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Spectral and thermal analysis of *Eucalyptus* wood drying at different temperature and methods

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**ABSTRACT**

In order to better understand the chemical changes after wood drying, *Eucalyptus* wood was dried to an absolutely dry state following the five types of treatment: oven-dried at 60, 90, 120, and 150 °C, and vacuum freeze-dried. The tangential shrinkage rate ($\beta$) of oven-dried specimens was increased from 7.63 to 9.90% as treatment temperature was increased, and the $\beta$ of the specimen submitted to vacuum freeze drying was 7.40%, scoring close to the specimen oven-dried at 60 °C. The chemical characteristics and thermogravimetric analysis of the specimens were studied based on the drying results. Here, the results confirmed that vacuum freeze drying has little effect on the chemical composition of wood and showed that, for oven-dried samples, the chemical composition of wood varies with the drying temperature. Concerning crystallinity of the oven-dried specimens, it was decreased from 38.57 to 26.22% as the treatment temperature was incremented. In turn, the crystallinity of the specimen processed with vacuum freeze drying was the lowest one.

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**KEYWORDS**

Wood drying temperature; spectral analysis; thermal analysis

**1. Introduction**

Wood performs an important role in our daily life, which is widely used for furniture, building, and outdoor greening due to its better comprehensive properties. Wood drying is a fundamental step in processing wood products. The moisture content of wood seriously influences their mechanical properties, so controlling the water content is a crucial step in the conversion of wood to any products. *Eucalyptus* has become one of the most important afforestation species in world plantation. As an industrial raw material, *Eucalyptus* wood is mainly used for the production of paper, particleboard, fiberboard, and plywood.

Similar to other types of wood, *Eucalyptus* wood is mostly composed of amorphous polymers. Drying is a crucial step in the manufacturing process as it contributes toward the dimensional stability, workability, and adhesive wettability of lumber. Several methods of drying wood are available in the market, including air drying, kiln drying, microwave drying, vacuum drying, vacuum freeze drying, high-frequency vacuum drying, and so on. While similar in general, the different drying conditions of these affect the drying rate, mechanical properties, samples quality, and the resulting economic efficiency. Salas et al. evaluated the moisture content variations, drying defects, and color changes of wood dried under three drying methods (kiln, solar, and air drying) during three seasons (dry, rainy, and transition season) in Costa Rica. According to their results, kiln drying had the fastest drying times, but both the number and magnitude of defects produced are highest. In turn, air drying led to a slower drying time and higher final moisture content than kiln drying. Bao et al. did the comparative study of moisture absorption and dimensional stability of Chinese cedar wood with conventional drying and superheated steam drying. Herrera-Diaz et al. studied the effect of wood drying and heat modification on some physical and mechanical properties of radiata pine, and showed that the dimensional stability of wood was improved but the modulus of rupture dropped during the drying process.

In recent years, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and thermogravimetric analysis (TGA) have been successfully used for analyzing wood materials. FTIR is a useful nondestructive or micro-destructive analytical technique providing information about chemical bonding...
Set A (60°C) for the first time. Absolutely dry state are thus presented and discussed. Eucalyptus and thermal analysis of spectroscopy, XRD, and TGA. The spectral analysis of the obtained dried wood were analyzed by FTIR by vacuum freeze-dried. The chemical characteristics cochemical properties of Eucalyptus, and molecular structure.[16] Li et al.[17] used TG and FTIR to analyze the changes of components of holo-cellulose, α-cellulose, and lignin which were extracted from the heat-treated and untreated milled wood. In order to obtain a detailed understanding of water adsorption mechanism of heat-treated wood, Xin Guo et al.[18] studied the molecular interaction between the absorbed water and heat-treated wood via micro-FTIR spectroscopy. XRD has been one of the most widely used techniques to investigate crystallinity index (CrI) and the crystallite size of wood materials. Dumanli et al.[19] used TG to study the combustion of fir wood and non-isothermal TG data were used to evaluate the kinetics of the combustion of this carbonaceous material. Lastly, Szubel et al.[20] also relied on TG to define the content of basic components and analyze the relations among the kinetics of devolatilization of different wood species and to determine the exhaust composition.

Despite the unquestionable worldwide importance of Eucalyptus wood in industrial applications where wood drying or moisture content is an unavoidable parameter to monitor, to the best of our knowledge there is no work in the literature reporting experimental data and technical insights on how different drying methods and temperature conditions are expected to affect the physicochemical properties of Eucalyptus wood.

