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Effect of Heat Treatment on Hygroscopicity of Chinese Fir (*Cunninghamia lanceolata* [Lamb.] Hook.) Wood

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Abstract: Chinese fir (*Cunninghamia lanceolata* [Lamb.] Hook.) is a widely planted species of plantation forest in China, and heat treatment can improve its dimensional stability defects and improve its performance. The wood samples were heat-treated at various temperatures (160, 180, 200, and 220 °C) for 2 h. To clarify the effect of heat treatment on wood hygroscopicity, the equilibrium moisture content (EMC) was measured, the moisture adsorption and desorption rates were determined, the hygroscopic hysteresis was examined, and the Guggenheim, Anderson, and de Boer (GAB) model was fitted to the experimental data. The moisture absorption isotherms of all samples belonged to the Type II adsorption isotherm, but the shape of the desorption isotherm was more linear for heat-treated wood samples, especially when the heat treatment temperature was higher. According to the results analyzed with ANOVA, there were significant differences in equilibrium moisture content between the control samples and the heat-treated samples under the conditions of 30%, 60%, and 95% relative humidity (RH, $p < 0.05$), and the results of multiple comparisons were similar. The decrease in hygroscopicity was more pronounced in wood treated at higher temperatures. The EMC of the 160–220 °C heat-treated samples of the control samples was 14.00%, 22.37%, 28.95%, and 39.63% lower than that of the control sample at 95% RH. Under low RH conditions (30%), water is taken up mainly via monolayer sorption, and multilayer sorption gradually predominates over monolayer sorption with the increase in RH. The dynamic vapor sorption (DVS) analysis indicated that the heat-treated wood revealed an increase in isotherm hysteresis, which was due to the change in cell wall chemical components and microstructure caused by heat treatment. In addition, the effective specific surface area of wood samples decreased significantly after heat treatment, and the change trend was similar to that of equilibrium moisture content.

Keywords: heat treatment; Chinese fir; dynamic vapor sorption (DVS); equilibrium moisture content (EMC); sorption hysteresis

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1. Introduction

Wood is a kind of natural macromolecular organism that is mainly composed of cellulose, hemicelluloses, and lignin. Wood has a high hygroscopicity due to the existence of a large number of accessible hydroxyl groups in the main substances constituting its cell walls. When temperature and humidity change, wood will absorb or release water from or into the surrounding air, causing its moisture content to change. The increase or decrease in the moisture content of wood will directly affect its dimensional stability, corrosion resistance, durability, mechanical properties, etc. Repeated dimensional changes caused by frequent variations in wood moisture content (MC) will eventually lead to crack formation in wood [1–3]. In order to reduce the hygroscopic property of wood and improve its serviceability, researchers have adopted various modification methods such as impregnation of resin, acetylation, esterification, and high-temperature heat treatment [4–6].

Among the many methods, high-temperature heat treatment is widely recognized because it can significantly improve the properties of wood without the use of chemicals.

Heat treatment is a modification technology that treats wood in an almost oxygen-free environment above 160 °C, which can change cell wall composition and in turn affect the physical properties of wood [7–9]. During the heat treatment process, hemicelluloses, lignin, and cellulose are all subject to change [10]. In contrast, hemicelluloses have poor thermal stability and are the first to degrade during heat treatment, resulting in acid hydrolysis and decarboxylation reactions [11,12]. The main change in cellulose due to heat treatment is the increase in crystallinity [13,14]. Lignin is the most thermally stable main cell wall component, but it is also subject to thermal degradation, with a variety of phenolic decomposition products produced during heat treatment [4]. All these changes will affect the pore structure of the wood cell wall and the amount of accessible hydroxyl group, which will change the moisture adsorption and desorption behavior of wood.

