Effect of Different Heat Treatment Temperatures on the Chemical Composition and Structure of Chinese Fir Wood

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The properties of wood can be improved after heat-treatment. There have been many studies dealing with mechanical properties and chemical modifications of heat-treated wood. The purpose of this paper is to provide a new analysis method, to give better insights on the hemicelluloses, cellulose, and lignin contents of heat-treated wood by using Fourier transform infrared (FT-IR) and two-dimensional infrared (2D-IR) spectroscopies. The FT-IR spectra results showed progressive degradation in the carbonyl groups of the glucuronic acid units and degradation of the pyranose of hemicelluloses. These changes were measured as the percentage decrease of crystalline cellulose and the loss of C=O and C=C groups linking together the aromatic skeleton of lignin. The 2D-IR spectra showed the appearance of 5 × 5 peak clusters in the 1000 to 1200 cm^{-1} region, which could account for the hemicellulose degradation. In addition, changes in the degree of sensitivity at 1627 and 1509 cm^{-1} coincided with cross-linking reactions among the aromatic units in the lignin molecules.

Keywords: Chinese Fir wood; Heat treatment; Chemical composition; FT-IR spectra; 2D-IR spectra

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INTRODUCTION

Wood is a cellular biomaterial with a complex, layered, and multi-component structure. The wood cell wall structure is primarily composed of cellulose, hemicellulose, and lignin. The structure and characteristics of the cell wall components, as well as the relationship between them, determines various properties of the wood. While wood has the advantages of high strength-to-weight ratio, impact resistance, and high processability, it has some disadvantages. It is very susceptible to weathering, and the nature of hygroexpansion, easy decay, and burning have limited its wide application (Li *et al.* 2015). Heat treatment of wood has been known as an effective method to improve wood properties (Esteves and Pereira 2009). Under high-temperature conditions, a series of complex chemical reactions takes place in the wood cell wall, such as degradation and condensation reactions (Yin *et al.* 2010). This leads to changes in the amount of the components of the wood and also in its physical and chemical properties. After the heat-treatment process, the dimensional stability and the durability of wood increase, which is strongly associated with the reduction in hygroscopicity (Bekhta and Niemz 2003; Cao *et al.* 2012; Olarescu *et al.* 2014). However, the loss of strength properties has always been one of the main drawbacks of thermal treatment, primarily impacting the strength, rigidity, and firmness of wood. On the contrary, some additional mechanical features of wood, such as the elasticity modulus, can be improved by heat treatment (Korkut *et al.* 2008a,b). The composition and micro-structure of wood have been changed through thermal processing, resulting in changes in wood's physical and mechanical performance. Biziks *et al.* (2013) found that white birch, after heat-treating at 180 °C, exhibited cell wall cracks and voids, which led to a decrease in its mechanical performance. Yin *et al.* (2010) found that improvement in the hygroscopic and micromechanical properties occurred with an elevation in the steam temperature, which correlated well with this pattern of degradation in the constituents of the biocomposite matrix in the cell wall. After the heat treatment of wood, relationships between the decomposition of cellulose, hemicellulose, lignin, and the mechanical and physical properties have been examined in several studies (Kocaefe *et al.* 2008; Windeisen *et al.* 2009; Mehrotra *et al.* 2010; Poletto *et al.* 2012; Kačíková *et al.* 2013).

Fourier transform infrared spectroscopy (FT-IR) is a simple and useful technique to rapidly obtain information about the structure of wood constituents and the chemical changes occurring in the wood. The FT-IR spectra have been used to study the chemical changes in the weathering of acrylic films and acrylic-coated lime wood (Popescu *et al.* 2013), and the structural changes of lime wood under biodegradation (Liu *et al.* 2014). Some researchers have achieved remarkable success in the food industry; traditional Chinese medicine research and the identification of precious tree species have been investigated using FT-IR analysis (Li *et al.* 2010; Yang *et al.* 2010).

