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Infrared Photoacoustic Spectra of Japanese Cedar (*Cryptomeria japonica* D. Don) Wood and Bark Heat-Treated at Temperatures Ranging from 200°C to 1100°C

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Abstract

Wood (xylem) and bark of Japanese cedar (*Cryptomeria japonica* D. Don) were pyrolyzed over a wide range of temperatures (200 – 1100°C) in a nitrogen atmosphere. The infrared spectra of the heat-treated samples were recorded by a photoacoustic method. The photoacoustic spectral contours of wood and bark were very similar, showing several noticeable changes of spectral features with increasing heat-treatment temperature (HTT). In particular, two drastic spectral changes occurred in the HTT ranges of 200-300°C and 600-700°C. It was indicated that O-H and C-H bonds remain in Japanese cedar heat-treated to 600°C. No vibrational band attributable to atomic groups containing O or H atoms could be found in the spectra obtained at 700°C or more.

Key words: Wood, Bark, Japanese cedar, *Cryptomeria japonica*, Heat treatment, Thermal degradation, Infrared spectroscopy, Photoacoustic spectroscopy

Introduction

The utilization of low quality wood and waste timber has recently become an important subject of discussion. The preparation of charcoal is one of the most promising usages of such lignocellulosics, and charcoal has attracted the attention of many workers as adsorbent rather than as fuel. Our group has also explored the ability of Japanese cedar (*Cryptomeria japonica* D. Don) bark heat-treated at various temperatures to adsorb halogenated organic compounds in water, and suggested that the heat-treated bark has the potential to be a good scavenger (Kurimoto *et al.*, 2001). However, more information on the adsorption mechanism is required to prepare better-quality charcoal or heat-treated lignocellulosics as adsorbent. We have, therefore, been studying the physical and chemical properties of heat-treated Japanese cedar by various means (Kurimoto *et al.* 2000; 2002; in press, Yamauchi *et al.* 2000).

Our aim here is to examine the atomic groups remaining in heat-treated wood and bark. Organic atomic groups should play an important role in chemical adsorption, and hence the analysis of these groups in heat-treated lignocellulosics is an approach to the study of adsorption mechanisms. Infrared spectroscopy provides a powerful tool for the identification of atomic groups in solid organic substances. However, for carbonaceous materials, it is difficult to obtain a spectrum that is satisfactory by ordinary infrared techniques such as the transmittance or diffuse reflectance method because black-body samples are an extreme absorber of infrared irradiation. Thus, to our knowledge, no infrared spectrum of wood heat-treated above 600°C has been reported in spite of several studies on the thermal degradation of wood in terms of infrared spectroscopy (Oren *et al.* 1984, Pakdel *et al.* 1988, Kato *et al.* 1997). The photoacoustic technique, however, enables one to record good infrared spectra of such samples.

In this study, we obtained infrared photoacoustic (IR-PAS) spectra of Japanese cedar wood (xylem) and bark heat-treated over the temperature range 200°C to 1100°C, and investigated chemical changes with increasing heat-treatment temperature (HTT).

Materials and Methods

Heat treatment

The wood and bark used in this study were taken from an 80-year old Japanese cedar grown in Akita Prefecture, Japan. Air-dried wood and bark were reduced to powder using a Wiley mill. The powder (12 g) was placed in a porcelain crucible. The crucible was put in an iron vessel and heated in an electric oven under a nitrogen atmosphere. In all heating runs, it took 30 - 40 min to reach the desired temperature, which was varied from 200°C to 1100°C at intervals of 100 degrees. The samples were maintained in the crucible at the desired temperature for 3 h, and then cooled to room temperature.

Fourier transform infrared photoacoustic spectroscopy

IR-PAS spectra were recorded using a JEOL JIR7000W spectrometer equipped with an IR-PAS module (IR-PAS 1000). All the spectra were obtained at 100 - 300 times accumulation and with a spectral resolution of 4 cm^{-1}. The powder of heat-treated samples was packed in a thin cell 10 mm in diameter.