The determination of equilibrium moisture content (EMC) is a commonly used method to evaluate the hygroscopicity of wood. The traditional method uses saturated salt solutions to determine the EMC of wood. Generally, the samples are placed in a desiccator filled with different kinds of saturated salt solutions, until a constant weight is reached. This method, however, has limitations in the selection of humidity. The Dynamic Water Vapor Sorption (DVS) technique has been recognized for its ability to measure the water absorption of wood with less labor and potential greater accuracy than traditional gravimetric methods [15,16]. A number of relevant studies have been carried out in recent years. Researchers suggested that the degradation of hemicelluloses and the increase in cellulose crystallinity during heat treatment led to the reduction of the available hydroxyl group, thus reducing the hygroscopicity of wood [17,18]. Brito et al. [19] evaluated the effect of thermal modification on wood at temperatures of 180 °C, 200 °C, and 220 °C and found a reduction of up to 51.4% in EMC when exposed to 21 °C and 65% RH. Bytner et al. [20] studied the hygroscopicity of thermally modified (in a nitrogen atmosphere) black poplar wood and found that at a temperature of 220 °C, the EMC was two times lower than the EMC of non-modified black poplar. However, Rautkari et al. [21] studied the accessible OH content and EMC of acacia (*Acacia mangium*) and sesendok (*Endospermum malaccense*) wood, which were heat treated at 180, 200, and 220 °C for 1, 2, or 3 h, and reported that the correlation between EMC and hydroxyl accessibility is poor. The decrease in the hygroscopic properties of heat-treated wood might not be explained by the accessibility of wood hydroxyl groups alone. Hill et al. [18,22] studied the Scots pine (*Pinus sylvesteris* L.), which was heat treated at 200 °C for 3 h and suggested that the water vapor sorption isotherms were changed after undergoing multiple hygroscopic resolution cycles. Endo et al. [23] studied the hygroscopicity of 120 °C hydrothermally treated Sitka spruce wood, and the results showed that the reduction of hygroscopic properties included reversible effects. Thus, it is also necessary to systematically study the effect of heat treatment on wood hygroscopicity.

Chinese fir is one of the most widely planted trees in China. As a fast-growing tree species, dimensional instability is the main drawback that limits its wide application [24]. Heat treatment could affect the hygroscopicity of the wood and, as a result, might improve its dimensional stability. In order to further optimize the heat treatment process and improve the dimensional stability of Chinese fir wood so that its products will have a wider range of applications in furniture, flooring, interior decoration, etc., changes in the hygroscopicity of heat-treated Chinese fir were systematically investigated in this paper. The DVS apparatus was employed to acquire the EMC of the specimens. ANOVA analysis and multiple comparisons were used to evaluate the effect of heat treatment on hygroscopicity. The EMC increment, EMC decrement, and sorption hysteresis were discussed as well. Furthermore, the GAB model was used to evaluate the adsorption isotherm.

2. Materials and Methods

2.1. Materials

Defect-free specimens with a dimension of 150 mm × 15 mm × 15 mm in the longitudinal (L), tangential (T), and radial (R) directions, respectively, were cut from the same growth rings of air-dried Chinese fir (*Cunninghamia lanceolata* [Lamb.] Hook.) heartwood. The heat treatments were processed in airtight equipment that was controlled with the condition of no more than 2% of the oxygen content at 160 °C, 180 °C, 200 °C, and 220 °C for 2 h. The treated specimens were then cooled down to room temperature inside the equipment and stored in a sealed container with P2O5 at room temperature. Only specimens of pure earlywood were used in this experiment. The samples were called HT160 (160 °C), HT180 (180 °C), HT200 (200 °C), and HT 220 (220 °C). For more detailed information, see the previously published paper [8].

2.2. Dynamic Vapor Sorption (DVS) Experiments

- Moisture absorption and desorption:

The experiments were conducted using a high-precision DVS instrument (DVS Intrinsic, Surface Measurement System Ltd., London, UK). A high-precision microbalance with an accuracy of 0.1 μg was equipped for the instrument, and the initial sample weight was about 25 mg. The relative humidity (RH) was controlled by N_2 and H_2O vapor, and the tests were performed at 25 °C. The sample mass was collected every 5 s during the test. When the sample mass changed less than 0.002% of the sample mass within 10 min, the test automatically entered the next stage. The steps for humidity change in the range of 0%–90% RH are 10%, and the step size for 90%–95% is 5%.

