Effect of Lignin Removal on Moisture Absorption of Wood

He Zhang¹,², Yuchen Chen²,*, Yongkuo Wang¹,³

¹Ministry of Civil Affairs of the People’s Republic of China, Beijing, China
²School of Laval University, Quebec

*Corresponding author e-mail: carmenchen24@outlook.com, mishanxixi@126.com, yongkuow@163.com

Abstract. In the study, we carried out heartwood and sapwood of fast-growing Chinese fir as research objects, the lignin was removed by sodium chlorite method, then the changes of wood chemical composition were detected by Raman spectra, the moisture absorption changes of wood were studied by saturated salt solution method, and the H-H model fitting data was used to analyze the effect of lignin removal. It aims to provide reference for the research and development of new wood modification technologies or wood-based products [4]. The results showed that there was no significant difference between sapwood and heartwood when the relative humidity was lower than 30%. With the increase of relative humidity in the environment, the water absorption capacity of sapwood cells was higher than that of heartwood. The water absorption capacity of heartwood and heartwood after delignification was significantly stronger than that of control wood, especially when the relative humidity was 95%, the equilibrium water content reached about 60%.

1. Introduction

Wood is one of the only four renewable materials in the world, and its processing and utilization have attracted more and more attention from the world. However, in order to meet the people's growing yearning for a better life, the pressure on China's timber supply is increasing. International timber trade bears more ecological risks and policy risks. Reducing dependence on tropical hardwood has become the consensus of many countries including China. China has also implemented a national reserve forest construction project, and forests play an important role in the construction of the ecological system of mountains, rivers, forests, fields, lakes and grasses. Therefore, the wood industry must accelerate two changes, one is the continuous acceleration of the transformation of raw material supply to fast-growing plantations, and the other is the acceleration of the transformation of utilization mode to high-quality utilization. However, these developments and changes have always been unable to avoid the fundamental problem of unsatisfactory wood properties of artificial forests. Due to the common problems of low density, poor dimensional stability, low mechanical strength and poor durability, this greatly limits the application of plantation wood, especially the use of high-quality solid wood.

In recent years, modification technologies based on wood chemical properties, or chemical-based materials derived from wood, have also attracted much attention from academia. The more advanced technologies include transparent wood, super-strong wood, sponge wood and so on. These studies have provided new angles and new ideas for the utilization of high quality wood. These studies are all...
based on the composition relationship of the basic chemical components of wood. This requires further exploration of the physical or chemical properties of cellulose, hemicellulose, lignin and extracts. This has become the focus and hotspot of wood scientists at home and abroad. Based on this, this paper takes fast-growing Chinese fir as the research object. The effect of lignin removal on moisture absorption of fast-growing wood was discussed. The physical and chemical properties of wood are mainly studied by Raman spectrometer. The effect of saturated salt solution method on hygroscopicity of heartwood and sapwood was studied. It aims to provide reference for the research and development of new wood modification technologies or wood-based products.

2. Materials and Methods

2.1. Materials

The tested fir wood is a clone of fir wood collected from Kaihua County Forest Farm in Zhejiang Province. Dam 8 planted in 1998, no CL-8-4. Cut 3.5m to 5.5m timber from the felled sample along the tree height direction, according to the sapwood and heartwood two parts respectively cut specimens, processing to 20 mm×20 mm×5 mm(R× T× L) for standby. The chemical reagent is sodium chlorite (98.0%, 500g), Chengdu aikeda chemical reagent limited company produces, Glacial acetic acid (analytically pure, mass fraction ≥99.5%), Guangdong Guanghua Sci-Tech Co.,Ltd produce. Self-made distilled water.

