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Determination of chemical changes in heat-treated wood using ATR-FTIR and FT Raman spectrometry



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ABSTRACT

In this study, attenuated total reflectance–Fourier transform infrared (ATR-FTIR) and Fourier-transform Raman (FT-Raman) spectroscopy techniques were used to determine changes in the chemical structure of heat-treated woods. For this purpose, scots pine (*Pinus sylvestris* L.), oriental beech (*Fagus orientalis* L.), and oriental spruce (*Picea orientalis* L.) wood species were heat-treated at different temperatures. The effect of chemical changes on the FT-Raman and ATR-FTIR bands or ratios of heat-treated wood was related with the OH association of cellulose, functional groups, and the aromatic system of lignin. The effects of heat treatment on the carbohydrate and lignin peaks varied depending on the wood species. The spectral changes that occurred after heat treatment reflected the progress of the condensation reaction of lignin. Degradation of hemicelluloses led to a decrease in free hydroxyl groups. High temperature caused crystalline cellulose to increase due to the degradation of amorphous cellulose.

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1. Introduction

Heat treatment is considered to be an effective technique for developing wood protection. However, chemical changes occur during heat treatment, which adversely affect wood structure. The use of heat treatment to change the chemical and anatomical structure of wood is not a new procedure. Heat treatment studies have been carried out since the early 20th century, and have improved quickly in developing countries, especially in Europe [1,2]. Following this development, the International ThermoWood Association was founded to promote its usage and to develop a heat treatment product in 2000 [3].

Heat treatment is reported to be an effective method since it is significantly resistant to fungal decay without the use of wood preservatives and improves the hydrophobic properties and dimensional stability of wood [4]. Furthermore, it is considered to be an environmentally friendly wood preservation method [5], which also increases the hardness and surface quality of wood [6]. However, heat treatment also has some drawbacks, with a major one being its potential to reduce some mechanical properties of wood [7].

Heat treatment also changes the wood structure and degrades cell wall compounds and wood extractives [8]. Some previous studies have reported that treatment duration and temperature, which are the principal factors for modification, affect the chemical composition

of wood. Boonstra and Tjeerdsma [9] pointed out significant chemical changes between the first and second stages of thermal modification. Fragmentation of hemicelluloses and hydrolysis dispersement of acetic acid from their acetyl groups occur mainly in the first stage of the process, and are found to be quite limited in the last stage [10]. The increased durability of wood can be explained by the strong interaction between the treatment temperature (especially above 200 °C) and high resistance against fungal decay [11]. Furthermore, chemical analysis of wood treated at 250 °C for long term indicates the presence of waste products as cellulose begins to disintegrate. The lignin amount of heat-treated wood changes, especially during the second stage [12, 13]. While hemicellulose degradation intensely influences the technological properties of wood, the separation of lignin and the crystallization of cellulose have relatively less effect [14–16].

Compared to conventional chemical analysis referred to as TAPPI standards, vibrational spectroscopy methods are relatively more rapid and reliable. The spectroscopic techniques presented both quantity and quality of wood cell wall components [17]. Vibrational spectroscopy methods such as the use of infrared and Raman spectroscopy are being more commonly performed for the chemical analysis of heat-treated wood because they are non-destructive, require few samples, and have a simple sample preparation step [13,18–20]. Unlike common spectroscopy techniques for biomaterials in literature, there have been very few Raman studies on the heat treatment or thermal modification of wood [21–23].

This study aims to develop a rapid and reliable analysis method for detecting the chemical modifications of heat-treated wood based on

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Table 1
The mass loss on the thermal treated wood samples.

Mass loss of thermal treated wood (%)		
Oriental beech	Scots pine	Oriental spruce
14.5 ± 1.1	17.4 ± 0.8	17.4 ± 0.7

the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) and Fourier-transform Raman (FT-Raman) spectra from wood powder. We studied the chemical structures of heat-treated samples of scots pine, oriental beech, and oriental spruce. The chemical modifications of cellulose, hemicelluloses, and lignin in these heat-treated woods were investigated using ATR-FTIR and FT-Raman spectroscopy.

2. Materials and methods

2.1. Preparation of wood samples

Raw materials in terms of oriental beech (*Fagus orientalis* L.), oriental spruce (*Picea orientalis* L.), and scots pine (*Pinus sylvestris* L.) wood species were provided from the Black-Sea Region in Turkey. Defect-free samples with dimensions of 150 mm (length) × 70 mm (width) × 20 mm (thickness) from the sapwood of the three species were kept in a climate-controlled room until they reached a moisture content of approximately 12%. A LOYKA NSP-100 MC meter (AKYOL Company, Istanbul, Turkey) was used to determine the moisture content of the three species.

2.2. Heat-treatment process

Ten wood samples were selected for each species. Heat treatment was then applied to four samples of each species in an oven whose temperature was controlled with a sensitivity of ± 1 °C at two temperatures (190 °C for oriental beech and 212 °C for oriental spruce and scots pine) under atmospheric pressure in the presence of air (so-called ThermoWood). Table 1 displays the mass loss percentage of wood following the heat-treatment process. After heat treatment, the wood samples were ground using a laboratory-scale Willey mill to obtain 40 to 60 mesh wood powders.