- Hysteresis ratio:

Wood hygroscopic hysteresis means that the hygroscopic equilibrium moisture content of wood is always less than the desorption equilibrium moisture content during the process of reaching equilibrium moisture content. The calculation of the hygroscopic hysteresis rate is performed by first calculating the absolute hysteresis value (obtained by subtracting the adsorption EMC from the desorption EMC values). The hysteresis ratio is the ratio of absolute hysteresis to the desorption EMC and the equation is as follows [17]:

$$R_{HR} = \frac{EMC_{de} - EMC_{ad}}{EMC_{ad}} \times 100 \quad (1)$$

where EMC_{ad} and EMC_{de} are the absorption EMC and desorption EMC under the same temperature and humidity conditions, respectively, %.

- GAB model:

In this study, the RH was varied from 0% to 95%, and the GAB model was used to fit the isotherms, as it is the most suitable method when RHs higher than 90% are included [25]:

$$EMC = M_m \frac{K_{GAB} \cdot C_{GAB} \cdot RH}{(1 - K_{GAB} \cdot RH)(1 - K_{GAB} \cdot RH + K_{GAB} \cdot C_{GAB} \cdot RH)} \quad (2)$$

where *RH* is the given relative humidity; M_m is the monolayer saturation moisture content; and K_{GAB} and C_{GAB} are the equilibrium constants related to multilayer and monolayer sorption, respectively.

- The internal specific surface area (S_{GAB}):

The S_{GAB} is obtained from the monolayer saturation moisture content Mm by the application of a relation [25]:

$$S_{GAB} = \frac{M_m \cdot L \cdot \sigma}{M} \quad (3)$$

where L is the Avogadro number, 6.022 × 1023, σ is the average area where water occupies the complete monolayer, and 0.114 nm^2, and M is the molar mass of water, 18 g/mol.

3. Results and Discussion

3.1. Water Vapor Sorption Behavior of the Samples

The moisture sorption isotherms of the wood samples are shown in Figure 1. According to the International Union of Pure and Applied Chemistry (IUPAC) classification method, all the moisture absorption isotherms of the samples were typical S-shaped curves, which belonged to Type II adsorption isotherms [26]. However, the shape of the desorption isotherms of the heat-treated samples, especially for HT220, was much more linear compared with the classic sigmoidal shape of untreated wood, which was consistent with that reported by Hill [4]. The EMC of the reference and the heat-treated samples showed a gradually increasing trend with the increase in RH during the process of moisture adsorption. Under the same RH, the EMC gradually decreased with the increase in treatment temperature for the heat-treated samples, and the EMCs of all the heat-treated samples were lower than those of the references, which was consistent with the results obtained by previous studies on the moisture adsorption performance of heat-treated wood using a dynamic water vapor adsorption instrument [17].

