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Raman Spectroscopic Characterization of Japanese Cedar Wood Heat-treated at Low Temperatures

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Abstract

Raman spectra of Japanese cedar (*Cryptomeria japonica*) sapwood and heartwood heated at low temperatures (50-160°C) were recorded, and spectral changes of Raman bands due to heat treatment were analyzed through a difference spectrum method. Although the heat treatment intensified fluorescence emitted from heartwood much more strongly than that from sapwood, there was no significant difference in vibrational Raman band contours between sapwood and heartwood. The Raman spectral changes associated with heat treatment of Japanese cedar were quite similar to those of Japanese larch (*Larix leptolepis*). The most characteristic and important spectral change was a decrease in intensity of the Raman band at 1655 cm⁻¹, which can be attributed mainly to stretching vibrations of C=C and C=O groups in lignin molecules. The intensity at 1655 cm⁻¹ decreased with increasing heat-treatment temperature and time, and the decrease rate had a strong dependence on water content.

Key words: Heat treatment, Japanese cedar, Lignin, Raman spectroscopy, Softening

Introduction

Heat treatment of wood at low temperatures has been applied to kiln-drying and various wood processing techniques. The process of heat-treating wood has progressed markedly since microwave or high frequency oscillators have been adopted as sources of heat. On the other hand, many studies have reported that physical and biochemical changes in wood properties are caused by heat treatment at low temperatures (Goring 1963, Ramiah and Goring 1967, Hatakeyama *et al.* 1969, Haw and Schultz 1985, Pakdel *et al.* 1989, Shukry *et al.* 1991, Ponder and Richards 1991, Masuku 1992, Scholze and Meier 2001, Kuroda 2007) and it has been pointed out that heat treatment leads to disadvantageous changes in lumber such as reductions in strength (Thompson 1969, Yoshida *et al.* 1999, Nakashima *et al.* 1999) or durability (Doi *et al.* 1998, 1999), and discoloring (Sumi 1978).

Some chemical changes probably happen in wood during long periods of heat-treatment even though the heat-treatment temperature is not so high because most wood constituents are organic compounds with functional groups. However, there are few reports on thermal chemical changes of wood at low temperature, especially lower than 100°C. Hence, it is necessary to perform further evaluation of heat-treated wood, e.g. kiln-dried lumber, to study chemical changes in the wood components caused by heat treatment at low temperatures.

In a preliminary study (Yamauchi *et al.* 2004), we found characteristic spectral changes in Raman bands of kiln-dried Japanese larch (*Larix leptolepis*) lumber.

In subsequent research on Japanese larch and beech (*Fagus crenata*) heat-treated at low temperatures (Yamauchi *et al.* 2005), we have reported the effect of heat-treatment temperature and water content on the chemical reactions in wood using Raman spectroscopic analysis. The most informative Raman spectral change common to both Japanese larch and beech was the decrease of Raman band intensity at 1655-1660 cm⁻¹, and it was concluded that this spectral change is due to decreases in the C=O groups in coniferaldehyde and C=C groups in coniferyl alcohol in lignin molecules. Moreover, we explained the effects of water content on the reactions in terms of the softening point of wood.

Our continued interest in the low temperature heat-treatment of wood has led us to explore the chemical changes in Japanese cedar (*Cryptomeria japonica*), which is the most popular plantation species in Japan. In Japan, kiln-drying for Japanese cedar lumber is one of the most noteworthy technologies in wood processing and the demand for kiln-dried Japanese cedar has increased rapidly because it is necessary to make the strain of the lumber smaller as a building material. Thus, it is of fundamental importance to obtain information on the chemical changes in Japanese cedar wood treated at low temperatures.

Our primary goal in this study is to explore the chemical changes in Japanese cedar arising from heat treatment in comparison with those in Japanese larch and beech through FT-Raman spectroscopy. In this article, we demonstrate the raw Raman and difference spectra of Japanese cedar heat-treated at low

temperatures (50-160°C) and discuss the chemical changes occurring in Japanese cedar wood. In addition, we reported the effects of heat-treatment time and temperature on the rate of decrease in Raman band intensity at 1655 cm^{-1} .