2.3. ATR-FTIR and FT-Raman spectroscopy measurements

The ATR-FTIR measurements were recorded using a Thermo Nicolet iS50 FTIR (Thermo Fisher Scientific Co., Waltham, MA, USA)

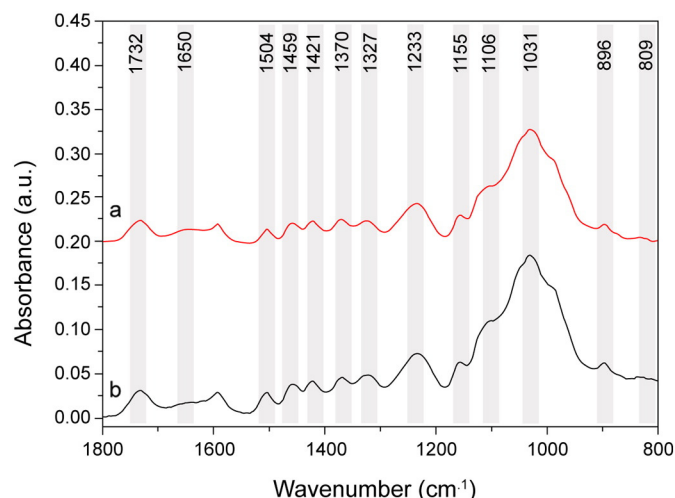


Fig. 1. FTIR spectra of oriental beech wood: (a) untreated; (b) heat-treated.

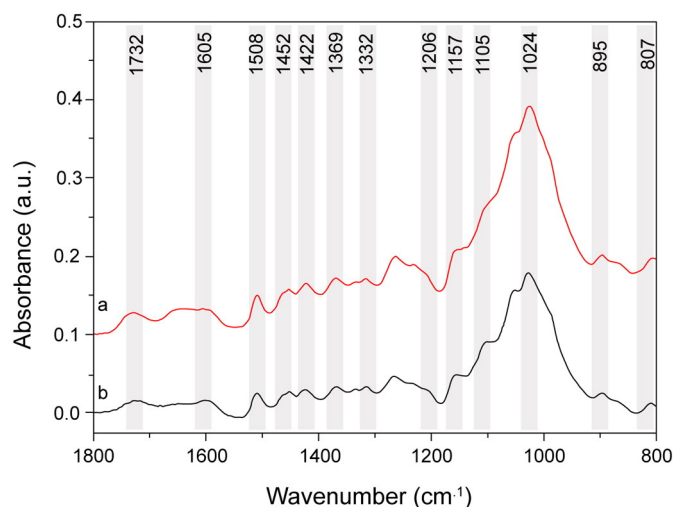


Fig. 2. FTIR spectra of scots pine wood: (a) untreated; (b) heat-treated.

spectrometer equipped with a single-bounce diamond crystal and a deuterated triglycine sulfate detector. The wood powder contacted the ATR crystal and the evanescent wave could be absorbed by the powder. The resulting attenuated radiation produced an ATR spectrum similar to a conventional absorption spectrum [24].

The FTIR spectra of all wood samples were determined to be in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} . Each spectrum was collected from 32 scans in the absorbance mode. FT-Raman spectra were determined using a Raman module mounted in the sample compartment of the Nicolet iS50 spectrometer (Thermo Fisher Scientific Co., Waltham, MA, USA). A 1064 nm diode laser was used as an excitation source fitted with an InGaAs detector. The laser power on the sample was set at 500 mW with a spot size of approximately 50 μm . The FT-Raman spectra of the samples were determined at a resolution of 8 cm^{-1} with 512 scans at room temperature. The Raman spectra of the wood samples were examined using OMNIC™ software (Thermo Electron Corporation, Madison, WI, USA). All spectral data were smoothed using a 25-point Savitsky–Golay algorithm in order to reduce noise. A 20-point second-order polynomial baseline correction was applied to the FT-Raman spectra of the samples. Three measurements were averaged to produce one spectrum for both FT-IR and FT-Raman analyses.

3. Results and discussion

3.1. ATR-FTIR analyses

In this study, the effect of heat treatment on the chemical properties of wood was found to be different depending on the temperature and wood species. ATR-FTIR spectra of data belonging to the main components of wood showed that samples treated at high temperatures (~200 °C) were different from those treated at low temperatures (<200 °C), as shown in Figs. 1–3 [25].

The FTIR spectra of the untreated and heat-treated wood samples exhibited absorption bands typical of wood components. Table 2 shows the assignments of substantial absorption bands in the region between 800 and 1800 cm^{-1} for various wood samples.

The changes in intensity of the bands or ratios of the ATR-FTIR spectra shown in Figs. 1–3 are related with the OH association of cellulose, functional groups, and the aromatic system of lignin. The bands at 1730–1732 cm^{-1} have been reported to be C=O stretching vibrations of the acetyl groups of galactoglucomannan, carboxyl- and aldehydes, and aromatic/conjugated aldehydes and esters [13,26]. While the bands at 1730–1732 cm^{-1} increased for heat-treated beech wood (Fig. 1), they decreased for heat-treated pine (Fig. 2) and spruce wood

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