In this study, Eucalyptus wood was oven-dried at four temperatures (60, 90, 120, and 150°C) as well as by vacuum freeze-dried. The chemical characteristics of the obtained dried wood were analyzed by FTIR spectroscopy, XRD, and TGA. The spectral analysis and thermal analysis of Eucalyptus wood dried to an absolutely dry state are thus presented and discussed for the first time.

### Table 1. Shrinkage rate in each direction of the specimens dried under different conditions.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Longitudinal shrinkage (%)</th>
<th>Radial shrinkage (%)</th>
<th>Tangential shrinkage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Set A (60°C)</td>
<td>0.16</td>
<td>5.76</td>
<td>7.62</td>
</tr>
<tr>
<td>Set B (90°C)</td>
<td>0.22</td>
<td>4.33</td>
<td>8.91</td>
</tr>
<tr>
<td>Set C (120°C)</td>
<td>0.17</td>
<td>4.48</td>
<td>9.36</td>
</tr>
<tr>
<td>Set D (150°C)</td>
<td>0.31</td>
<td>5.42</td>
<td>9.90</td>
</tr>
<tr>
<td>Set E (vacuum freeze-dried)</td>
<td>0.21</td>
<td>4.24</td>
<td>7.40</td>
</tr>
</tbody>
</table>

and molecular structure.[16] Li et al.[17] used TG and FTIR to analyze the changes of components of holo-cellulose, α-cellulose, and lignin which were extracted from the heat treated and untreated milled wood. In order to obtain a detailed understanding of water adsorption mechanism of heat-treated wood, Xin Guo et al.[18] studied the molecular interaction between the absorbed water and heat-treated wood via micro-FTIR spectroscopy. XRD has been one of the most widely used techniques to investigate crystallinity index (CrI) and the crystallite size of wood materials. Dumanli et al.[19] used TG to study the combustion of fir wood and non-isothermal TG data were used to evaluate the kinetics of the combustion of this carbonaceous material. Lastly, Szubel et al.[20] also relied on TG to define the content of basic components and analyze the relations among the kinetics of devolatilization of different wood species and to determine the exhaust composition.

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### 2. Materials and methods

#### 2.1. Materials

The raw material used for this study was Eucalyptus urophylla wood (four years old) obtained from Guangdong Province, China. Specimens were taken from a green tree, with a high moisture content of over 100%. The wood specimens (dimensions: radial about 3.5–3.6 mm, tangential about 70–85 mm, and longitudinal about 80–95 mm) were prepared, and all specimens were without obvious flaws. Specimens were evenly divided into six paired sets A to F, with ten sheets of veneer. Each specimen was labeled with its own number.

Specimens from Set A were oven-dried at 60°C (for 120 min). Set B specimens were oven-dried at 90°C (for 95 min). Set C specimens were oven-dried at 120°C (for 90 min). Set D specimens were oven-dried at 150°C (for 75 min). Finally, Set E specimens were vacuum freeze-dried (vfd, for 12 hours) to reach an absolute dry state. For the latter, the time for freezing was defined as 4 h under ~20°C, a vacuum pressure of 00000–00007 Pa, and a temperature during sublimation rate of about ~18.3°C.

Before drying, each specimen weight and each direction size was recorded. During oven drying, the weight and each direction size of the specimens were measured and recorded every 5 min. All specimens were dried until the measured property difference did not exceed the previous measurement by 0.5%. In this way, the specimens were dried to an absolutely dry state. The shrinkage rate in each direction was calculated using the following definition:

\[
\beta = \frac{L_{\text{max}} - L_0}{L_{\text{max}}} \times 100\%
\]

where \(\beta\) is the shrinkage rate of each direction, including longitudinal shrinkage, radial shrinkage, tangential shrinkage. \(L_{\text{max}}\) is the size of each direction before drying, and its unit is in millimeters. \(L_0\) is the size of each direction when finishing drying, and its unit is in millimeters. The drying results of each group are shown in Table 1.

Specimens of each group were milled to powder and sieved in a sieve with a mesh number of 200 (controlling the particle diameter no longer than 75μm).