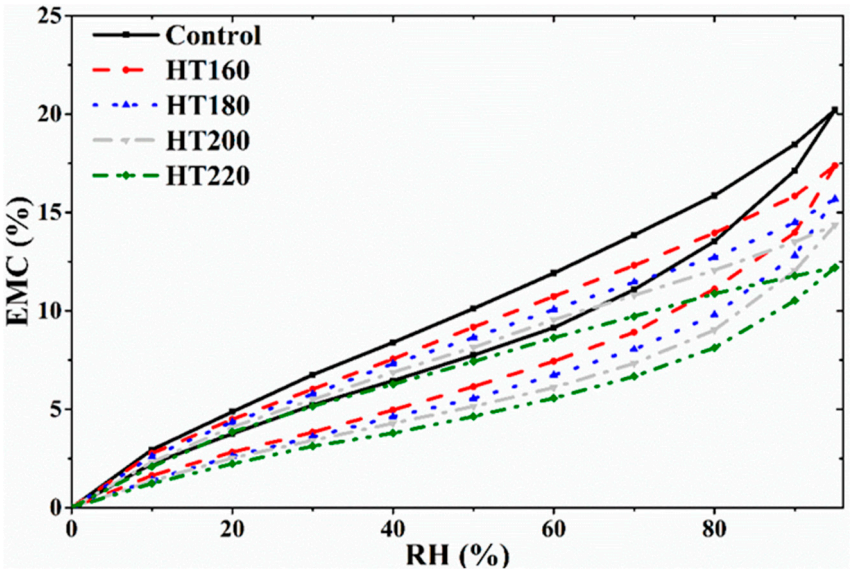

Figure 1. Adsorption and desorption isotherms of the samples.

According to the shape of the isotherms, the moisture absorption curve of each sample did not show an obvious rapid rise after the RH was greater than 90%. Therefore, under the current test conditions, there may not be obvious capillary condensation inside each sample. Similar results were found in the study of Norway spruce by Thygesen et al. [27], and they also showed that below the fiber saturation point, capillary condensation had no significant contribution to EMC. The Type II adsorption isotherm was characterized by monolayer adsorption under low humidity conditions, and the second layer adsorption and multilayer adsorption gradually appeared with the increase in RH. According to the above results, high-temperature heat treatment might influence both monolayer adsorption and multimolecular layer adsorption in the process of wood moisture absorption, since multimolecular layer adsorption was carried out on the basis of the monomolecular layer. Previous studies have shown that heat treatment reduces the number of hygroscopic groups in the cell wall components of wood, which affects the wood hygroscopicity, causing a reduction in the amount of monolayer water, which in turn reduces the amount of multilayer water [28]. In addition, Phuong et al. (2007) [29] found that the number of hydroxyl groups decreased with the increase in heat treatment intensity, and the change

in the number of accessible hydroxyl groups was positively correlated with the change in wood hygroscopicity; however, the study of Rautkari et al. [21] came to contradictory conclusions. Therefore, the change in the number of accessible hydroxyl groups may only be one of the factors affecting the hygroscopicity of wood. As mentioned above, in addition to the hygroscopic groups, the crosslinking of lignin and the change in the crystallinity of cellulose during heat treatment may all affect the hygroscopicity of wood. Therefore, the reasons for the reduction in wood hygroscopicity by heat treatment need to be further explored.

In order to explore the difference in the EMC between the reference samples and the heat-treated samples under different RH conditions, the EMC of the samples under 30%, 60%, and 95% RH was selected for analysis to reflect the effect of heat treatment temperature on the EMC of wood under low, medium, and high RH conditions. Under the condition of 30% RH, the average EMC of the references was 5.21%, and for heat treatment samples, it was 3.83% (HT160), 3.60% (HT180), 3.42% (HT200), or 3.13% (HT220), respectively. Compared with the control material, EMC decreased by 26.49%, 30.90%, 34.36%, and 39.92%, respectively. When the RH increased to 60%, the EMC of the control samples was 9.15%, which was 18.68% (HT160), 26.34% (HT180), 33.33% (HT200), and 39.12% (HT220) higher than that of the 160–220 °C heat-treated samples, respectively. Under the condition of 95% RH, the EMC of the 160–220 °C heat-treated samples was 14.00%, 22.37%, 28.95%, and 39.63% lower than that of the control sample. From the data, it can be seen that with the increase in relative humidity, the difference in the EMC between the references and the samples heat-treated at relatively low temperatures gradually decreased. However, the difference in the EMC between HT220 and the references was always about 40%. The results analyzed with ANOVA are shown in Table 1. The results of the ANOVA in Table 2 indicate that the EMC of the heat-treated samples and that of the control samples are significantly different, indicating that heat treatment at 160–220 °C all had significant effects on the hygroscopicity of wood under the same RH conditions.

