--------------|----------|------------------|---------------|------------------|---------------|
| | | A/D ^a | Average | A/D ^a | Average |
| 4 | 1 | 0.878 (0.033) | | 0.866 (0.053) | |
| | 6 | 0.893 (0.027) | 0.869 (0.022) | 0.916 (0.010) | 0.887 (0.020) |
| | 24 | 0.835 (0.041) | | 0.878 (0.034) | |
| 10 | 1 | 0.911 (0.011) | | 0.861 (0.021) | |
| | 6 | 0.854 (0.022) | 0.879 (0.021) | 0.883 (0.019) | 0.884 (0.018) |
| | 24 | 0.872 (0.009) | | 0.908 (0.011) | |

^aAverage values of all cycles.

Data provided as the average (standard deviation) per cycle from several replicate experiments.

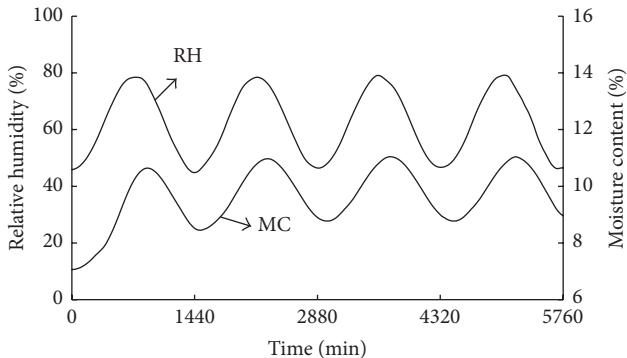


FIGURE 1: Plots of moisture contents (MC) changes and relative humidity (RH) against cyclic time for 10 mm thick poplar wood (25°C, 24 h).

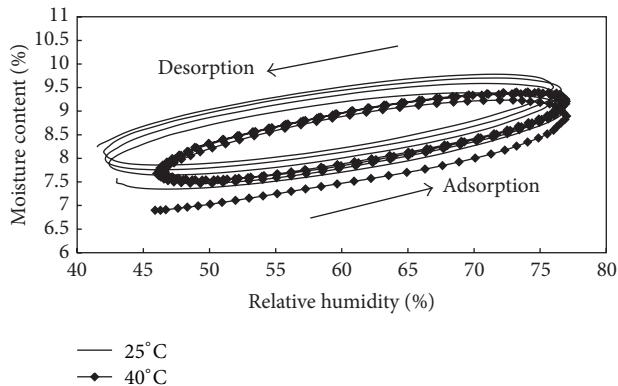


FIGURE 2: Dynamic moisture sorption isotherms for 10 mm thick poplar wood under both 25°C and 40°C at cyclic period of 6 h.

3.2. Moisture Sorption Hysteresis. Figure 2 presents dynamic sorption isotherms of 10 mm thick poplar wood under both 25°C and 40°C at cyclic period of 6 h. It is obvious that moisture sorption hysteresis occurs under varying RH, and it becomes weak as temperature increases due to the softening of hemicelluloses [2]. To investigate the sorption hysteresis quantitatively, maximum hysteresis ratio A/D for each cycle was calculated and summarized in Table 2. As shown in the table, A/D ratio falls into the normal range of 0.8–0.9

[15], with no consistent effect of cyclic period and specimen thickness. Compared with A/D ratio at 25°C, the values under 40°C get higher slightly, and the phenomenon was also observed by Weichert [16] in static condition. This was because an increase in temperature promoted the softening of hemicellulose [2], which weakened the difference in MC between adsorption and desorption, causing sorption hysteresis to decrease as a result.

3.3. Thermodynamic Properties of Adsorbed Water. Figure 3 shows changes of the Q_L and $T\Delta S$ against moisture content during dynamic adsorption cycled at different periods for 10 mm thick poplar wood as an example. It is clear that the Q_L and $T\Delta S$ have similar tendency against moisture content. This indicates the bonding energy between water molecules and wood substance is closely related to the arrangement of water adsorbed in wood. First, both the Q_L and $T\Delta S$ decrease as moisture content increases, which suggests a reduction in bonding energy and arranging order of the adsorbed water with rising moisture content, due to a decrease in the attraction of water molecules by wood [17] because of the gradual growth of multilayer water with lower activation energy [8, 15] within the study range. Positive data of Q_L in the figure implies the forming of hydrogen bonds between water and its surrounding sorption sites in wood, while negative values from $T\Delta S$ at larger moisture content state that adsorbed water in wood was disordered, even less ordered than liquid water [11, 12]. Secondly, at a given moisture content, both the Q_L and $T\Delta S$ become greater as cyclic period extends, which could be attributed to the fact that with longer period, water adsorbed in wood has more time to rearrange and bond, resulting in higher arranging regularity and bonding energy. However, compared with static study, the dynamic Q_L and $T\Delta S$ were only about half of the values from Cao's results [11, 12] obtained at the corresponding times during adsorption under similar temperatures.