2.2. Method

2.2.1. Lignin Removal. Selecting the prepared sample, Drying at 103 °C for 24 hours, Obtaining the absolute dry quality before delignification, Based on every 150ml distilled water, 1:2 mixed sodium chlorite and glacial acetic acid solution, To configure, Put the test piece into the mixed solution. Water bath heating at 85 °C for 12 hours, and then put into a drying box after air drying for several days. Dry at 103 °C for 24h, the absolute dry quality after delignification is obtained, the weight loss rate (%) of delignification treatment was calculated. The removal of lignin is specifically carried out according to the method in “Chemical Components Effect on Mechanical Properties of Wood Cell Wall” [1].

2.2.2. Hygroscopicity experiment. First, the sample was dried for 24 hours. Weigh, Then 100ml of magnesium chloride, sodium bromide, potassium chloride and potassium nitrate are added respectively at 20°C to prepare saturated salt solution. The ambient humidity is 30%, 60%, 80% and 95% respectively. The quality is weighed after the time interval of 24 hours and 48 hours. Wait until equilibrium is reached and remove it. Data processing and calculation methods refers to “Wood Drying Science” [5].

On the premise of a certain temperature, the equilibrium water content in the sample cells is:

\[ M_S = \frac{(W_{moist} - W_{dry})}{W_{dry}} \]  

In the formula:

- \( M_S \) — Equilibrium moisture content of samples;
- \( W_{moist} \) — The sample weight at a certain relative humidity;
- \( W_{dry} \) — Absolute dry weight of sample.

3. Results and Discussion

3.1. Weight Loss Rate after Treatment

Table 1 shows the changes of heartwood and sapwood before and after delignification. After being treated by sodium chlorite method, Lignin is effectively removed.
Table 1. Sample quality before and after treatment

| Type       | Sample number | Pre-treatment quality (g) | Quality after treatment (g) | Weight Loss Rate (%) |
|------------|---------------|---------------------------|----------------------------|----------------------|
| heartwood  | X1            | 0.4845                    | 0.3341                     | 31.04%               |
|            | X2            | 0.8021                    | 0.5506                     | 31.36%               |
|            | X3            | 0.6332                    | 0.4333                     | 31.57%               |
|            | X4            | 0.6189                    | 0.4421                     | 28.57%               |
|            | X5            | 0.6056                    | 0.4073                     | 32.74%               |
|            | Average (standard deviation) | -                      | -                          | 31.06%(0.0137)        |
| sapwood    | B1            | 0.8278                    | 0.5927                     | 28.40%               |
|            | B2            | 0.6812                    | 0.4865                     | 28.58%               |
|            | B3            | 0.5346                    | 0.3653                     | 31.67%               |
|            | B4            | 0.6547                    | 0.4658                     | 28.85%               |
|            | B5            | 0.6453                    | 0.4367                     | 32.33%               |
|            | Average (standard deviation) | -                      | -                          | 29.97%(0.0168)        |

3.2. Raman Spectrum Analysis

In this study, Raman spectroscopy was used to further analyze the effect of delignification on wood spectroscopy. Table 2 shows the Raman spectrum characteristic peaks of Chinese fir cell wall in 4000-400 cm$^{-1}$ band. The Raman spectrum after treatment is shown in Figure 1.

Table 2. Characteristic peaks of Raman spectra of cell wall of Chinese fir

| Wavelength(cm$^{-1}$) | Spectral peak attribution |
|------------------------|---------------------------|
| 1273                   | Telescopic vibration of benzene ring |
| 1604                   | Telescopic vibration of benzene ring |
| 1655                   | C=C bond and γ-C=O bond |
| 2942                   | Methoxy C-H bond |
| Cellulose              | 917                        | C-H deformation |
|                        | 1095                       | CC and CO vibrations |
|                        | 1463                       | HCH and HOC plane bending vibration |
|                        | 2889                       | CH and CH$_2$ Telescopic Vibration |
| glucomannan            | 1340                       | Mannose skeleton vibration |