Table 1. ANOVA of the effect of heat treatment temperature on EMC.

Relative Humidity/%	Source	DF	SS	MS	F Value	Sign.
30	Inter-group	4	7.362	1.840	42.531	*
	Intra-group	10	0.433	0.043		
	Total	14	7.795			
60	Inter-group	4	23.250	5.812	211.933	*
	Intra-group	10	0.274	0.027		
	Total	14	23.524			
95	Inter-group	4	110.381	27.595	572.804	*
	Intra-group	10	0.482	0.048		
	Total	14	110.863			

Note: * means a significant difference at the 0.05 level.

Table 2. Multiple comparisons for the EMC of samples after heat treatment at different temperatures.

Temperature/°C	30% RH		60% RH		95% RH	
	EMC/%	Duncan Grouping	EMC/%	Duncan Grouping	EMC/%	Duncan Grouping
Control	5.21	A	9.15	A	20.21	A
160	3.83	A	7.44	B	17.38	B
180	3.60	AB	6.74	C	15.69	C
200	3.42	B	6.10	D	14.36	D
220	3.26	C	5.57	E	12.20	E

Note: significance level: $\alpha < 0.05$.

To further analyze the influence of heat treatment temperatures on the hygroscopicity of wood, the EMCs of heat-treated wood samples and references under the RH conditions

of 30%, 60%, and 95% were investigated. For multiple comparisons, the average EMC and Duncan grouping analysis of the samples are shown in Table 2. As shown in the table, at 30% relative humidity, there is no significant difference in EMC between the reference samples and the samples heat-treated at 160 °C and 180 °C, nor are the samples heat-treated at 180 °C and 200 °C. However, there were significant differences in the EMC between the untreated samples and HT200 and HT220. Under the conditions of 60% RH and 95% RH, the EMCs of the control samples and the heat-treated samples were significantly different from each other. Under the condition of low relative humidity, a heat treatment temperature higher than 200 °C would have a significant effect on the hygroscopicity of wood, and under the environment of relatively high humidity, heat treatment at 160–220 °C had a significant effect on the hygroscopicity of wood.

3.2. Moisture Adsorption and Desorption Rate

The EMC increment and decrement during the moisture adsorption (left) and desorption (right) processes of the samples are shown in Figure 2. When the RH was lower than 30%, the values of the EMC increment of the samples showed a decreasing trend with the increase in RH, which was consistent with previous studies [30]. With the increase in RH from 30% up to 90%, the overall trend of the EMC increment was a gradual increase but it differed slightly from sample to sample. After the RH was higher than 90%, the EMC increment decreased again. According to the previous study, when moisture adsorption was under low RH conditions, the fast process appeared to be associated with the formation of monolayer water [31,32]. Therefore, the gradual decline of the EMC increment in the lower RH range mainly reflects the change in monolayer adsorption at the sorption sites inside the wood. At this stage, the EMC increment of the references was significantly greater than that of the heat-treated wood samples, and it was especially obvious at 10% RH. It was indicated that the control samples began rapid monolayer adsorption under the condition of low RH, and the adsorption amount under each RH condition was larger than that of the heat-treated samples. Multi-molecular layer adsorption began to form inside the wood and gradually dominated with the increase in RH. At an RH above 60%, the range of the variation in the EMC increment for each sample increased significantly, which should be due to the softening of hemicelluloses. Researchers pointed out that at room temperature, hemicelluloses begin to soften in the range of 65%–70% RH, and the glass transition of cell wall amorphous substances at higher RHs may significantly affect the hygroscopic behavior of wood [33]. Since the amorphous substance in the cell wall changes from a glassy to a highly elastic state, the rigidity of the network structure becomes weaker as the modulus changes from high to low, and the decrease in the viscosity between the macromolecular chains makes the relative slip easier. Thus, more moisture sorption sites appear, resulting in significantly greater moisture absorption [34,35]. At this stage, the changes in the EMC increment of the control wood samples and HT160 were similar, being higher than that of HT180 and HT200, and the EMC increment of HT220 was significantly lower than that of other samples. Heat treatment may lead to an increase in the stiffness of wood cell walls [17], which in turn increases the difficulty of relative slippage between macromolecular chains, thereby reducing the number of resulting sorption sites. The effect of heat treatment on cell wall stiffness became more obvious as the heat treatment temperature increased, so the range of variation of the EMC increment for each sample at this stage decreased with an increase in the heat treatment temperature. Since the RH was increased by 5% at the end of the test and changed by 10% during the previous test, a decrease in the increase in the EMC was observed in Figure 2.