#### 2.2. Fourier transform infrared spectroscopy

Specimens for the FT-IR analysis were prepared by grinding in a 0.2 mm mesh size Wiley mill (IKA MF10, IKA-Werke, Staufen, Germany).[21] For this, the specimens (3.5–4.0 mg) were pre-ground and subsequently dried KBr (350 mg) and placed in an agate mortar, mixed well, and pulverized.[22] The mixture was dried at 60°C for 4 hours and then poured into a tableting die to obtain completely transparent tablets. Infrared spectra of the specimens were obtained by a
2.3. Thermogravimetric analysis (TGA)

TGA was used to determine the pyrolytic characteristics of Eucalyptus wood with different drying conditions. The thermogravimetric experiments were performed by using the sensitive thermobalance (PerkinElmer, Diamond, China). The weight of the furnace and temperature was calibrated according to the manufacturer’s recommendation. Temperature calibration was performed by measuring Curie points of indium, tin, and gold. In this study, specimens with initial masses of 10 mg were placed in the pan of the TGA microbalance, which was enough to fill the pan because of the low density of the ground specimens. Nitrogen gas was used as carrier gas. Experiments were carried out on thermobalance at a linear heating rate of 10 °C/min, with the temperature range from 25 to 800 °C, at a steady nitrogen flow of 30 mL/min.

3. Results and discussion

3.1. Fourier transform infrared spectroscopy

Studies using FT-IR were carried out to determine the extent of structural changes in the spectra of different drying conditions. The respective spectra of specimens are shown in Figure 1. The main reason for poor wood dimensional stability is that the main polymer (cellulose, hemicelluloses, lignin) in the wood contains a large number of free hydroxyl groups, which have a strong moisture absorption. The hydroxyl groups are the function chemical bond in cellulose. They may form two kinds of hydrogen bond, including intramolecular and intermolecular hydrogen bond. Hemicelluloses contain many hydroxyl groups in main chain and side chain. Multiple formations of an intermolecular hydrogen bond were between biphenol and other phenolic groups in lignin. As shown in Figure 1, with the increase of drying temperature, the intensity of hydroxyl absorption in cellulose (3411–3423 cm⁻¹) decreased, and the change of hydroxyl absorption peak was more obvious. This is probably due to the

![FTIR spectra](image.png)

**Figure 1.** FTIR spectra of different drying conditions: A – oven-dried at 150 °C; B – oven-dried at 120 °C; C – oven-dried at 90 °C; D – oven-dried at 60 °C; E – vacuum freeze-dried.

The crystallinity index (CrI) was calculated using the Segal method according to the following equation:

\[
CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%
\]

where \(I_{002}\) is the intensity of the diffraction from the (002) plane, which is the maximum diffraction intensity, and \(I_{am}\) is the intensity of the diffraction from the plane at 2\(\theta\) = 18°, representing only amorphous material.

The crystallite size was evaluated using the Scherrer equation:

\[
d(hkl) = \frac{k \cdot \lambda}{\beta \cdot \cos \Theta}
\]

where \(d(hkl)\) is the crystallite size in the direction perpendicular to the hkl reflection plane, \(k\) is the Scherrer constant (0.89), \(\lambda\) is the X-ray wavelength (1.54 nm), \(\beta\) is the full-width half-maximum, and \(\Theta\) is the corresponding Bragg angle.
high drying temperature, free hydroxyl between the cellulose molecules in the wood would react, removing one molecule of water to form an ether bond, resulting in a significant reduction in the number of free hydroxyl groups. In addition, under the higher temperature condition, the acetyl groups of hemicelluloses easily hydrolyzed to produce acetic acid, decreasing a degree of carbonyl (C=O). Then under this acidic condition, the lignin would undergo the esterification reaction, which reduces the hydroxyl groups and increases the carbonyl groups. It means that replacing the hydroxyl groups (in cellulose) with carbonyl groups, and the moisture absorption was reduced.

The absorption peaks of C–H stretching vibration in the methyl and methylene groups were found in 2902 cm\(^{-1}\) (60 °C), 2885 cm\(^{-1}\) (90 °C), 2875 cm\(^{-1}\) (120 °C), 2885 cm\(^{-1}\) (150 °C), 2902 cm\(^{-1}\) (vfd), respectively. The functional groups of these absorption peaks are abundant in cellulose and hemicelluloses. Significant differences in this absorption band in the spectra were found among spectrum E and others (Figure 1). The peak at about 2900 cm\(^{-1}\) in the spectra A to E was strengthened gradually, with spectrum E being the most intense of all. This result is evidence that as drying temperature rises, the effect of cellulose and hemicelluloses in specimens was increased, while specimens dried by vacuum freeze drying evidence the least effect on cellulose and hemicelluloses. The absorption band of non-conjugated carbonyl C=O stretching of hemicelluloses appeared at 1735 cm\(^{-1}\), the C–H bending vibration and C–O–C stretching vibration in cellulose and hemicelluloses appeared at 1383 and 1161 cm\(^{-1}\), and the absorption band of C–H vibration and C–O stretching vibration of cellulose of all specimens had the same position at 899 and 1050 cm\(^{-1}\). The absorbance at 1505 cm\(^{-1}\) arising from the aromatic skeletal vibration, the band at 1242 cm\(^{-1}\) assigned to methoxyl groups, and the absorbance at 1327 and 1127 cm\(^{-1}\) corresponding to syringyl unit were all attributed to the groups of lignin. As we can see in Figure 1, all specimens at the absorption peaks of lignin were essentially the same, which is representative that different drying conditions have little effect for the lignin skeleton of wood. To sum up the upside analysis, vacuum freeze drying has little influence on the chemical composition of specimens; however, under oven-dried, chemical composition of wood would change with the drying temperature increasing. These results should be crossed with the non-negligible shrinkage rate results of Table 1, as existing research efforts to model wood drying phenomenon typically assume that no chemical reaction or shrinking occurs during wood drying\(^{[27,28]}\) Our results show that these two aspects might not be applicable either to vacuum drying or to oven drying and thus should be taken into account differently depending on the drying method.