Two-dimensional correlation infrared spectroscopy (2D-IR) could provide new information about the variation of molecular structure and enhance the resolution of the traditional infrared spectra (Popescu and Simionescu. 2013). It has been applied in the investigation of traditional Chinese medicines and identification of precious tree species (Lei *et al.* 2010; Zhang *et al.* 2014). Some researchers have used 2D-IR to study the characterization of fungal degradation and photo-degraded lime wood (Popescu *et al.* 2010, 2011). Popescu and Simionescu (2013) used the 2D-IR method, combined with FT-IR and principal component analysis to investigate the structural modifications of *Tilia cordata* wood during heat treatment. Li *et al.* (2015) employed FT-IR spectra, combined with second-derivative infrared spectra and 2D-IR spectra, to analyze the chemical modifications in heat-treated teak wood.

Chinese Fir (*Cunninghamia lanceolata* (Lamb.) Hook.) wood is widely used in furniture, floor and paper pulp production in China. The aim of this study is to provide a new method, by employing FT-IR and 2D-IR spectroscopies, to evaluate the effect of heat treatment on the chemical structure and composition of Chinese Fir wood, investigating the changes in the hemicelluloses, cellulose, and lignin contents.

EXPERIMENTAL

Materials Treatment

Chinese Fir wood samples were sawn into 100 × 50 × 20 mm (length × width × height) dimensions and dried to a moisture content of approximately 8% in a high-frequency vacuum dryer. The steam/heat treatment was conducted at 190 or 230 °C for 2 h in an air-tight chamber with less than 2% oxygen. Steam was used as the heating medium and shielding gas. The untreated wood sample (reference) was kept in normal environmental conditions.

After heat treatment, the specimens were conditioned at a temperature of 20 °C and a relative humidity of 65%, until their weights attained stability.

A wet chemical analysis method was employed to obtain the holocellulose, cellulose, and lignin, according to the following standards: GB/T2677.10 (1995), Nitric acid ethanol method (Wang and Cheng 2011), and GB/T 2677.8 (1994).

Test Methods

The FT-TR spectral analysis was performed by grinding the wood samples into a powder with dimensions between 80 and 100 meshes. Then, 2.0 mg of wood powder was mixed with 100 mg of KBr. The mixture was pressed into a tablet, 13 mm in diameter. The tablet was tested to obtain the FT-IR spectra using a Spectrum GX Fourier-transform infrared spectrometer (Perkin-Elmer, USA), equipped with a deuterated triglycine sulfate (DTGS) detector. The scanning range was 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}, and a total accumulation of 32 scans.

Two-dimensional infrared spectra (2D-IR spectra) analysis was performed on similar wood tablets. The tablets were placed inside a portable, programmable temperature controller (Model 50-886, Love Controls, China), which was connected to the spectrometer. The 2D-IR spectra were obtained from a series of temperature-dependent dynamic spectra at temperatures ranging from 50 to 120 °C, at a heating rate of 10 °C, with 2D-IR correlation analysis software programmed by the Department of Chemistry of Tsinghua University, Beijing, China.

The holocellulose is the sum of cellulose and hemicelluloses. In this study, by comparing the FT-IR spectra and 2D-IR spectra of the holocellulose and the cellulose, the changes of hemicelluloses were found.