The characteristic peak representing lignin at 1604 cm$^{-1}$ in Figure 1 is very significant, after acid treatment of lignin, it is found that the characteristic peak at this location is obviously lower than that of the control material. Almost disappeared, indicating that lignin is removed, further observe the spectrum near 1604 cm$^{-1}$ (Figure 1), it can be seen that there is a peak at 1655 cm$^{-1}$. Corresponding to C=C bond on coniferyl alcohol and γ-C=O bond on coniferyl aldehyde in lignin unit, this peak disappeared almost completely after delignification treatment. The results showed that sodium chlorite method did cause the cleavage of carbonyl groups on lignin units. The peaks at 1273 cm$^{-1}$ and 2942 cm$^{-1}$ respectively correspond to the hydroxyl or C-H bond on methoxy and methoxy groups connected to lignin and phenyl, after delignification, the peak heights of the two positions are obviously reduced, It shows that sodium chlorite method can remove methoxy group from lignin. 1340 cm$^{-1}$ represents the characteristic peak of hemicellulose and 917 cm$^{-1}$, 1095 cm$^{-1}$, 1463 cm$^{-1}$, 2889 cm$^{-1}$ represents the characteristic peak of cellulose without obvious reduction. It shows that after sodium chlorite treatment, Hemicellulose and cellulose have not been largely removed, based on the data analysis in
Table 1, it can be concluded that: After being treated by sodium chlorite method, almost all lignin was removed from the specimen [2].

![Raman spectroscopic local map](image)

**Figure 1.** Raman spectroscopic local map

As can be seen from the results of Raman spectrum, the chemical composition between heartwood and sapwood is the same but the content is not the same. The heartwood and sapwood after delignification treatment, the characteristic peaks of lignin at 1510 cm\(^{-1}\) and 1423 cm\(^{-1}\) are obviously lower than those before treatment, the characteristic peak representing lignin at 1510 cm\(^{-1}\) even disappears, however, there are still differences between heartwood and sapwood after treatment. Presumptive reason: During xylem formation of trees, various types of cells in cambium region and xylem have undergone obvious changes in cell morphology, structure and function. This also leads to different contents of heartwood and sapwood although their chemical compositions are the same. However, the samples treated by sodium chlorite method mainly change the chemical structure of lignin and remove it, with little influence on other chemical components.

### 3.3. Hygroscopicity Analysis

Figure 2 and Table 3 show the moisture absorption equilibrium moisture content of the treated material and the control material at different relative humidity at room temperature. As can be seen from figure 2, when the humidity of heartwood of fir wood is 30%, there is little difference in moisture absorption performance. However, as the humidity increases, sapwood absorbs more water than heartwood, and after lignin is removed, the moisture absorption capacity of wood cells has little difference at lower humidity (30%). When in an environment of higher humidity (higher than 60%), the acid treated sample has significantly higher hygroscopicity than the untreated sample. But when the humidity reaches 95%, with surprising results, samples treated by sodium chlorite method, the hygroscopic capacity is much higher than that of untreated samples. The equilibrium moisture content is as high as 60%. However, only about 22% of them were untreated. This shows that: Firstly, delignification treatment improves the hygroscopicity of wood, with the increase of relative humidity, the hygroscopic capacity becomes more obvious. Second, when it is not treated, the hygroscopicity of heartwood is lower than that of sapwood. This may be mainly due to the difference in contents
between the two [3]. After treatment, the moisture absorption rate of heartwood is higher than that of sapwood, especially at high relative humidity.

| Relative humidity | Heartwood treatment | Contrast treatment | Sapwood treatment | Contrast treatment |
|-------------------|--------------------|--------------------|-------------------|--------------------|
| 30%               | 5.76±0.23          | 5.33±0.23          | 5.80±0.41         | 6.14±0.27          |
| 60%               | 10.07±1.48         | 9.46±0.22          | 9.19±0.58         | 10.03±0.22         |
| 85%               | 15.34±0.96         | 12.46±0.38         | 14.82±0.54        | 13.79±0.14         |
| 95%               | 69.83±6.75         | 21.32±0.64         | 51.79±3.86        | 24.11±0.79         |

Figure 2. Wood hygroscopicity before and after delignification

(1) Evaluation of fitting effect

The fitting effect of the model was evaluated by determining coefficient ($R^2$) and average relative error [6]. Among them:

$$R^2 = 1 - \frac{SSE}{SST}$$  \(2\)

In the formula: SSE—residual sum of squares; SST—total sum of squares. $R^2$ represents the degree of curve fitting between experimental data and model functions. The closer its value is to 1, the better the fitting effect of the curve is [6].