Changes of the Q_L and $T\Delta S$ against moisture content for both 4 mm and 10 mm thick poplar wood during dynamic adsorption cycled at 24 h are given in Figure 4. An adverse effect of specimen thickness can be found on differential sorption heat as well as differential entropy, which means Q_L and $T\Delta S$ are lower for thicker specimens at a certain moisture content. This is probably because there is not sufficient time for the thicker specimens, especially their inner part, to

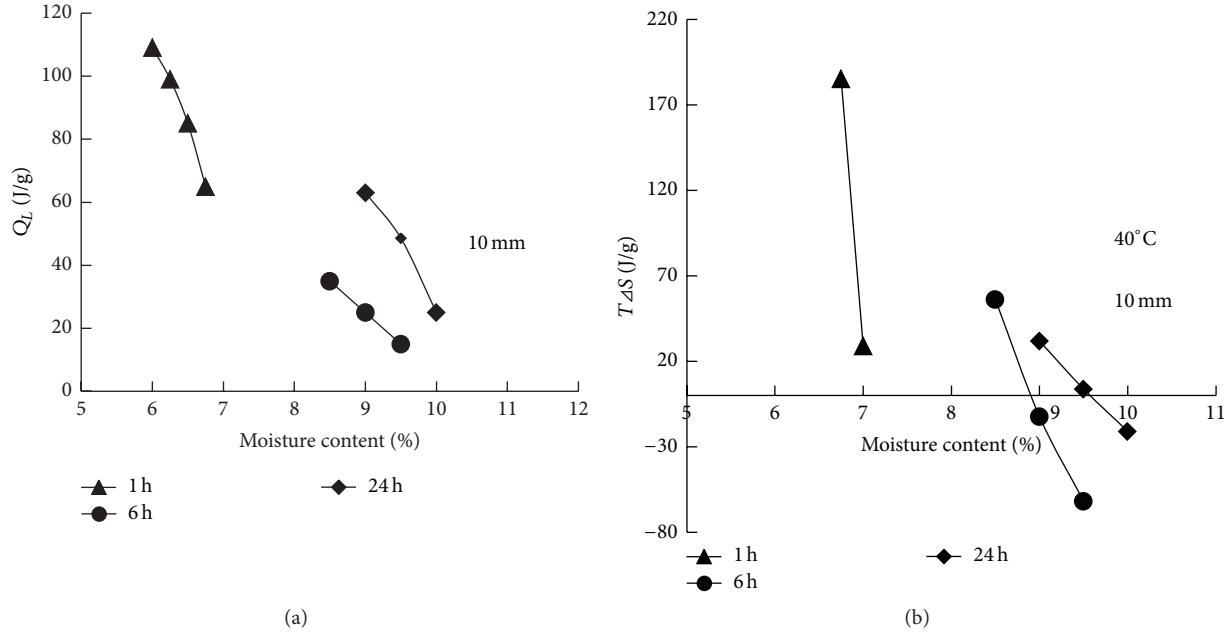


FIGURE 3: Differential heat of sorption Q_L (a) and differential entropy $T\Delta S$ (b) against moisture content during dynamic adsorption cycled at different periods for 10 mm thick poplar wood.