RESULTS AND DISCUSSION

FT-IR Spectral Analysis of the Wood Samples and their Main Components

Within the range of 1800 to 800 cm^{-1} (Fig. 1), cellulose, hemicelluloses, and lignin have their own characteristic absorption peaks. The peak near 1734 cm^{-1} in holocellulose showed strong intensity; however, the corresponding position in the FT-IR spectra of cellulose showed almost no absorption peak. Therefore, it was speculated that this absorption peak could be assigned to hemicelluloses. Similarly, the peak at 1268 cm^{-1} was derived from hemicelluloses and lignin. The peak at 1636 cm^{-1} signified both hemicelluloses and cellulose because it was not present in the FT-IR spectra of lignin. Through comparative analysis, two bands, namely the C=O stretching vibration in the O=C-OH group of the glucuronic acid (GlcA) unit at 1734 cm^{-1} and the C-O stretching in the O=C-O group at 1268 cm^{-1}, belonged to hemicelluloses. The C-H bending vibrations at 1372 cm^{-1}, the O-H bending vibration of water sorption at 1636 cm^{-1}, and the glucose ring stretching vibration at 1110 cm^{-1}, were characteristics of cellulose. The band of the aromatic skeletal vibrations, together with the C=C stretch vibrations in lignin, were clearly identified at 1603 cm^{-1}. Three other bands of lignin, *i.e.*, the aromatic skeletal vibration at 1509 cm^{-1}, C-O stretching of guaiacyl unit at 1268 cm^{-1}, and the vibration of the syringyl ring, together with the C-O stretching at 1215 cm^{-1}, were also characteristic peaks of lignin.

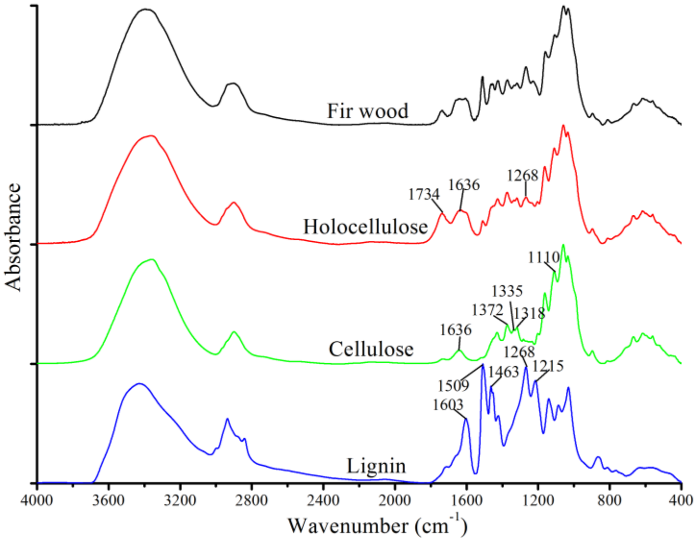

Fig. 1. FT-IR spectra of control fir wood and its holocellulose, cellulose, and lignin contents (4000 to 400 cm^{-1})

FT-IR Spectral Analysis of Wood Samples at Different Heat Treatment Temperatures

The FT-IR spectra of the control and heat-treated wood (190 and 230 °C) were analyzed, with the results shown in Fig. 2. As the heat-treatment temperature increased, the intensity of the absorption peaks at 1734 and 1636 cm^{-1} gradually decreased. Similarly, a continuous decrease in the peak intensity at 1229 cm^{-1}, assigned to C-O-C stretching vibration in pyranose, was also observed. These changes in the intensity of this three bands showed that the chemical bonds in the molecular structure of cellulose and hemicelluloses had changed, which led to the thermal degradation of these two components.

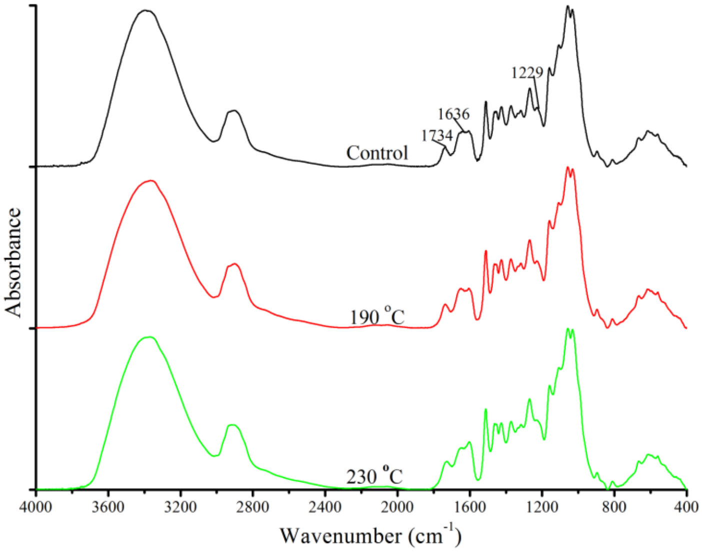

Fig. 2. FT-IR spectra of control wood and heat-treated wood samples in the region of 4000 to 400 cm^{-1}