The EMC decrement of the samples during the desorption process is shown in the right part of Figure 2. As shown in the figure, an increase was found in the EMC decrement as the RH changed from 90% to 80%. The increase is due to the decreased target RH step (from 5% to 10%). The EMC decrement of each sample basically showed a trend of first decreasing and then increasing along with the decrease in RH. However, the decreasing trend of the EMC decrement of the control samples in the initial stage of desorption was

more obvious. Since the desorption process can be viewed as the inverse of the hygroscopic process, the difference between the two is mainly related to the rate of response of the cell wall to the ingress or egress of moisture, and the effect of hygroscopic hysteresis needs to be taken into account [22]. In general, within the same range of RH, the increase or decrease in the value of the EMC of the heat-treated wood samples was smaller than that of the control samples, that is, under the same environmental conditions, the change in the EMC with RH in the control samples was larger than that in heat-treated samples, which was an important reason for the superior dimensional stability of the heat-treated wood over that of the untreated wood.

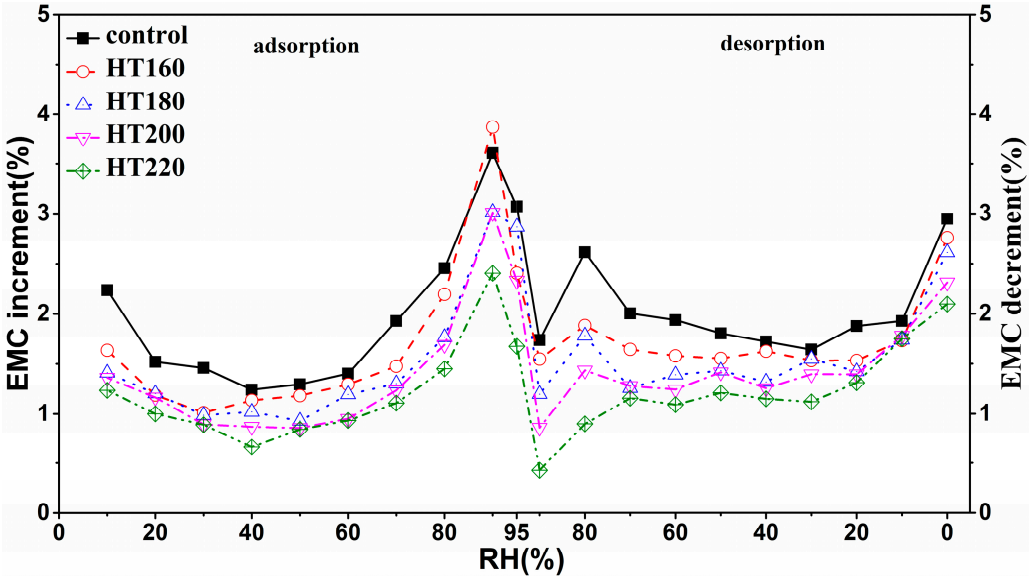

Figure 2. EMC increment and decrement of the samples.