Materials and Methods

Wood samples and heat treatments

The test samples of sapwood and heartwood, 25(T) $\times$ 25(R) $\times$ 5(L) mm, were taken from an 80-year-old Japanese cedar planted in Akita prefecture. Five replicate samples were selected randomly from sapwood and heartwood, and then the average water contents at 25°C and 60% relative humidity (RH) were determined by an oven-drying method (105°C, 48 h).

Three heat-treatment procedures were employed as follows: (I) samples conditioned at 25°C and 60% RH were heated in an open vessel, (II) samples kept at 25°C and 90% RH for 2 days were heated in a Teflon cell with a small glass beaker filled with 1.5 ml water, and (III) water-swollen samples were heated in the Teflon cell. The Teflon cell was sealed in a stainless steel vessel and the cross-sectional view of the cell and vessel was illustrated in the previous report (Yamauchi *et al.* 2005). All the heat-treatment runs were carried out using an electric oven, and the cell and vessel were preheated to the desired temperature before the heating run. The wood samples treated by procedure I were heated at atmospheric pressure (ca. 0.10 MPa). The cell pressure in procedure II should be equal to that in procedure III, and the pressures at 70°C, 100°C, and 120°C were estimated to be 0.15 MPa, 0.23 MPa, and 0.33 MPa, respectively. The water contents of the samples before and after heat treatment were calculated from weight measurements. The heat-treated wood samples were cooled and dried at ambient conditions (23 $\pm$ 2°C, 50-70% RH) for more than 2 days, and then used for Raman measurements.

Raman measurements

FT-Raman spectra were recorded with a Jeol JIR 7000W spectrometer equipped with an RS-RSU-200 Raman module and a TGS detector. The excitation source was an Nd³⁺: YAG laser (1064.1 nm) in the 180° back-scattering configuration. The laser beam diameter was about 0.5 mm and the incident laser power was 200 mW, which is low enough to prevent irreversible damage to the wood samples. To obtain good-quality spectra, more than 1000 scans were required at about 2 cm^{-1} intervals (spectral resolution, ca. 4 cm^{-1}). All the Raman measurement spots were located on earlywood at the center of a transverse sectional surface of the Japanese cedar samples. Raman spectra were measured twice at the same spot on the surface of the wood sample before and after heat treatment.

Difference spectra

A difference spectrum was calculated by subtracting Raman spectrum A of a wood sample before heat treatment from spectrum B after heat treatment as follows.

$$\text{Difference spectrum} = \text{Spectrum B} - k \times \text{Spectrum A} \quad (1)$$

where k is a constant ($k \approx 1$), which is calculated when the intensity of an internal reference in a difference spectrum is zero. The base line of the difference spectrum was corrected to be free from bending due to fluorescence.

Results and Discussion

Water content of wood samples

There were no significant differences in water content between Japanese cedar sapwood and heartwood samples from each heat-treatment procedure. In procedure II, water in the glass beaker was hardly reduced when the heat treatment was completed, indicating that the inside of the Teflon cell was maintained at a saturated-water-vapor pressure during the heating run. The water content of Japanese cedar samples prior to heating lay within the ranges of 10.6-12.1% (25°C, 60% RH), 18.6-21.1% (25°C, 90% RH), and 230-320% (water-swollen state) in heat treatments I, II, and III, respectively. Immediately after the heating runs, the water content was in the ranges of 16.9-21.4% and 190-300% in procedures II and III, respectively. Thus, it can be concluded that the cedar samples possessed sufficient free water during procedure III but only bound water during procedure II because the fiber-saturation point of wood is generally in the water-content range of 22-35% (Takahashi and Nakayama 1992).

Raman spectra of Japanese cedar sapwood and heartwood heat-treated at low temperatures

Figure 1 demonstrates the Raman spectra in the wavenumber range from 1000 cm^{-1} to 3600 cm^{-1} of Japanese cedar sapwood (Fig. 1A) and heartwood (Fig. 1B) samples heat-treated for 22 h using procedure II. The most remarkable spectral change is base-line bending due to fluorescence arising from wood constituents in the wavenumber range below 2500 cm^{-1} . A noticeable increase in fluorescence intensity from the heartwood sample started at 80°C (Spectrum b in Fig. 1B). For sapwood, the base-line bending was not so large up to 100°C (Spectrum d in Fig. 1A), but bending developed rapidly from 110°C (Spectrum e in Fig. 1A). Hence, the results suggest that wood constituents other than the main components in the heartwood contribute strongly to fluorescence emission when the heat-treatment temperature is below 100°C. Moreover, both Japanese cedar sapwood and heartwood exhibited a tendency that heat treatment intensifies fluorescence in the order procedure I < II < III, at the same heat-treatment temperature, which is similar to Japanese larch and beech (Yamauchi *et al.* 2005).