The relationship between wood and water is the basic theory in wood science. It has always been the focus, hotspot and difficulty of research in the industry. However, with the progress of related technologies, Not only does wood as a whole pay attention to water properties and apply mathematical models to analyze water adsorption properties, new methods such as low-field nuclear magnetic resonance and DSC are used to explore the wood-water relationship. Thybring (2013) in the review, it is suggested that the fiber saturation point FSP can even be as high as 40%.

In order to better analyze the moisture absorption of Chinese fir heartwood and sapwood after delignification, Using Hailwood-Horrobin moisture absorption model (H-H model), According to the following formula, the sorption isotherm is constructed to visually represent the changes before and after treatment.
In the formula, $a_w$ is relative humidity ($\%$), $A$, $B$, $C$, $k_1$, $k_2$, $w$ are constants, and $m$ is equilibrium moisture content ($\%$). Among them, $k_1$ and $k_2$ respectively represent the equilibrium constants of water-wood system during adsorption of single and multi-molecular layers. And the larger the value, the stronger the adsorption capacity. $18/W$ reveals the moisture content of wood when the effective sorption group is saturated with hydration water. The larger W, the less water adsorption sites on the polymer surface.

(2) Results Analysis

Figure 3. Hygroscopicity isotherm of wood before and after Delignification
Table 4. Fitting parameters of curve before and after treatment

| Parameter | Sapwood treatment | Heartwood treatment | Sapwood untreated | Heartwood untreated |
|-----------|-------------------|---------------------|-------------------|---------------------|
| A         | 15.322            | 15.201              | 17.225            | 18.321              |
| B         | 0.668             | 0.668               | 0.768             | 0.765               |
| C         | 0.006             | 0.006               | 0.004             | 0.003               |
| \( k_1 \) | 0.048             | 0.048               | 0.045             | 0.037               |
| \( k_2 \) | 0.763             | 0.764               | 0.471             | 0.378               |
| W         | 16.261            | 16.239              | 16.745            | 16.261              |
| 18/W      | 1.107             | 1.108               | 1.074             | 1.107               |
| \( R^2 \) | 0.9743            | 0.9656              | 0.9833            | 0.9835              |

As can be seen from Figure 3 and Table 4, at different relative humidity, both treated and untreated materials conform to the H-H model of \( \ln m = \left( \frac{A}{\alpha e} + B - C\alpha e \right) \). It can be seen from the Figure that the moisture absorption equilibrium moisture content of the treated and untreated materials almost completely coincides with the theoretical value of the H-H model. The fitting degree \( R^2 \) is above 0.96, the curve type is similar to the typical "S(II)" isothermal adsorption line. This shows that the adsorption process of water on the specimen and control material treated by sodium chlorite method includes both monolayer adsorption and monolayer adsorption, there is also multi-molecular layer adsorption. In addition, in the area where the relative humidity is 80%-95%, the sample treated by sodium chlorite method, the slope of the curve is close to 1. Indicates that within this relative humidity range, after sodium chlorite treatment of part of the water vapor in the specimen gathered into liquid water.