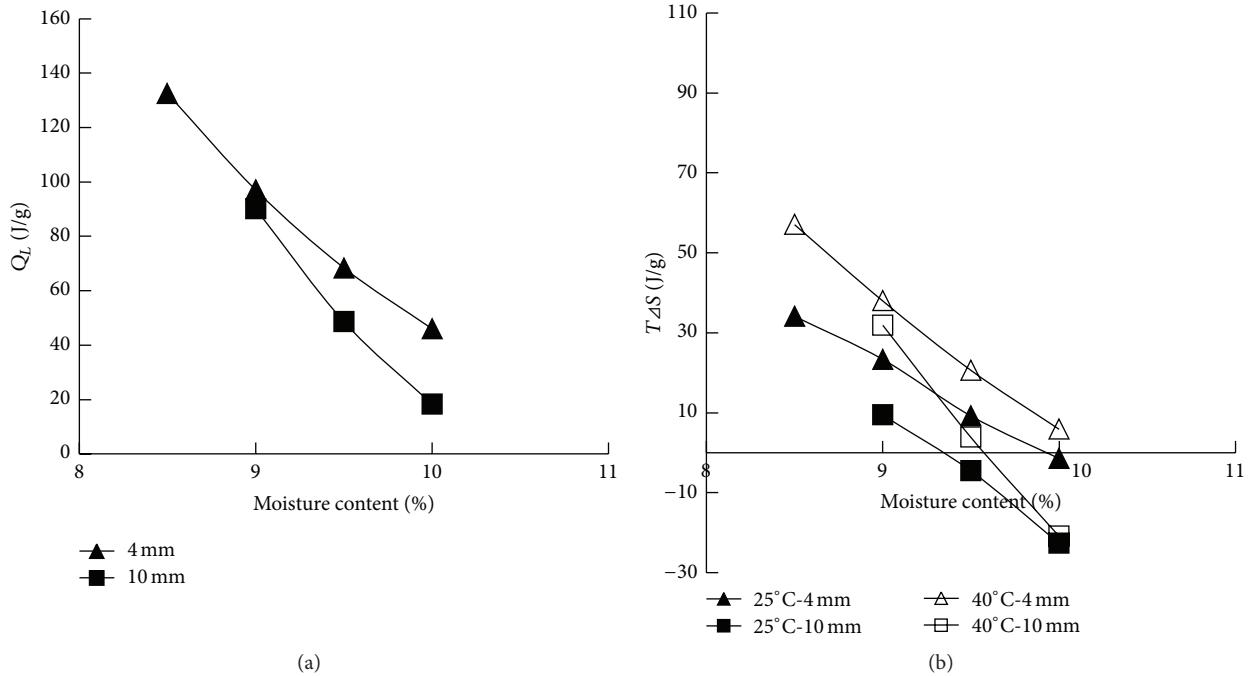


FIGURE 4: Differential heat of sorption Q_L (a) and differential entropy $T\Delta S$ (b) against moisture content for 4 mm and 10 mm thick poplar wood during dynamic adsorption cycled at 24 h.

respond. Therefore, the thicker specimens especially their inner part have no sufficient time to rearrange and bond, resulting in lower arranging regularity and bonding energy. In addition, $T\Delta S$ increases with higher temperature, mainly owing to the fact that the arrangement of adsorbed water in wood could be promoted by temperature.

Figure 5 illustrates the ΔG against moisture content in process of adsorption. As shown in Figure 5(a), like the Q_L and $T\Delta S$, ΔG decreases as moisture content increases. This is because the plasticity of wood increases with moisture content and less work was involved in making sorption sites available [11, 12]. On the contrary to $T\Delta S$, however, ΔG is