The most important spectral change caused by heat treatment, which has already been reported previously (Yamauchi *et al.* 2004, 2005), was the decrease in intensity of the vibrational Raman band at about 1655 cm^{-1} with increasing heat-treatment temperature. The band at about 1655 cm^{-1} is due mainly to stretching vibrations of the C=O and C=C bonds in coniferaldehyde and coniferyl alcohol units,

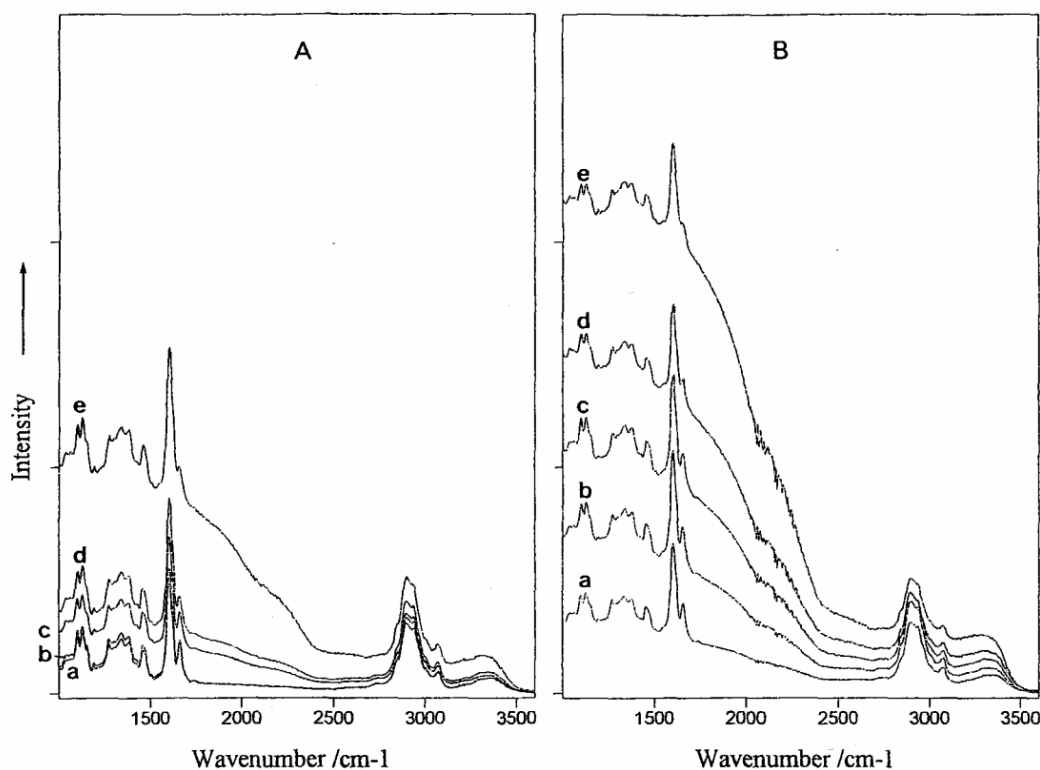


Fig. 1. Raman spectra of Japanese cedar sapwood (A) and heartwood (B) heat-treated by procedure II.
(A) sapwood; (a) 60°C, (b) 80°C, (c) 90°C, (d) 100°C, (e) 110°C,
(B) heartwood; (a) 60°C, (b) 80°C, (c) 90°C, (d) 100°C, (e) 110°C

respectively, in lignin molecules (Agarwal and Atalla 1993, Agarwal *et al.* 1995). We have explained the reduction in the band intensity in terms of the decrease in the C=O and C=C groups arising from the progress of chemical reactions in lignin (Yamauchi *et al.* 2005). Unlike Japanese larch, the growth of band intensity at 1635 cm^{-1} was not observed clearly in the raw Raman spectra of heat-treated Japanese cedar.