As can be seen from Table 4, the W value after delignification is smaller than that of the control material. The results showed that the number of water adsorption sites in delignified wood was higher than that of control wood. The moisture adsorption content of the specimens treated by sodium chlorite method increased. The values of \( k_1 \) and \( k_2 \) are positive values, this means that the adsorption capacity of the multi-molecular layer is greater than that of the single-molecular layer [7]. From the analysis in Table 4, the \( k_1 \) value of the treated specimen is larger than that of the control material. It means that the moisture absorption capacity of the single molecular layer of fast-growing Chinese fir after delignification is stronger than that of the control material. Therefore, after lignin removal, in the lower humidity range (below 30%), the difference between the samples before and after treatment is not obvious. However, in the higher humidity range (above 60%), there are obvious changes. The phenomenon that the treated sample absorbs more water than the sample before treatment. The water adsorption capacity of wood monolayer is mainly due to the existence of free hydroxyl groups, which are relatively hydrophilic. However, the existence of lignin previously hindered the hygroscopic ability of hydrophilic groups. With the removal of lignin, the proportion of effective hydroxyl in the treated specimen increases. Therefore, the moisture absorption capacity of the treated test piece is improved, this also explains the difference in hygroscopicity before and after delignification. In Table 4, it can be found that the \( k_2 \) value of the specimen treated by sodium chlorite method is greater than that of the control material. This indicates that the adsorption capacity of the multi-molecular layer of the sample after delignification treatment is enhanced compared with that of the control material. To sum up, after delignification treatment, the adsorption capacity of the monolayer of the specimen to water is improved, and at the same time, the secondary adsorption sites in the specimen are also increased.

The hygroscopicity of wood is not only affected by the accessibility of hydroxyl groups, but also by the microscopic pores of wood. Vitas (2019) study shows that delignification treatment can increase the proportion of macro pores, that is, Nakatani (2008) study points out that the pores in lignin are mainly micro pores below 0.6nm. There are three reasons why delignification treatment increases hygroscopicity: First, the removal of hydrophobic substance lignin improves the accessibility
of water molecules of wood cell wall substance hemicellulose and cellulose amorphous region. Secondly, the removal of lignin increases the proportion of macro pores in the distribution of wood pore system, making the condensation effect in macro pores significantly increase under the condition of high relative humidity. Thirdly, the quality of wood per unit volume decreases and the content of hygroscopic substances (hydroxyl) in cell wall components increases significantly.

4. Conclusion
Fast-growing wood is the main material for wood processing in China. However, due to the limitation of experimental conditions, only the influence of delignification treatment on moisture absorption performance of wood is discussed in this paper. The research results in this paper are of high value for exploring the microstructure and properties of cell walls, providing a better research perspective and some interesting entry points for subsequent research. The main research conclusions are as follows:

1) Through spectral analysis, it can be found that the average weight loss rate after sodium chlorite treatment is 32%. It is presumed that most lignin has been removed, and there may be a small amount of hemicellulose removed, which is confirmed by Raman spectra.

2) Hygroscopicity test shows that: When the relative humidity is lower than 30%, the hygroscopicity change is not obvious. With the increase of relative humidity, the exposure of hydrophilic groups, the increase of cell wall microscopic voids and the increase of the mass ratio of hygroscopic substances caused by delignification treatment lead to a significant increase of moisture absorption equilibrium moisture content. Even at 95% high relative humidity, the equilibrium moisture content reaches an amazing 60%. It is believed that it is caused by condensation of microcapillary, but it needs further verification.

3) There are some differences in hygroscopicity between heartwood and sapwood. Combined with H-H model fitting of hygroscopicity data, the reason is inferred: When the humidity is high, the difference of moisture absorption ability between sapwood and heartwood mainly comes from the moisture absorption of multi-molecular layer (adsorbed water and condensed water). However, the moisture absorption capacity of heartwood and sapwood after delignification is obviously enhanced. Mainly because lignin is a relatively hydrophobic chemical component, mainly because lignin is a relatively hydrophobic chemical component. The lignin content directly affects the moisture absorption capacity of wood. After lignin removal, the number of hydrophilic groups in the cell wall increases and the moisture absorption capacity of wood increases.

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