FT-IR Spectral Analysis of Holocellulose and Cellulose at Different Heat Treatment Temperatures

When quantifying the progress of degradation, changes in the relative intensities of specific bands were analyzed. The FT-IR spectra of control and heat-treated fir wood holocellulose (190 and 230 °C) are shown in Fig. 3. The relative change in the hemicellulose content was calculated by using the C=O stretching vibration at 1738 cm^{-1}, the C-O stretching at 1268 cm^{-1}, and the C-O-C stretching vibration in pyranose at 1232 cm^{-1}. The absorption band at 1372 cm^{-1}, primarily attributed to the C-H bending vibrations in cellulose, was used for the spectrum reference, where the peak intensity exhibited almost no change in intensity during the heat treatment process.

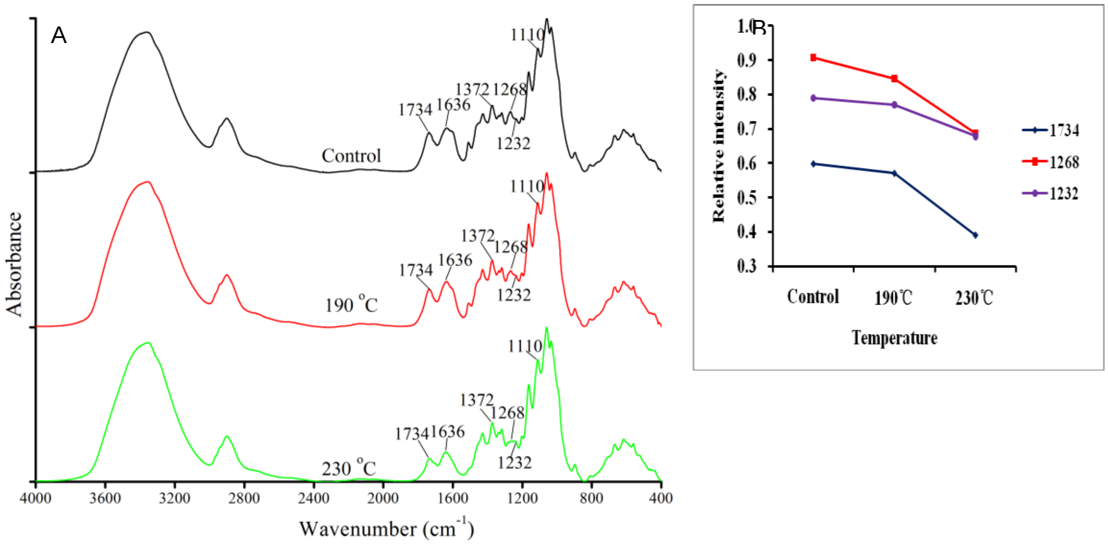

Fig. 3. (A) FT-IR spectra of holocellulose from the control and heat-treated samples (4000 to 400 cm^{-1}); (B) relative intensities of the absorption peaks at 1736, 1268, and 1232 cm^{-1} for the control and heat-treated samples

The relative intensity of the C=O stretching vibration of the glucuronic acid (GlcA) unit at 1734 cm^{-1} showed small changes when heat-treated at 190 °C (< 3%) and a continuous decrease of 21% at 230 °C. The clear progressive change in the intensity of the 1736 cm^{-1} peak indicated a strong degradation of this carbonyl group when the heat treatment temperature reached 190 °C or higher. In this process, the hemicelluloses reacted and the acetyl group was broken down from the hemicellulose molecular chain to form acetic acid (Xing and Li 2014). The absorption band at 1268 cm^{-1} had a slight decrease of 6% at 190 °C, and was followed by a decline of 16% at 230 °C. The C-O-C stretching vibration at 1232 cm^{-1} showed a decrease of 2% at 190 °C and an obvious decrease of 11% at 230 °C. These changes most likely show a degradation of pyranose at the highest treatment temperature of 230 °C.