### 3.2. Thermal decomposition characteristics

TG and DTG curves of different drying treated Eucalyptus wood specimens pyrolysis at a heating rate of 10 °C/min are shown in Figure 2. Wood is mainly composed of cellulose, hemicellulose, and lignin, and its decomposition reaction is essentially the sum of the three major chemical components of the thermal decomposition reaction. The pyrolysis decomposition process was mostly affected by the effect of cellulose.\(^{[29]}\) Each wood specimen showed four distinct stages of weight loss during the thermal degradation. The first stage (dehydration), the second stage (pre-carbonization), the third stage (carbonization), and the fourth stage (calcination) were ranged from 25 °C to about 100 °C, 150 °C to about 310 °C, 310 °C to about 430 °C, and 430 °C to 800 °C, respectively. Based on the independent-parallel-reactions hypothesis, the stages 2 and 3 referred to hemicelluloses and cellulose decomposition, respectively.\(^{[30,31]}\) The decomposition temperature of the cellulose ranged from about 325 to 375 °C, while the hemicelluloses’ decomposition temperature ranged from 225 to 325 °C.

In Figure 3, a peak, a shoulder, and a long tailing can be observed for each DTG curve. As can be seen, the thermal degradation rate of vacuum freeze-dried is faster than that of oven-dried in the initiation of the pyrolysis. However, the thermal degradation rate did not exhibit an obvious difference in relation to
the oven-dried temperature treatments, with the maximum decomposition rate scoring about 11.73%/min (reported in Table 2). This result might be associated with the extractive contents in the wood, which suggested that vacuum freeze-dried can reduce more extractive contents than oven-dried due to the sublimation process during vacuum freeze drying. Moreover, the different oven drying treatments showed a negligible influence on the thermal degradation rate of the specimens.

Analyzing Figure 3, the temperature ranges can be linked to different process stages (hemicellulose, cellulose, lignin). The thermal decomposition characteristics of lignocellulose can be quantified through several parameters (listed as below), related to the temperature ranges of the different zones of the weight loss curves: $T_{\text{onset}}$ is the initial temperature of wood sample decomposition; $T_{\text{onset(hc)}}$ is the extrapolated temperature for the beginning of hemicellulose decomposition; $T_{\text{shoulder}}$ is the temperature corresponding to the hemicellulose shoulder, marking the peak top of the hemicellulose decomposition; $T_{\text{peak}}$ is the temperature of the maximum devolatilization rate; $T_{\text{offset(c)}}$ is the extrapolated temperature for the termination of cellulose decomposition and the beginning of lignin tail. Table 3 shows different characteristic temperatures among specimens. $T_{\text{onset}}$ values increased with the increase of drying temperature, which indicated that drying at the highest temperature can increase the beginning temperature of wood degradation. The $T_{\text{onset(hc)}}$ and $T_{\text{shoulder}}$ value of the specimens treated at different drying temperatures were almost the same, illustrating that drying temperature had little effect on the pyrolysis of the specimens hemicellulose. The $T_{\text{peak}}$ values were almost identical among all specimens, and all of the maximum decomposition rates were about 11.73%/min. As per the $T_{\text{offset(c)}}$ values, they increased with the enhancement of the drying temperature, indicating that the higher drying temperatures increase the termination temperature of the hemicellulose and cellulose. On the other hand, the termination temperature of lignocellulose pyrolysis was increased through the start temperature, illustrating that the temperature range of decomposition procedure for the specimens was extended.