Difference spectra

Although the decrease in band intensity at 1655 cm^{-1} was visible as shown in Fig. 1, other spectral changes may be concealed in the Raman spectra. However, it was difficult to identify spectral changes thoroughly from the raw Raman spectra alone. In the previous paper (Yamauchi *et al.* 2005), we adopted a difference spectrum method to understand more exactly the Raman spectral changes and calculated two kinds of difference spectra independently of each other using two internal references. One reference was the strong band at about 1600 cm^{-1} due to a totally symmetric vibration of an aromatic ring (reference A). The other was a group of several bands around 1100 cm^{-1} (reference B), which are assigned to stretching vibrations of C-C and C-O bonds in cellulose or hemicellulose (Agarwal and Atalla 1993, Agarwal and Ralph 1997). Japanese cedar showed difference spectra similar to Japanese larch in both cases using references A and B. We considered that reference B was more reliable than reference A because the band intensity at 1600 cm^{-1} may grow by a pre-resonance effect, and

hence discuss here only the difference spectra of Japanese cedar calculated using reference B.

1. Japanese cedar sapwood

Figure 2 depicts the difference spectra of Japanese cedar sapwood after heat-treatment procedures I (Fig. 2A), II (Fig. 2B), and III (Fig. 2C) for 22 h. The characteristic changes in difference spectra with increasing heat-treatment temperature were as follows.

- (1) Decrease in Raman intensity at 1655 cm^{-1}
- (2) Increase in Raman intensity at 1635 cm^{-1}
- (3) Rapid growth of Raman band around 1600 cm^{-1} above 150°C in procedure I
- (4) Appearance of a very weak peak or shoulder at about 1612 cm^{-1} in procedures II and III

These spectral changes have been already observed in the difference spectra of Japanese larch and beech heat-treated at low temperatures (Yamauchi *et al.* 2005). The explanation of decrease in Raman intensity at 1655 cm^{-1} was described above. This decrease became observable from 110–120°C in procedure I, 70°C in procedure II, and 60°C in procedure III. The intensity at 1655 cm^{-1} showed an accelerating decrease with the increasing heat-treatment temperature. In general, the cooking (delignification) of wood in pulping processes is carried out at much higher than ambient temperature and pressure. Thus, for procedures II and III, it is suggested that the increase in cell pressure may also contribute to the softening of lignin. The increase in the