For cellulose (Fig. 4), a small decrease was seen in the absorption band at 1636 cm^{-1}; however, the peak intensity at 1110 cm^{-1}, assigned to the glucose ring stretching vibration (Popescu and Simionescu 2013), decreased by 23% when the temperature reached 190 °C. It is possible that cellulose degraded, and this may have led to a percentage decrease in crystalline cellulose. From 190 °C to 230 °C, the peak intensities at 1630 and 1110 cm^{-1} exhibited little change, which indicated that the cellulose remained relatively stable.

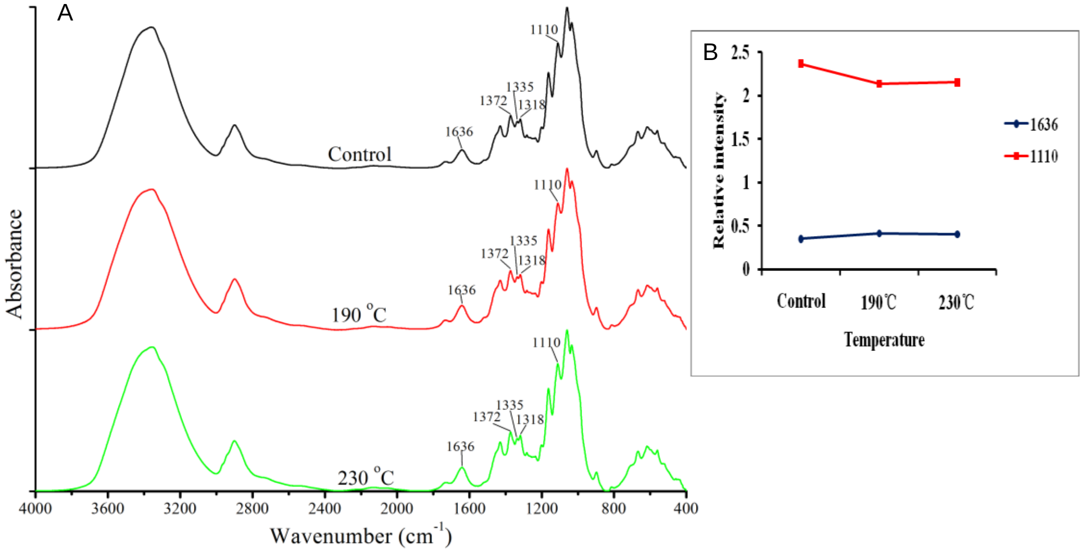

Fig. 4. (A) FT-IR spectra of cellulose from control and heat-treated samples (4000 to 400 cm^{-1}); (B) relative intensities of the absorption peaks at 1639 and 1110 cm^{-1} for the control and heat-treated samples

FT-IR Spectral Analysis of Lignin at Different Heat-Treatment Temperatures

The FT-IR spectra of control and heat-treated lignin (190 and 230 °C) are shown in Fig. 5. The absorption band at 1509 cm^{-1} was assigned to the aromatic skeletal vibration of lignin and was used as the spectrum reference. By comparison, the peak relative intensities at 1268 and 1215 cm^{-1} exhibited small decreases. This may have resulted from cleavage of the ether bond in the lignin structure during the thermal treatment, which led to the removal of methoxy functions. The intensity at 1708 cm^{-1} showed an increase of 10% and 15% at 190 °C and 230 °C, respectively. Meanwhile, the slight changes in the intensity of the peaks of 1603 cm^{-1} showed that a loss of the C=C group linked to the aromatic skeleton probably occurred, which indicated that the occurrence of a cross-linking had been formed among the aromatic units in the lignin when the heat temperature reached 190 °C or higher (Yin *et al.* 2013).