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Photoacoustic signals were collected on purging a cell bench with helium gas. Moving-mirror velocity was fixed at 0.16 cm/s through all the measurements. Carbon black was adopted as a reference sample.

Results and Discussion

Wavenumber region from 1900 cm^{-1} to 800 cm^{-1}

A number of the fundamental vibrations due to the atomic groups in wood constituent molecules are positioned in this wavenumber region. Figures 1 and 2 depict the IR-PAS spectra from 1900 cm^{-1} to 800 cm^{-1} of the heat-treated Japanese cedar bark and wood, respectively. The top spectrum in each figure corresponds to the air-dried sample.

As with other wood species, the constituents of bark are considerably different from those of wood (xylem) in Japanese cedar (Migita 1968, Uemura 1973) and the differences appear clearly in the line shape of IR-PAS spectra (Figures 1-a and 2-a), especially in the 1700 – 1400 cm^{-1} region. The spectral differences are still observed in the samples heat-treated at 200°C and 300°C. Moreover, as for the air-dried samples, the vibrational bands of bark are broader or less resolved than those of wood throughout the overall region, and this can be ascribed to a wide variety of chemical compounds contained in the bark.

Almost all of the vibrational bands detected in the air-dried samples are also observed in the samples heat-treated at 200°C. The result is predictable from the thermal analysis (Graham *et al.* 1984) showing that the thermal degradation or depolymerization of hemicellulose, cellulose and lignin begins 200-250°C, 240-350°C and 280-500°C, respectively. However, a change caused by heat-treatment at 200°C is commonly observed as a reduction of relative intensity in the 1700-1530 cm^{-1} region corresponding to C=O stretchings and O-H deformations. This is most likely due to the decrease of water molecules and/or the variation of hydrogen bond distance, C=O···H and H-O···H.

Another notable result at 200°C, which is observed in the bark sample alone, is the narrowing or resolving of several bands below 1530 cm^{-1}. This spectral change may be explained in terms of a decrease of the kinds of compounds remaining in the bark. Some of the relatively low-molecular-weight compounds contained only in the bark would be evaporated or decomposed through the heat-treatment at 200°C, while macromolecules such as cellulose and lignin show little chemical change. Actually, the segments that had turned black were seen in the bark through an optical

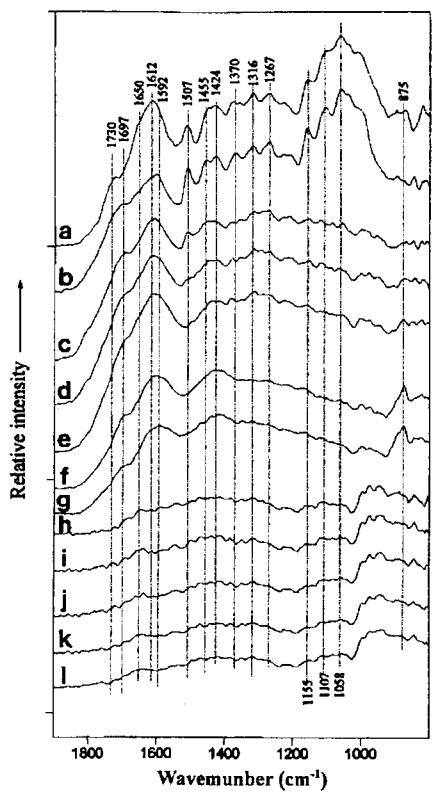

Fig. 1. IR-PAS spectra in the 1900-800 cm^{-1} region of Japanese cedar bark heat-treated at various temperatures
(a) untreated bark, (b) 200°C (c) 300°C, (d) 350°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C, (i) 800°C, (j) 900°C, (k) 1000°C, (l) 1100°C