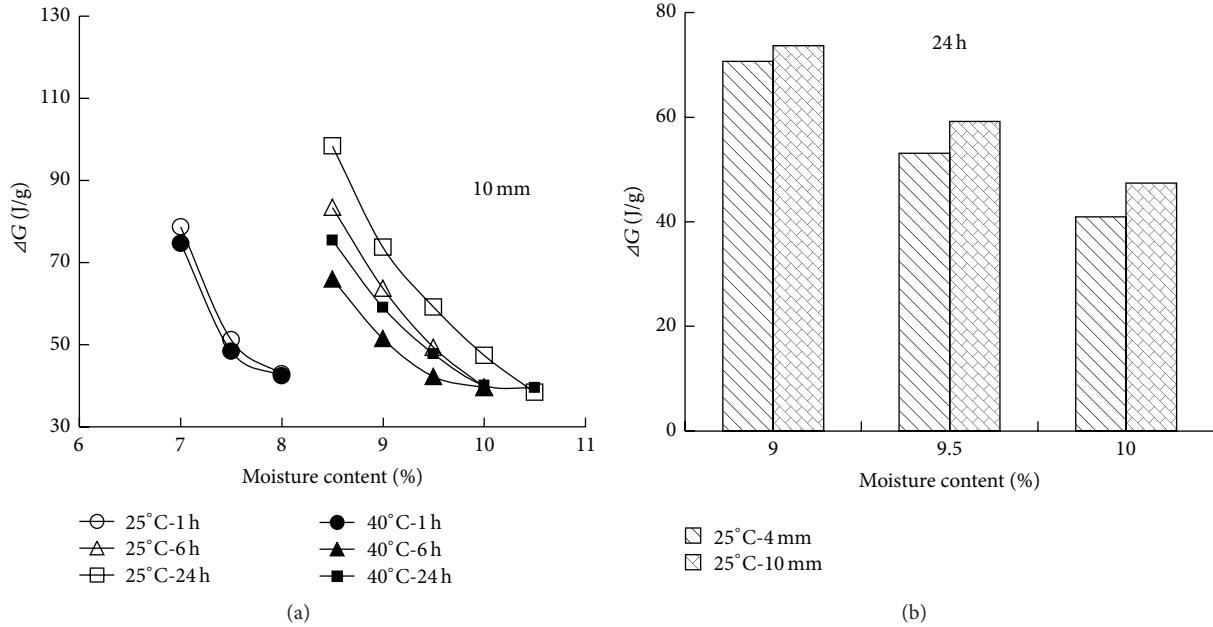


FIGURE 5: Free energy change ΔG against moisture content during dynamic adsorption by the effect of temperature and cyclic period (a) and specimen thickness (b).

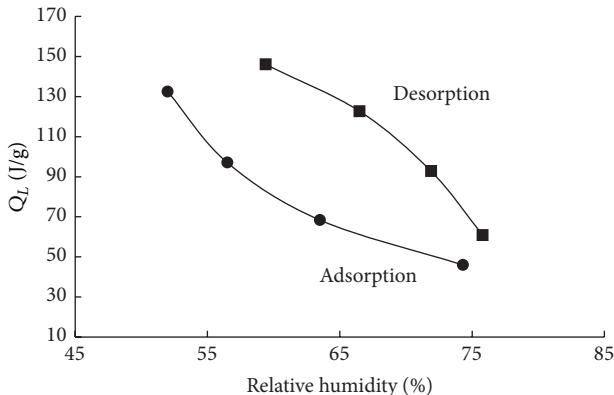


FIGURE 6: Differential heat of sorption Q_L for 4 mm thick poplar wood against relative humidity during dynamic adsorption cycled at 24 h.

lower at a higher temperature, as a result of heat added to the work to cut hydrogen bonds among wood structure probably. In addition, ΔG tends to reduce with the decreasing cyclic period or increasing specimen thickness (Figure 5(b)), the same as Q_L and $T\Delta S$ also.

3.4. Thermodynamic Sorption Hysteresis. By use of the correlation between moisture content and the imposed RH, relationship between thermodynamic parameters of the adsorbed water and RH can be worked out. And Figure 6 demonstrates Q_L for both adsorption and desorption of 4 mm thick poplar wood against RH cycled at 24 h. Thermodynamic sorption hysteresis, being interpreted as the difference in the

average number of hydrogen bonds formed on sorption sites in wood at a specific moisture content between adsorption and desorption, could be observed under dynamic condition as well, which can be explained reasonably by the effective hydroxyl group [11, 12].

Therefore, the hysteresis in Q_L , ΔG , and $T\Delta S$ of the adsorbed water, calculated by the difference between desorption and adsorption at certain RH, was defined here as Q_{Lp} , ΔG_p , and $T\Delta S_p$, respectively. Figure 7 displays effects of temperature, specimen thickness, and cyclic period on the Q_{Lp} of the adsorbed water in wood. It can be found in Figure 7(a) that, in contrast to moisture sorption hysteresis, thermodynamic sorption hysteresis becomes stronger with rising temperature. In addition, as shown in Figure 7(b), Q_{Lp} is lower for thinner specimens while it is inversely related to cyclic period.

Figures 8 and 9 express various effects on the ΔG_p and $T\Delta S_p$ of the adsorbed water in poplar wood against RH during dynamic sorption. Similar to the Q_{Lp} , ΔG_p and $T\Delta S_p$ increase as temperature and specimen thickness increase, or cyclic period decreases.