3.3. Effect of Heat Treatment on Sorption Hysteresis

The hygroscopic hysteresis rate of the samples was calculated using Equation (1) and is shown in Figure 3. From the figure, it can be seen that the hysteresis rate of the wood was increased by the heat treatment, which is consistent with the results of previous studies [17,33,36]. The hysteresis rate of moisture absorption basically showed a gradual increase with the increase in the heat treatment temperature. In the process of hygroscopicity, the wood cell wall would be swelling and forming micropores, and these micropores would be reclosed in the process of desorption. The changes in the pores would affect the number of accessible hydroxyl groups, and the hysteresis was related to the response rate of the cell wall to the ingress or egress of moisture [22]. For the hysteresis phenomenon, researchers [17,29] suggested that it might be possible that the swelling of cell walls would be restrained during water adsorption due to the effect of the cross-linking of less organized wood constituents. The cross-linking of cell wall components leads to a stiffer matrix, and in the process of moisture adsorption, the process of opening the inner surface of cell walls that makes the sorption sites available for bonding water molecules was affected. In the process of moisture desorption, the stiffer matrix also influenced the closure of the inner surface, which hindered water desorption. Elevated heat treatment temperatures would lead to the decomposition of hemicelluloses and increase the additional cross-linking of lignin. Thus, the stiffness of the cell wall matrix must be increased, resulting in a higher adsorption hysteresis.

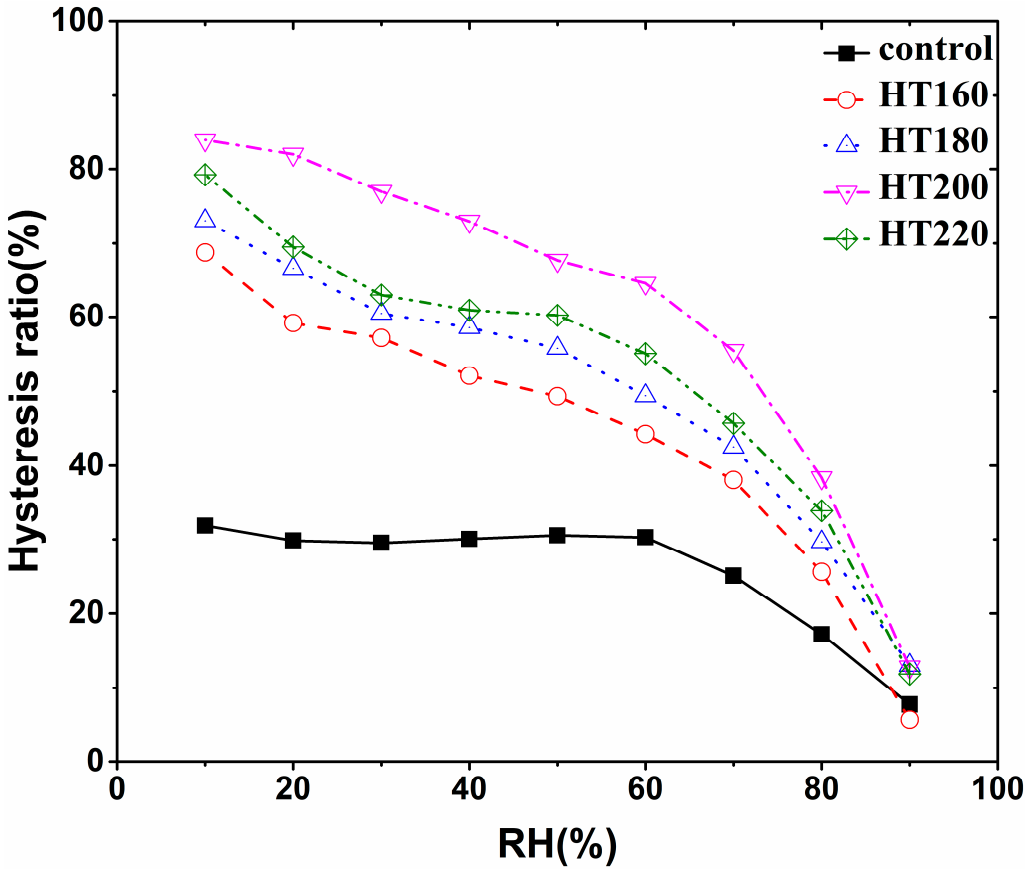

Figure 3. Hysteresis ratio of the wood samples.