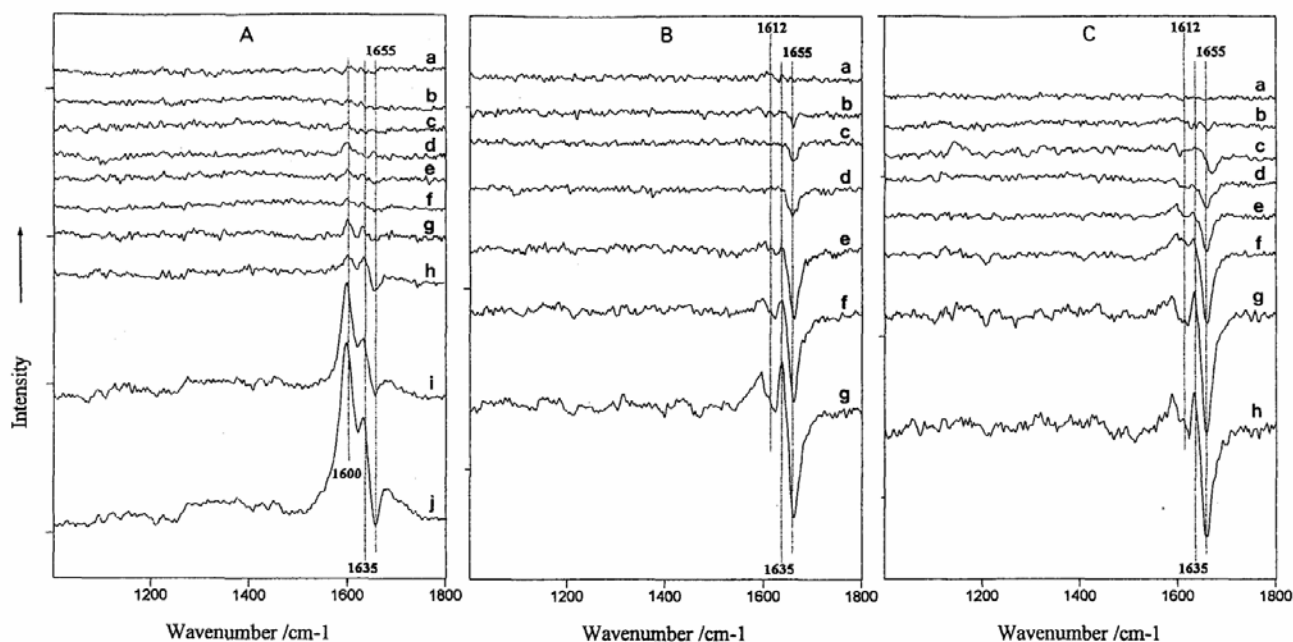


Fig. 2. Difference spectra calculated from the Raman spectra of Japanese cedar sapwood before and after heat-treatment procedures I, II, and III using internal reference B.

(A) procedure I; (a) 70°C, (b) 80°C, (c) 90°C, (d) 100°C, (e) 110°C, (f) 120°C, (g) 130°C, (h) 140°C, (i) 150°C, (j) 160°C,

(B) procedure II; (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C, (e) 100°C, (f) 110°C, (g) 120°C,

(C) procedure III; (a) 50°C, (b) 60°C, (c) 70°C, (d) 80°C, (e) 90°C, (f) 100°C, (g) 110°C, (h) 120°C

intensity at 1635 cm^{-1} may be attributable to the formation of stilbene derivatives (Agarwal and Atalla 2000). The growth of the band at 1600 cm^{-1} is possibly caused by a pre-resonance effect. A possible explanation for the weak peak at 1612 cm^{-1} is the slight shifting of the strong band at 1600 cm^{-1} due to the presence of substitution product of the benzene ring.

2. Japanese cedar heartwood

The Raman spectra of Japanese cedar heartwood showed strong base-line bending due to intense fluorescence in comparison to sapwood, and thus it was difficult to correct the bent base-line exactly. However, the same spectral changes as sapwood were confirmed in the difference spectra of heartwood treated by heat treatment I, II, or III. Therefore, it could be concluded that no significant differences in the Raman spectral features between sapwood and heartwood were observed in the wavenumber range from 1000 cm^{-1} to 1800 cm^{-1} when Japanese cedar was treated at low temperature.

3. Effects of heat-treatment time

Figure 3 demonstrates the Raman spectra of Japanese cedar sapwood heat-treated at 90°C by procedure II for various times. The base-line bending below 2500 cm^{-1} increases clearly and the Raman intensity at 1655 cm^{-1} decreased with increasing heat-treatment time. Figure 4 shows the difference spectra calculated using reference B. The contours of the difference spectra reveal that the decrease in intensity at 1655 cm^{-1} becomes larger as heat-treatment