4. Conclusions

Thermodynamic approach was applied in this study to investigate the interaction between wood and water during dynamic sorption for two thicknesses of poplar wood specimens. Main conclusions can be summarized as follows:

- (1) The moisture content changed sinusoidally with the imposed RH and was inversely related to specimen thickness as well as temperature, but in a positive correlation with cyclic period.

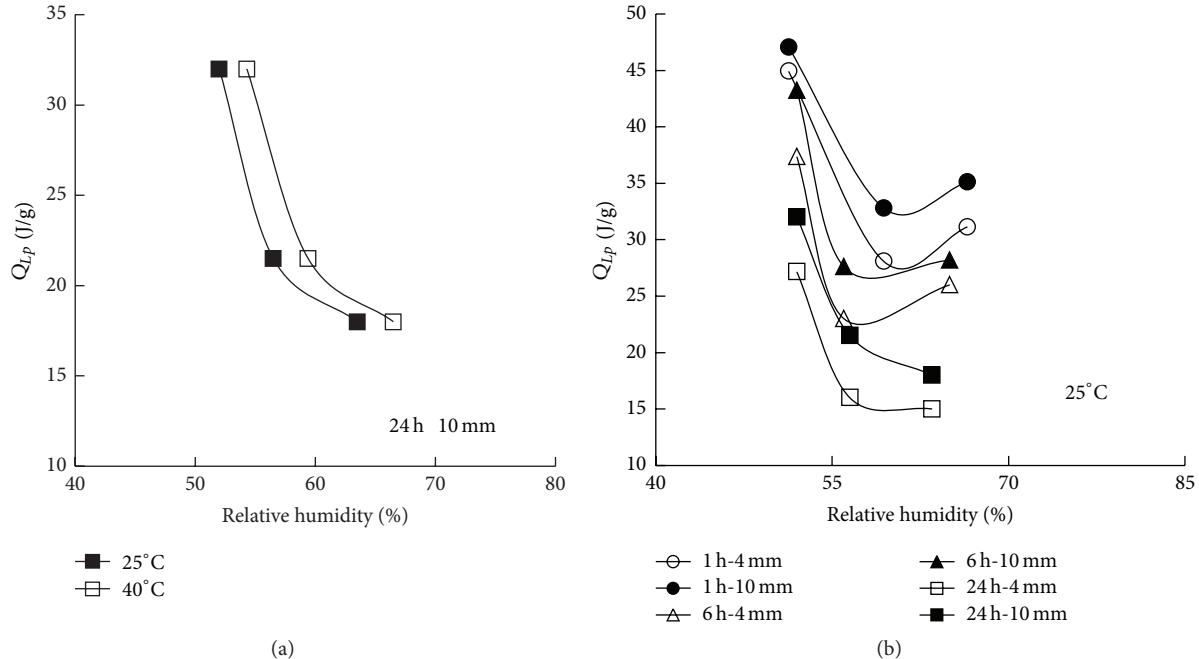


FIGURE 7: Effect of temperature (a) and specimen thickness and cyclic period (b) on differential sorption heat hysteresis Q_{Lp} of the adsorbed water.