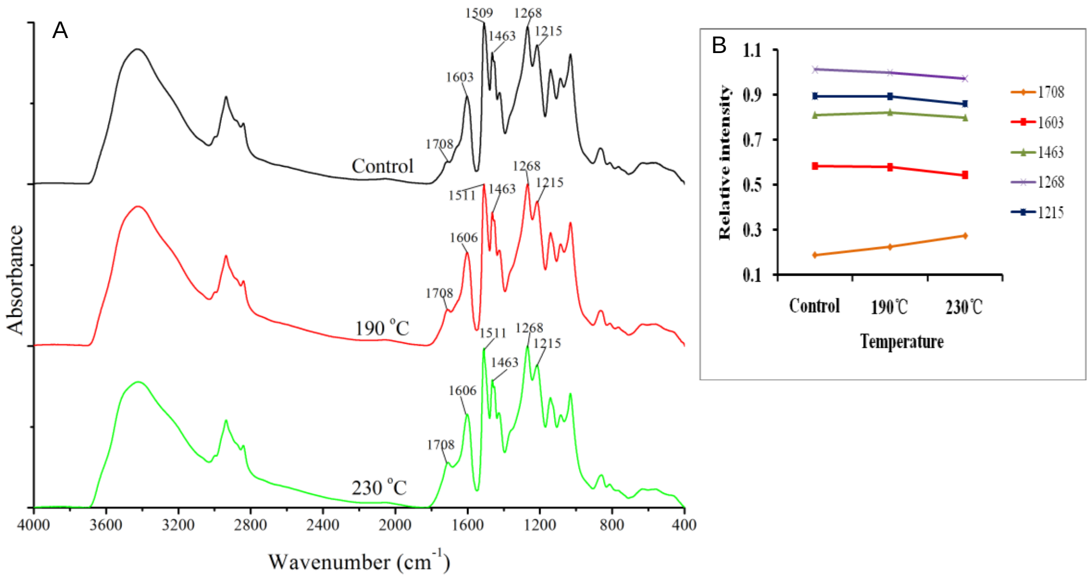

Fig. 5. (A) FT-IR spectra of lignin from control and heat-treated samples (4000 to 400 cm^{-1}); (B) relative intensities of the absorption peaks at 1708, 1603, 1463, 1268, and 1215 cm^{-1} for the control and heat-treated samples

Two-Dimensional-IR Spectral Analysis of the Wood Samples

A 2D-IR spectrum can usually enhance the spectral resolution in comparison to what can be obtained using a FT-IR spectrum alone. In 2D-IR, color indicates the degree of sensitivity of the samples to the thermal perturbation; the brighter the color looks, the greater the sensitivity.

The 2D-IR spectra of the wood samples are shown in Fig. 6. After heat treatment, the wood samples became increasingly sensitive, with a positive correlation between treatment temperature and sensitivity. The intensity of the peak around 1647 cm^{-1} was consistently the strongest in both the control and heat-treated wood samples. When the temperature reached 230 °C, the 5 × 5 peak cluster between 1000 and 1200 cm^{-1}, assigned to the C-O-C stretching vibration in hemicelluloses and cellulose, appeared. The appearance of this peak cluster could most likely be interpreted as the result of degradation in hemicelluloses and/or cellulose.