### Table 2. Maximum decomposition rates exhibited by the specimens submitted to different processing conditions.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Set A (60° C)</th>
<th>Set B (90° C)</th>
<th>Set C (120° C)</th>
<th>Set D (150° C)</th>
<th>Set E (VFD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum decomposition rate (%/min)</td>
<td>11.61</td>
<td>11.73</td>
<td>11.65</td>
<td>11.48</td>
<td>11.63</td>
</tr>
</tbody>
</table>

### Table 3. Thermal degradation characteristic of wood specimens dried by different drying conditions.

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$T_{\text{O}}$ (°C)</th>
<th>$T_{\text{onset(hc)}}$ (°C)</th>
<th>$T_{\text{shoulder}}$ (°C)</th>
<th>$T_{\text{offset(c)}}$ (°C)</th>
<th>$T_{\text{peak}}$ (°C)</th>
<th>$T_{\text{offset(c)}}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>160</td>
<td>251</td>
<td>299</td>
<td>353</td>
<td>446</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>165</td>
<td>253</td>
<td>301</td>
<td>358</td>
<td>457</td>
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<tr>
<td>120</td>
<td>170</td>
<td>252</td>
<td>299</td>
<td>355</td>
<td>464</td>
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<tr>
<td>150</td>
<td>170</td>
<td>251</td>
<td>298</td>
<td>355</td>
<td>462</td>
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</tr>
<tr>
<td>VFD</td>
<td>168</td>
<td>251</td>
<td>301</td>
<td>358</td>
<td>479</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3. XRD

Cellulose is the main component of wood, and the number of crystalline areas in the fiber has a great impact on the physical and chemical properties of wood. With the increase of crystallinity, the tensile strength, elastic modulus, hardness, density, and dimensional stability of the cellulose increase. For a better understanding of the effect of *Eucalyptus* wood with different drying conditions, the relative crystallinity and crystallite size of wood were determined by XRD. Accordingly, Figure 4 shows the X-ray diffractograms of *Eucalyptus* wood. In turn, Table 4 provides a summary of the values of the crystalline index and crystalline sizes of the materials with different drying conditions. In general, the *Eucalyptus* wood specimens displayed a typical X-ray diffractogram, having the major crystal planes of (101), (101), and (002) at around 15.5°, 16.5°, and 22.3°, respectively.

As shown in Figure 4, the similarity in the five XRD patterns shows that the different drying treatments of the *Eucalyptus* wood do not affect the natural cellulose-1 polymorph structure. From Table 4, after different drying conditions, the crystallinity of *Eucalyptus* wood was noticeably different. As the drying temperature increased from 60 to 150 °C, the crystallinity of *Eucalyptus* wood was decreased from...
38.57% to 26.22%. This might be due to the deacetylation on hemicellulose to form acetic acid, and acetic acid causes partial acid hydrolysis of cellulose at high temperature, which destroys the structure of cellulose and resulting in a decrease in the degree of polymerization of it, and finally leading to decrease in crystallinity. With regard to vacuum freeze drying, water of wood was pre-frozen into ice, and then by heating the samples, the ice was directly sublimated. During this process, samples suffered a heat and mass transfer at a low temperature and low pressure. When undergoing vacuum freeze-dried, a low-temperature drying, the Eucalyptus wood crystallinity was 23.63%, which may be because during the VFD process, wood cell wall suffered damage and destroyed crystalline cellulose.\(^{[34]}\) As reported in Table 4, the crystalline size changed according to the different treatments but did not show a regular change, which suggests that there is no significant relationship between crystalline size and crystallinity.

### 4. Conclusion

In order to better understand the chemical changes after wood drying, Eucalyptus wood was dried to an absolutely dry state following the five types of treatment: oven-dried at 60, 90, 120, and 150°C, and vacuum freeze-dried. The obtained results showed that after oven-dried at different temperatures, the chemical composition of wood specimens could be changed. However, the vacuum freeze drying method showed little effect on the chemical composition of the samples. After drying at high temperature, the pyrolysis of hemicellulosases and cellulose in the specimens started and terminated at higher temperatures. However, after vacuum freeze-dried, the pyrolysis of hemicellulosases and cellulose in specimens started at 168°C, which is a higher temperature than those of oven-dried specimens (at 60 and 90°C), and terminated at 479°C, i.e., higher than the other treated specimens. In addition, our study also showed that different drying temperatures and method were not able to change cellulose crystal form. With the increase of oven-drying temperature, the crystallinity of cellulose decreased from 38.57 to 26.22%; however, the crystallinity of cellulose of specimens dried by vacuum freeze drying was the lowest, scoring 23.63%.

### Acknowledgments

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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