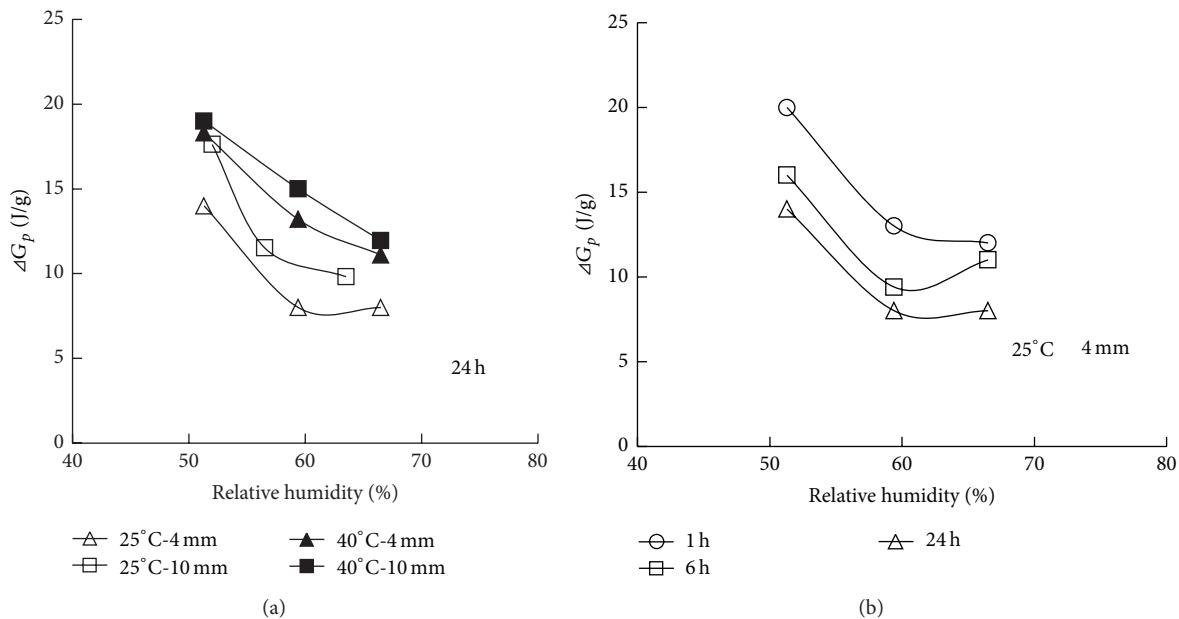


FIGURE 8: Free energy change hysteresis ΔG_p of the adsorbed water against RH by the effect of temperature and specimen thickness (a) and cyclic period (b).

- (2) Q_L , ΔG , and $T\Delta S$ of the adsorbed water during dynamic sorption all decreased with increasing moisture content or specimen thickness and decreasing cyclic period. However, temperature had opposite effects on ΔG and $T\Delta S$.
- (3) Both moisture sorption hysteresis and thermodynamic sorption hysteresis could be found. The former

became weak with rising temperature or thicker specimens, while the latter got clear when temperature or specimen thickness increased.

And an attempt will be made to test the generalization of these results and comparison will be further made to make the study more scientific and practical in the future work.