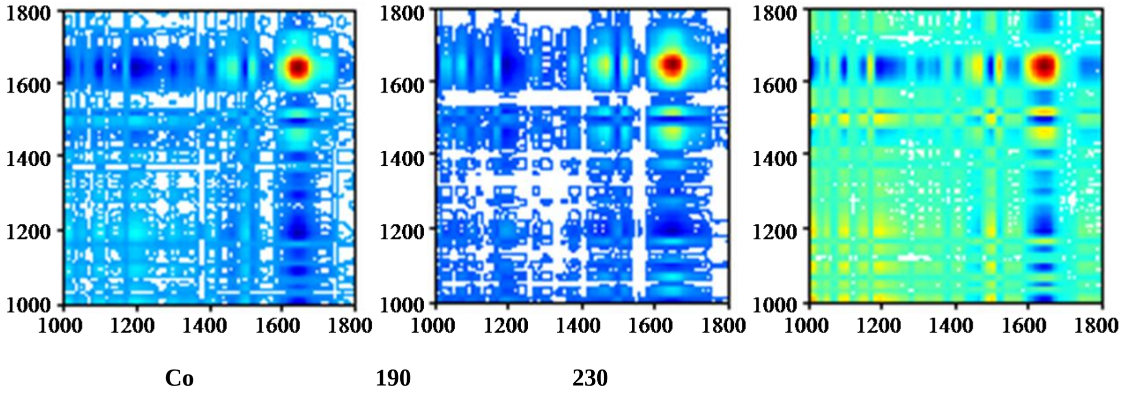

Fig. 6. 2D-IR spectra of control and heat-treated samples (1800 to 1000 cm^{-1})

The 2D-IR spectra of holocellulose and cellulose from control and heat-treated samples are shown in Figs. 7 and 8. By comparison, the intensity of the peak around 1648 cm^{-1} may suggest O-H bending vibration in the adsorbed water. This absorption band was always the strongest in the 2D-IR spectra. In the 1000 to 1200 cm^{-1} region, a 5 × 5 peak cluster appeared in the 2D-IR spectra of holocellulose, when the temperature reached 230 °C, while the 2D-IR spectra of cellulose did not show a 5 × 5 peak cluster at this heat treatment temperature. Therefore, the appearance of this peak could indicate the degradation of hemicelluloses.

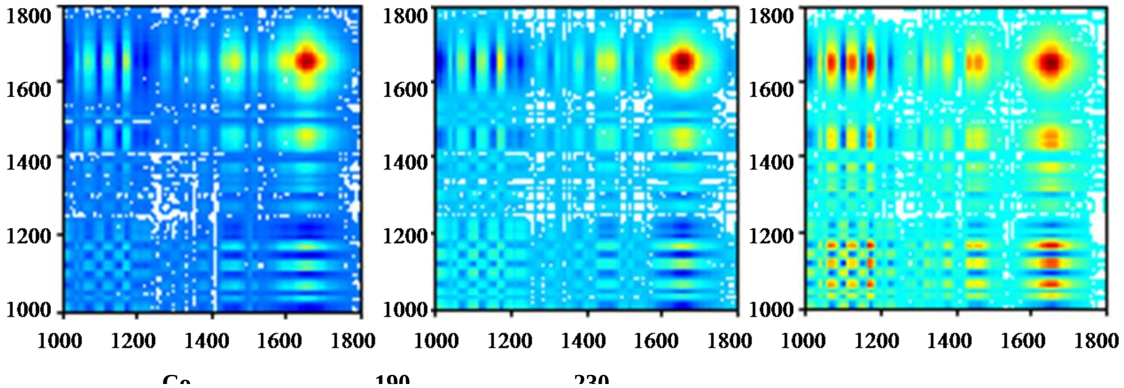

Fig. 7. 2D-IR spectra of holocellulose from control and heat-treated samples (1800 to 1000 cm^{-1})