3.4. Fitting the GAB Model to the Data

The results of the GAB model fitting are presented in Table 3. All the R^2 values were above 99.0%, indicating that the fits were considered to be valid. GAB parameters can reflect the effect of heat treatment on the hygroscopic properties of wood. Among them, C is an equilibrium constant associated with monolayer adsorption, and its value is always positive [37]. The K is the correction coefficient associated with multimolecular layer adsorption, and its value should be no greater than 1 [38]. In this study, the values of K ranged from 6.68 to 7.86 and C ranged from 0.76 to 0.80, which is consistent with what was reported in the literature above. In addition, the Mm is the maximum monolayer water absorption, which reflects the impact on the water absorption of the monolayer. The obtained Mm value ranged from 5.73% for untreated samples to 3.51% for HT220 samples, which reflected the influence of heat treatment on the water absorption of the monolayer. The amount of monolayer water adsorption decreased gradually with the increase in heat treatment temperature, but the change was not obvious when the treatment temperature was increased from 200 °C to 220 °C. The internal specific surface area (S_{GAB}), which corresponds to the monolayer capacity, could be estimated by Mm. According to Table 3, the obtained internal specific surface area ranged from 171 m^2/g to 134 m^2/g, along with the heat-treated temperature increasing from 160 °C to 220 °C, which is equivalent to about 78.08%, 69.41%, 62.56%, and 61.19% of the untreated samples. This trend was consistent with that of the EMC mentioned above. The S_{GAB} was calculated based on the amount of monolayer water absorption. However, the amount of monolayer water absorption is directly related to the amount of accessible hydroxyl groups, so the effective specific surface area actually depends on the amount of effective hydroxyl group.

Table 3. Fitted model parameters for the samples obtained from the GAB model.

Treated-Temperature/°C	M_m (%)	K	C	R^2	S_{GAB} (m^2/g)
Control	5.73	0.7651	7.38665	0.999	219
160	4.47	0.78991	6.46471	0.997	171
180	3.96	0.79440	7.04448	0.998	152
200	3.58	0.79874	7.86002	0.998	137
220	3.51	0.76497	6.67798	0.999	134

4. Conclusions

The hygroscopicity of heat-treated wood at 160, 180, 200, and 220 °C, as well as their reference samples, were investigated in this study. The EMCs under different RH conditions were obtained by DVS, and the shape of the desorption isotherm was more linear for heat-treated wood samples. This phenomenon suggests that the hygroscopic behavior of wood changes after heat treatment, and the reason for this change should be related to the changes in the chemical components and pore structure of the wood cell wall due to heat treatment. Heat treatment at 160 °C would affect wood hygroscopic properties, especially under high relative humidity conditions. As the heat treatment temperature increased, wood hygroscopicity was affected more obviously. The results analyzed with ANOVA and multiple comparisons showed that heat treatment can be very effective in reducing the hygroscopicity of wood when the heat treatment temperature reaches 200 degrees Celsius, and the relative humidity is high. Under lower relative humidity conditions, the EMC increment of the control samples was significantly greater than that of the heat-treated wood samples, and at this stage, moisture adsorption appeared to be mainly associated with the formation of monolayer water. Multimolecular layer water adsorption gradually dominated with the increase in RH, and the difference in the EMC increment was related to the change in the chemical component content of each sample due to the heat treatment. The hysteresis ratio of the wood samples increased with the increasing heat treatment temperature due to the change in the cell wall chemical components and microstructure caused by heat treatment. The GAB fitting results showed that the effective specific surface area of the heat-treated wood samples decreased significantly, and the declining trend of the effective specific surface area was similar to that of the EMC.

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