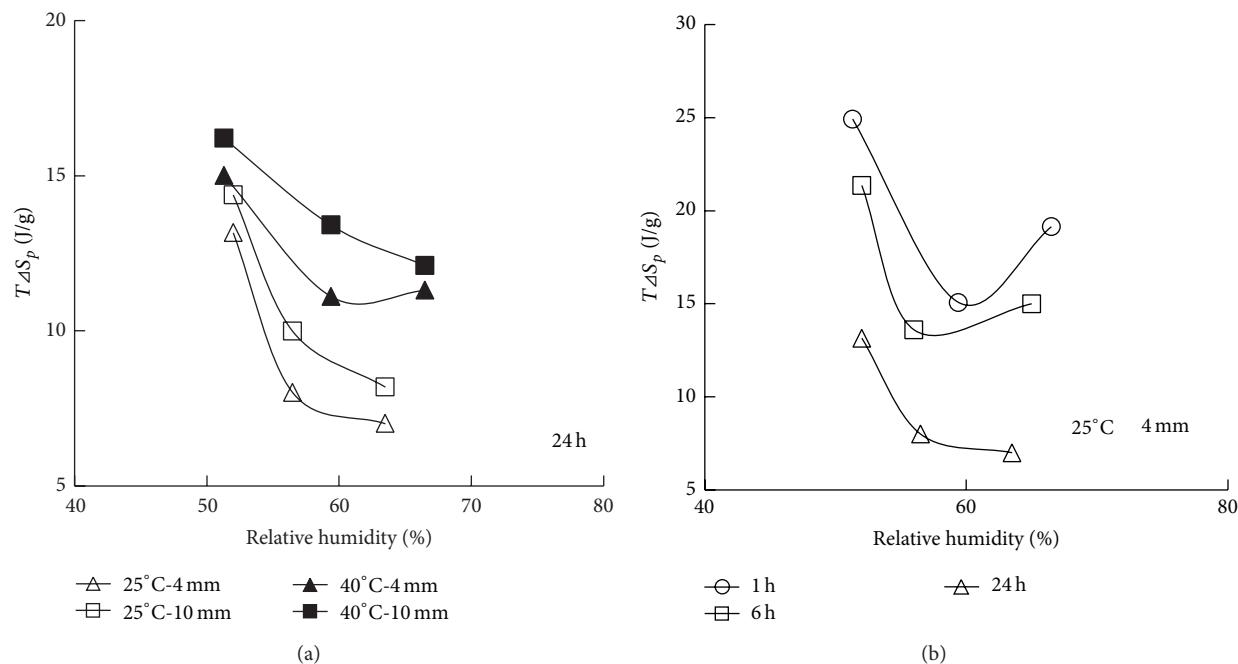


FIGURE 9: Differential entropy hysteresis $T\Delta S_p$ of the adsorbed water against RH by the effect of temperature and specimen thickness (a) and cyclic period (b).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] E. N. Ma and G. J. Zhao, *Special Topics on Wood Physics*, China Forestry, Beijing, China, 2012.
- [2] E. T. Engelund, L. G. Thygesen, S. Svensson, and C. A. S. Hill, "A critical discussion of the physics of wood-water interactions," *Wood Science and Technology*, vol. 47, no. 1, pp. 141–161, 2013.
- [3] R. M. Gong, J. Shen, L. Z. He, Y. L. Liu, and L. Y. Xu, "The effect of temperature on moisture movement and microstructure of larch wood in man-made forest," *Journal of Northeast Forestry University*, vol. 29, no. 5, pp. 31–33, 2001.
- [4] E. Ma, T. Nakao, G. Zhao, H. Ohata, and S. Kawamura, "Dynamic sorption and hygroexpansion of wood subjected to cyclic relative humidity changes," *Wood and Fiber Science*, vol. 42, no. 2, pp. 229–236, 2010.
- [5] W. Willem, "Hydrostatic pressure and temperature dependence of wood moisture sorption isotherms," *Wood Science and Technology*, vol. 48, pp. 483–498, 2014.
- [6] T. T. Yang and E. N. Ma, "Dynamic sorption and hygroexpansion of wood by humidity cyclically changing effect," *Journal of Functional Materials*, vol. 23, no. 44, pp. 3055–3059, 2013.
- [7] T. Zhao, E. Ma, and W. Zhang, "Moisture and temperature changes of wood during adsorption and desorption processes," *Wood and Fiber Science*, vol. 45, no. 2, pp. 187–194, 2013.
- [8] W. A. M. McMinn and T. R. A. Magee, "Thermodynamics properties of moisture sorption of potato," *Journal of Food Engineering*, vol. 60, no. 2, pp. 157–165, 2003.
- [9] S. Kadita, "Studies on the water sorption of wood," *Wood Research*, vol. 23, pp. 1–61, 1960.
- [10] A. J. Stamm, *Wood and Cellulose Science*, Ronald, New York, NY, USA, 1964.
- [11] J. Z. Cao, *Interaction between Water and Wood during Adsorption and Desorption Processes-from Dielectric and Thermodynamic Approaches*, Beijing Forestry University, Beijing, China, 2001.
- [12] J. Z. Cao and D. P. Kamdem, "Moisture adsorption thermodynamics of wood from fractal-geometry approach," *Holzforschung*, vol. 58, pp. 274–279, 2004.
- [13] K. E. Kelsey and L. N. Clarke, "The heat of sorption of water by wood," *Australian Journal of Applied Science*, vol. 7, pp. 160–175, 1956.
- [14] A. J. Stamm and W. Karl Loughborough, "Thermodynamics of the swelling of wood," *The Journal of Physical Chemistry*, vol. 39, no. 1, pp. 121–132, 1935.
- [15] C. Skaar, *Wood-Water Relations*, Springer, Berlin, Germany, 1988.
- [16] L. Weichert, "Investigations on sorption and swelling of spruce, beech and compressed beech wood at temperatures between 20° and 100°," *Holz Roh-Werkst*, vol. 21, no. 8, pp. 290–300, 1963.
- [17] A. Koumoutsakos and S. Avramidis, "Enthalpy-entropy compensation in water sorption by various wood species," *Holz als Roh- und Werkstoff*, vol. 57, no. 5, pp. 379–382, 1999.
- [18] G. Francisco, L. G. Fernandez, P. D. P. Esteban, S. A. G. Cristina, and F. Javier, "Sorption and thermodynamic properties