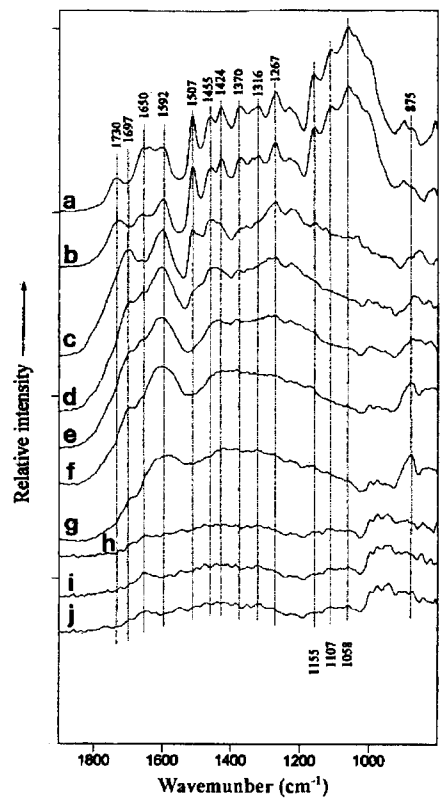

Fig. 2. IR-PAS spectra in the 1900-800 cm^{-1} region of Japanese cedar wood heat-treated at various temperatures
(a) untreated wood, (b) 200°C (c) 300°C, (d) 350°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C, (i) 800°C, (j) 900°C

microscope, although the wood heat-treated at 200°C scarcely changed color.

The first drastic change occurs in both the spectra at 300°C. The bark and wood heat-treated above 300°C were completely black to the naked eye. The vibrational bands due to cellulose and/or hemicellulose at 1424, 1370, 1316, 1155, 1107 and 1058 cm^{-1} (Liang *et al.* 1960, Harrington *et al.* 1964, Michell *et al.* 1965) disappear nearly completely. Remarkably, the strong bands in the 1180-900 cm^{-1} region vanish suddenly. Although the peaks attributed to lignin are certainly detectable at 1507 and 1267 cm^{-1}, their relative intensities become much smaller. The result supports the notion that partial decomposition in a lignin molecule is caused by the heat-treatment at 300°C. Moreover, a new peak appears at about 1700 cm^{-1} in both spectra, although it is not clear whether this peak is due to a shift of the band at 1730 cm^{-1} or different vibrational mode.

As is evident from Figures 1 and 2, there exists no appreciable difference between the bark and the wood at 350°C or more. The bands at 1507 and 1267cm^{-1} become less intense with increasing HTT and disappear completely at 500°C. This proves that the thermal degradation of lignin molecules had reached an advanced stage. The broad peak at about 1590 cm^{-1} with a shoulder around 1700 cm^{-1} is observed even at 600°C. Also noteworthy is that a band at 875 cm^{-1} is observed as a prominent peak in the spectra at 500 and 600°C.

The second drastic change occurs between 600 and 700°C. At 700°C, the peaks at 1590, 1240 and 875 cm^{-1} vanish abruptly and there remain only a few weak bands below 1000 cm^{-1}. The spectral contour is nearly independent of HTT from 700°C to 1100°C.

Wavenumber region from 3600 cm^{-1} to 2500 cm^{-1}

In general, for wood constituent molecules, only the fundamental modes of O-H and C-H stretchings appear in this region. We show only the IR-PAS spectra of the heat-treated bark in Figure 3, since no significant difference could be found in spectral features between the wood and bark over the overall HTT.

The O-H stretching vibrations of the air-dried bark appear as an extremely broad band due to hydrogen bonds (H-O $\cdots$ H) at around 3400 cm^{-1}. The C-H stretching vibrations are also detected as a single peak at about 2930 cm^{-1} with a shoulder on the low wavenumber side and the peak is normally regarded as an overlap of the stretching modes of CH, CH_2 and CH_3 groups being composed of a saturated carbon with hydrogen. The IR-PAS spectrum at 200°C maintains the same line shape as that of the air-dried bark.

Both the O-H and C-H stretching bands show clear spectral changes when the HTT moves beyond the first point of drastic change described earlier. At 300°C, the band of O-H stretchings decreases in intensity, and seems to shift to a higher wavenumber. This decrease is mainly ascribed to the reduction of OH groups with thermal degradation of cellulose and hemicellulose, and the shift can be due to the breaking of the hydrogen bond. The intensity of the O-H stretching band decreases with increasing HTT and becomes undetectable at 700°C.