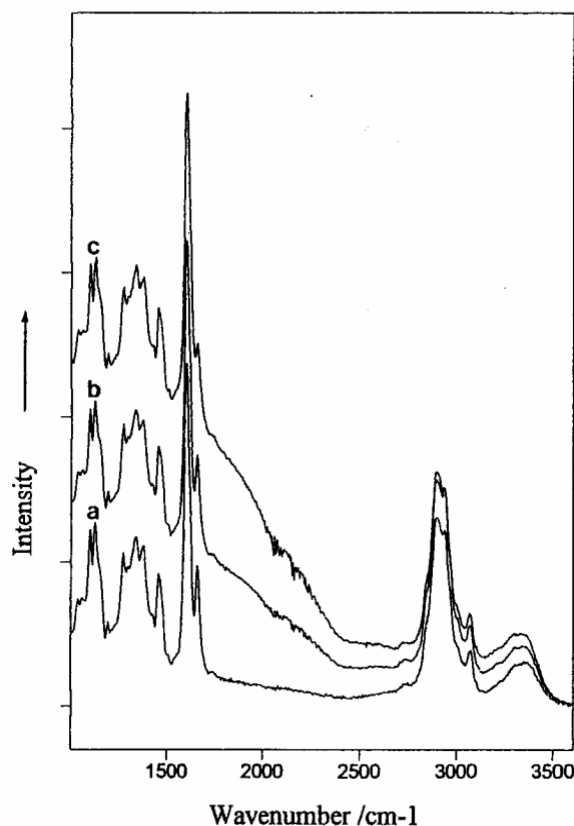


Fig. 3. Raman spectra of Japanese cedar sapwood heat-treated at 90°C by procedure II.
(a) 25 h, (b) 48 h, (c) 120 h

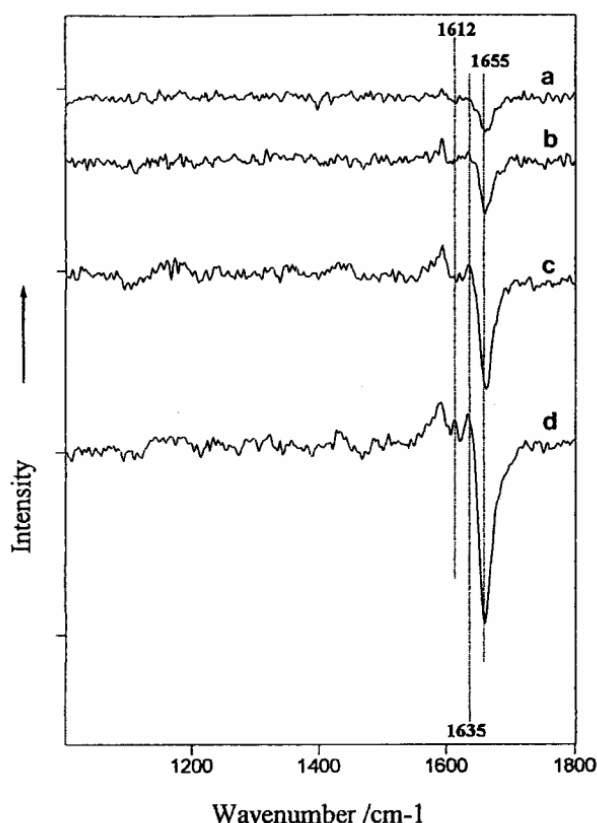


Fig. 4. Difference spectra calculated from the Raman spectra of Japanese cedar sapwood before and after heat-treatment procedure II (90°C). (a) 12 h, (b) 25 h, (c) 48 h, (d) 120 h

time increases. Moreover, weak peaks at about 1612 cm^{-1} (Spectrum d in Fig. 4) and 1635 cm^{-1} (Spectra c and d in Fig. 4) became observable with increasing heat-treatment time. These spectral changes are very similar to those with increasing heat-treatment temperature.

We investigated the progress of the chemical reaction of the C=O and C=C groups in lignin during heat treatment on the basis of the decrease in Raman intensity at 1655 cm^{-1} . To avoid interference by fluorescence, the ratio of peak height at 1655 cm^{-1} after heat treatment (h') to that before heat treatment (h) was determined as described previously (Yamauchi *et al.* 2005) and the value of h'/h , which expresses the total residual rate of the C=O and C=C groups, was plotted against heat-treatment time in Fig. 5.

As can be seen from Figs. 1 and 3, it becomes more difficult to obtain an exact value of peak height at 1655 cm^{-1} as heat-treatment time or heat-treatment temperature increases. Thus, Figure 5 shows the h'/h values in the range from 70°C to 100°C and below 80 h. The h'/h values decreased smoothly and curve-linearly with increasing heat-treatment time and the decreasing rate was elevated by increasing heat-treatment temperature. Assuming that the reduction in Raman intensity at 1655 cm^{-1} is due to the decrease of the C=O and C=C groups, it follows that the chemical reactions in lignin molecules proceed more rapidly as heat-treatment temperature increases. Moreover, as

mentioned above, the increase in cell pressure may contribute to decrease in the softening point of lignin. The results from Fig. 5 reveal that in heat treatment II the reactions accelerated above 70°C, especially above 90°C, and support the view that the reaction rate is closely related to softening of lignin because water-swollen lignin has a softening point near 80°C (Furuta 2000).