- of Terminalia superb Engl. & Diels and Triplochiton scleroxylon K. Schum. through the 15, 35 and 50°C sorption isotherms,” *European Journal of Wood and Wood Products*, vol. 72, pp. 99–106, 2014.
- [19] E. Tsami, “Net isosteric heat of sorption in dried fruits,” *Journal of Food Engineering*, vol. 14, no. 4, pp. 327–335, 1991.
 - [20] J. Z. Cao, G. J. Zhao, and Z. Y. Lu, “Thermodynamic characteristics of water absorption of heat-treated wood,” *Journal of Beijing Forestry University*, vol. 19, no. 4, pp. 26–33, 1997.
 - [21] L. G. Esteban, P. D. Palacios, F. G. Fernández, A. Guindeo, and N. N. Cano, “Sorption and thermodynamic properties of old and new pinussylvestris wood,” *Wood and Fiber Science*, vol. 40, no. 1, pp. 111–1121, 2008.
 - [22] A. P. Schniewind, “Creep-rupture life of Douglas-fir under cyclic environmental conditions,” *Wood Science and Technology*, vol. 1, no. 4, pp. 278–288, 1967.
 - [23] Macromolecule Academy, *Physical Properties of Macromolecule*, Kyoritsu Press, Tokyo, Japan, 1958.
 - [24] P. N. Peralta, A. P. Bangi, and A. W. C. Lee, “Thermodynamics of moisture sorption by the giant-timber bamboo,” *Holzforschung*, vol. 51, no. 2, pp. 177–182, 1997.
 - [25] K. E. Kelsey, “The sorption of water vapour by wood,” *Australian Journal of Basic and Applied Sciences*, vol. 8, pp. 42–54, 1957.
 - [26] Y. X. Liu and G. J. Zhao, *Wood Resources in Materials Science*, China Forestry Publishing House, Beijing, China, 2004.
 - [27] Q. F. Zhou, D. Y. Tu, L. Liao, and Q. Guo, “Variation of equilibrium moisture content of heat-treated *Couratari oblongifolia*, *Fraxinus excelsior*, and *Quercus rubra* wood,” *BioResources*, vol. 8, no. 1, pp. 182–188, 2012.



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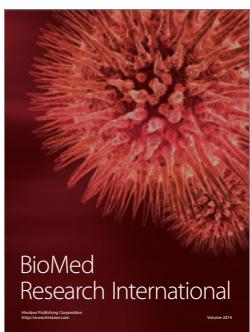
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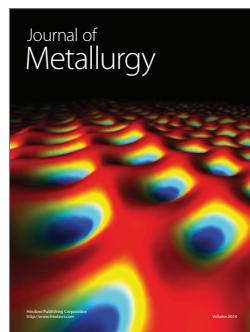
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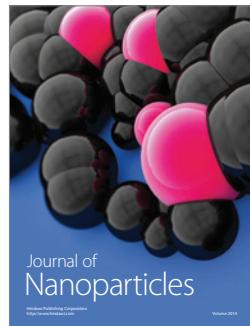
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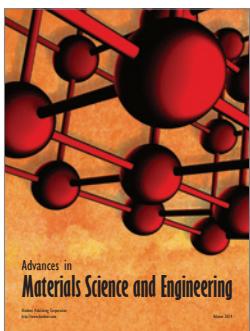
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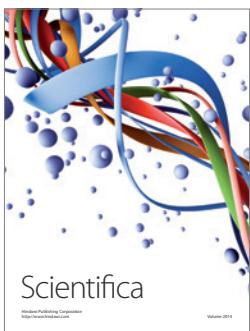
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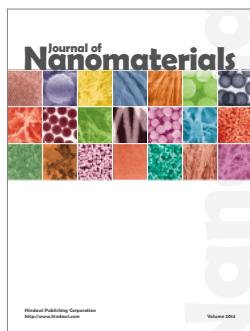
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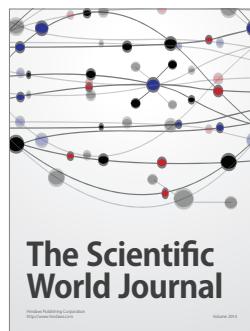
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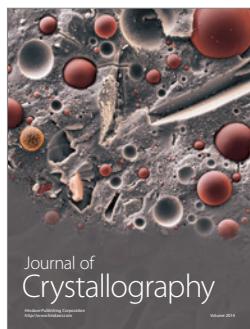
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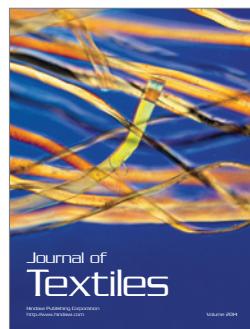
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