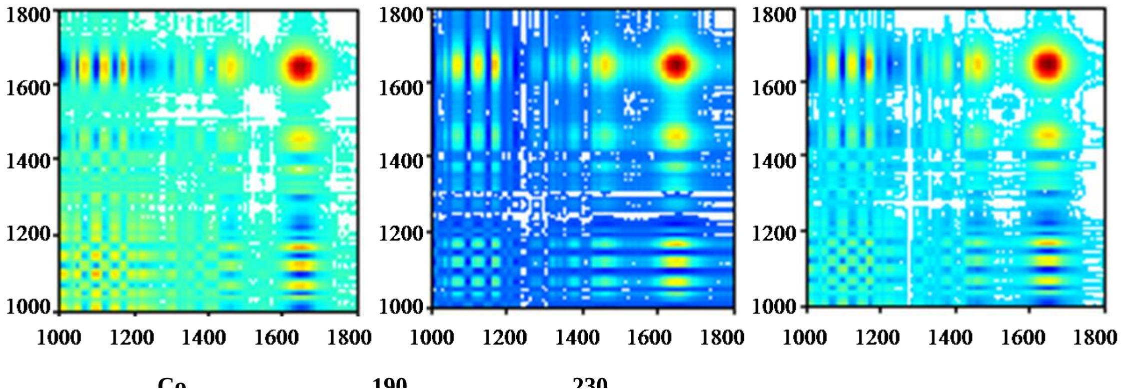

Fig. 8. 2D-IR spectra of cellulose from control and heat-treated samples (1800 to 1000 cm^{-1})

The sensitivity of the band at 1627 cm^{-1} gradually decreased with increasing temperature (Fig. 9), which was interpreted as a loss in the C=C groups linking the aromatic skeleton in lignin. Meanwhile, the sensitivity of the band at 1509 cm^{-1}, assigned to aromatic skeletal vibration, became stronger. This could also indicate the occurrence of cross-linking between the aromatic units in the lignin when the temperature reached 190 °C or higher.

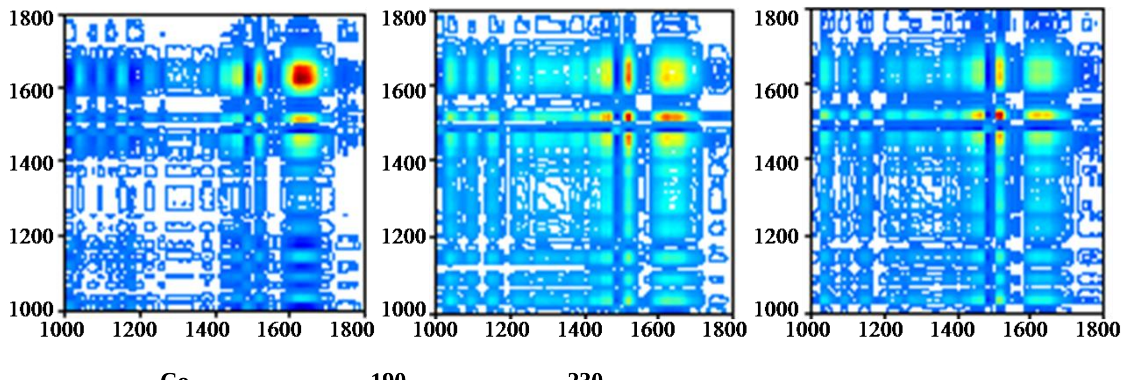

Fig. 9. 2D-IR spectra of lignin from control and heat-treated samples (1800 to 1000 cm^{-1})

CONCLUSIONS

The new method investigated in this work, by employing FT-IR combined with 2D-IR spectroscopies, can provide effective analysis of heat-treated wood and give better insights on hemicelluloses, cellulose, and lignin. The conclusions go as following:

1. Changes in the chemical structure of the hemicelluloses, cellulose, and lignin of Chinese fir wood were observed from the FT-IR spectra. These deviations included a progressive decline in carbonyl groups of the glucuronic acid unit, the degradation of pyranose in hemicelluloses, a decreasing crystalline cellulose content, and a loss of C=O and C=C groups in the aromatic skeleton.
2. In the 2D-IR spectra, the appearance of a 5 × 5 peak cluster in the 1000 to 1200 cm^{-1} region was consistent with hemicellulose degradation. The changes in the sensitivity at 1627 and 1509 cm^{-1} also indicated cross-linking among the aromatic units of lignin.

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