Table 1 summarizes the h'/h data of Japanese cedar shown in Fig. 5 (treatment time 23–25 hours) and of Japanese beech reported previously. It is evident that the rate of decrease in the band intensity at 1655 cm^{-1} of Japanese cedar was faster than that of beech at each heat-treatment temperature. According to Iida (1986), there was no significant difference in the softening point between Japanese hardwood and softwood in the range 63–80°C when the wood sample was water swollen. However, Raman measurements made it clear that Japanese cedar lignin chemically changed more easily than beech lignin in heat treatment II.

The kinetic approach of the reactions corresponding to the reduction of Raman band intensity at 1655 cm^{-1} is certainly very important, because a temperature-dependence of the reaction rate is clearly shown in Fig. 5. However, we have not obtained sufficient information on the mechanisms and products of the reactions of the C=O and C=C groups; therefore, we will not kinetically analyze the reaction here.

Concluding Remarks

Based on the Raman spectral changes, we investigated the chemical changes in Japanese cedar sapwood and heartwood caused by heat treatment at low temperatures, and discussed the effects of heat-treatment temperature and time on the chemical reactions.

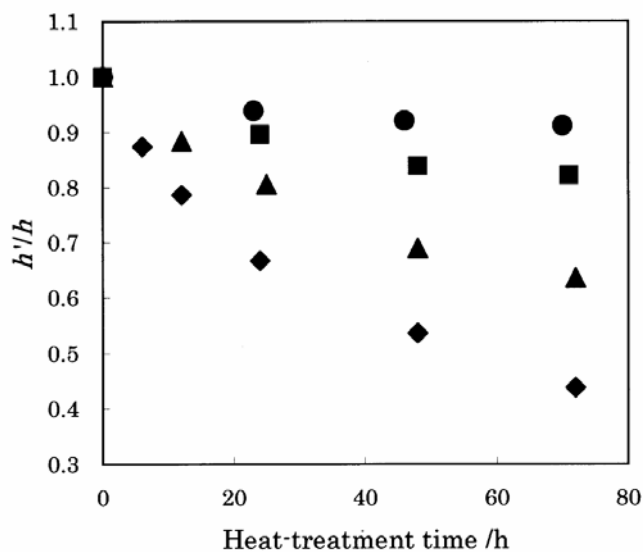


Fig. 5. Decrease in Raman intensity at 1655 cm^{-1} by heat-treated procedure II at various temperatures. (●) 70°C, (■) 80°C, (▲) 90°C, (◆) 100°C

Table 1. Comparison of the decrease in Raman intensity at 1655 cm⁻¹ of Japanese cedar and beech (Yamauchi *et al.* 2005) treated by procedure II.

Heat-treatment temperature (°C)	70		80		90		100	
	Cedar	Beech	Cedar	Beech	Cedar	Beech	Cedar	Beech
Heat-treatment time (h)	23	22	24	22	25	22	24	22
<i>h</i> '/ <i>h</i>	0.94	1.00	0.90	1.00	0.81	0.95	0.67	0.81

Fluorescence intensity was enhanced by increases in heat-treatment temperature or time. Although the enhancement of fluorescence in heartwood was much stronger than that in sapwood, there were no significant differences in the spectral changes of vibrational Raman bands in the range from 1000 cm⁻¹ to 1800 cm⁻¹ between sapwood and heartwood. Thus, the main chemical reactions during low temperature heat-treatment in heartwood are the same as those in sapwood. In the three heat-treatment procedures with different water content conditions, the overall spectral changes of Japanese cedar were very analogous to those of Japanese larch.

The most important spectral change of Raman band arising from heat treatment was the reduction in intensity at 1655 cm⁻¹, corresponding to the decrease in C=O and C=C groups in lignin molecules. The rate of decrease clearly increased with increasing heat-treatment temperature in the range from 70°C to 100°C, suggesting that the softening of lignin is closely involved with the acceleration of the chemical reactions. By comparing with the *h*'/*h* data of Japanese beech, evidence was obtained which shows that Japanese cedar lignin begins to change chemically at a lower heat-treatment temperature than beech.

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