As regards the peak coming from the C-H stretchings, a new shoulder appears at around 2960 cm^{-1} at 300°C and further the peak seemingly splits into three bands at 2960, 2930 and 2855 cm^{-1} in the spectrum at 350°C. These bands decrease in intensity with increasing HTT and disappear at 600°C. A new band that should be attributable to C-H stretching vibration between unsaturated carbon and hydrogen instead occurs near 3050 cm^{-1} at 500 and 600°C. A similar occurrence of a vibrational band at about 3050 cm^{-1} was reported with respect to lignite by use of diffuse reflectance method (Yoo *et al.* 1993), although it was found at higher HTT. It is interesting that the band near 3050 cm^{-1} is not detected at 400°C or less despite the presence of lignin molecules containing aromatic rings and ethylenic double bonds and inversely, it is observed clearly above the decomposition temperature of lignin.

The new band also becomes undetectable at 700°C. It is indicated that all of the C-H stretching bands vanish when the HTT moves beyond the second point of drastic change. In other words, the IR-PAS measurements revealed that C-H bonds remain in Japanese cedar samples heat-treated at 600°C.

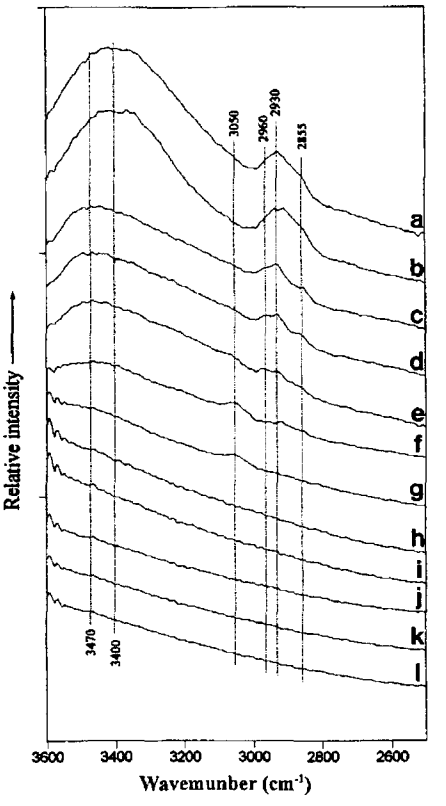

Fig. 3 IR-PAS spectra in the 3600-2500 cm^{-1} region of Japanese cedar bark heat-treated at various temperatures
(a) untreated bark, (b) 200°C (c) 300°C, (d) 350°C, (e) 400°C, (f) 500°C, (g) 600°C, (h) 700°C, (i) 800°C, (j) 900 °C, (k) 1000°C, (l) 1100°C

Concluding Remarks

Several important conclusions can be drawn from the IR-PAS spectra of Japanese cedar wood and bark heat-treated under a nitrogen atmosphere from 200°C to 1100°C. The heat-treated wood and bark showed the same IR-PAS spectral changes with HTT above 350°C, and this implies that both undergo similar chemical changes and then are carbonized. The fact that a decrease in band intensities at 1592 and 1507 cm^{-1} was observed in the spectrum at 300°C suggested the partial decomposition of a lignin molecule. It was elucidated that the heat-treated Japanese cedar samples contain both OH and CH groups at 600°C. In the IR-PAS spectra at 700°C or more, we could found no vibrational band attributable to atomic groups containing O or H atoms.

From a methodological viewpoint, it is anticipated that the spectral change of characteristic vibrational bands in the IR-PAS spectra will be used as an indicator of HTT. The estimation of HTT is likely useful in preventing the contamination of dioxins when charcoal is prepared from wood-based materials containing synthetic resins, because the decomposition of dioxins is not accelerated until the temperature is raised above 700°-800°C.

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