J Wood Sci (2005) 51:498–506
DOI 10.1007/s10086-004-0691-6

ORIGINAL ARTICLE

Shigeru Yamauchi · Yasuo Iijima · Shuichi Doi

Spectrochemical characterization by FT-Raman spectroscopy of wood heat-treated at low temperatures: Japanese larch and beech

Received: March 19, 2004 / Accepted: November 5, 2004

Abstract Test samples of Japanese larch (*Larix leptolepis*) heartwood and Japanese beech (*Fagus crenata*) sapwood were heated for 22 h at constant temperatures (50°–180°C) under three water content conditions. Raman spectra of the samples were recorded before and after the heat treatments, and spectral changes in the range from 1000 cm^{-1} to 1800 cm^{-1} were evaluated using the difference spectrum method. For both wood species, the Raman band intensity at 1655–1660 cm^{-1} due mainly to the C=C and C=O groups in lignin clearly decreased with increasing heat-treatment temperature (HTT). The spectral change was thought to reflect the progress of condensation reactions of lignin molecules during the heat treatment. Moreover, the decrease in band intensity was considerably facilitated by the presence of water in the cell wall, suggesting that the condensation is closely related to the softening of lignin. From the spectral changes in the wavenumber region of 1200–1500 cm^{-1}, it was considered that wood constituents are partially decomposed at the higher HTT.

Key words Raman spectroscopy · Heat treatment · Japanese larch · Japanese beech · Lignin

Introduction

Heat treatment of wood and wood-based materials has been directed toward not only artificial drying but also dimensional stabilization, deformation and fixation, separation of extracts, and others. Although wood scarcely loses weight up to 200°C, a number of studies[1–9] have pointed out that the physical and biochemical properties of wood change during heat treatment at lower temperatures. Such treatment leads to undesirable changes, such as reduction in strength[10–12] or durability,[13,14] and discoloring.[15] Therefore, it is of fundamental importance to investigate the changes of wood constituents at the molecular level to develop the heat-treatment techniques for producing high-quality wood.

To do this, it is desirable that the analysis of heat-treated wood includes no wet process, because the products of heat treatment are not always chemically stable. In the past decade, the application of Raman spectroscopy suitable for nondestructive analysis has been extended to many kinds of woody materials by employing Fourier transform (FT) techniques and a near-infrared laser. We have used this spectroscopic tool for local analysis of materials made from lignocellulosics because it probes only a small laser spot, and we have obtained much information on the chemical behavior of adhesives[16,17] and preservatives[18] in wood. Moreover, we recently reported the Raman spectra of artificially dried Japanese larch (*Larix leptolepis*) lumber.[19] The preliminary study showed not only important and intriguing aspects of chemical changes in wood during artificial drying but also several problems to be clarified.

The aim of the present article is to examine the effects of heat-treatment temperature (HTT) and water content on the chemical changes in wood. Small block samples of Japanese larch, softwood, were heat-treated at temperatures ranging from 50° to 180°C under three water content conditions. Japanese beech (*Fagus crenata*), hardwood, was also explored in the same way as Japanese larch, because there are distinct differences in hemicellulose and lignin between softwood and hardwood. We describe here the Raman spectra of larch and beech samples that were heat-treated at low temperatures (≦180°C), and further discuss the chemical changes in both wood species during heat treatment based on the spectral changes.

S. Yamauchi (✉) · Y. Iijima
Institute of Wood Technology, Akita Prefectural University, 11-1 Kaieisaka, Noshiro 016-0876, Japan
Tel. +81-185-52-6985; Fax +81-185-52-6976
e-mail: sigeru@iwt.akita-pu.ac.jp

S. Doi
Graduate School of Life and Environmental Sciences, University of Tsukuba, Tsukuba 305-8572, Japan

---

Part of this article was presented at the 53rd Annual Meeting of the Japan Wood Research Society, Fukuoka, March 2003

Experimental

Wood samples and heat treatments

The wood blocks used as test samples were taken from Japanese larch heartwood and Japanese beech sapwood. The blocks of larch and beech measured 15 (T) × 15 (R) × 5mm (L) and 25 (T) × 25 (R) × 5mm (L), respectively. Prior to heat treatment, all the samples were weighed at 25°C and 60% relative humidity (RH). Five replications were selected from the samples of each wood species and the average water contents at 25°C and 60% RH were based on the assumption that water content of the wood samples was approximately zero after 48h of oven-drying at 105°C. On the basis of these average values, the water contents of the samples before heat treatment were calculated from the weights.

Three different procedures of heat treatment were employed as follows: (I) the samples were conditioned at 25°C and 60% RH, and then were heated in an open vessel at the desired temperature for 22h, (II) the samples were kept at 25°C and 90% RH for 2 days, and immediately were put in a sealed vessel together with a small glass beaker containing 1.5ml of water and heated for 22h (Fig. 1a), and (III) water-swollen samples were heated in the sealed vessel for 22h (Fig. 1b). All heat treatments were carried out using an electrical oven, and the desired temperature was varied from 70° to 180°C in procedure I and from 50° to 130°C in procedures II and III at intervals of 10°C. The 22-h heat treatment was adopted in this study, because the period of heating at the highest temperature in artificial drying of wood is generally about 1 day. It was difficult to perform reliable analysis of Raman spectra due to intense fluorescence when the HTT exceeded the upper limit. The sealed vessel consisted of an outer stainless-steel vessel and an inner Teflon cylindrical cell (diameter 34mm, 55mm high), as shown in Fig. 1. After heat treatment, the wood samples were cooled and dried at ambient conditions (23° ± 1°C, 50%–70% RH) for more than 2 days, and then used for Raman measurements.

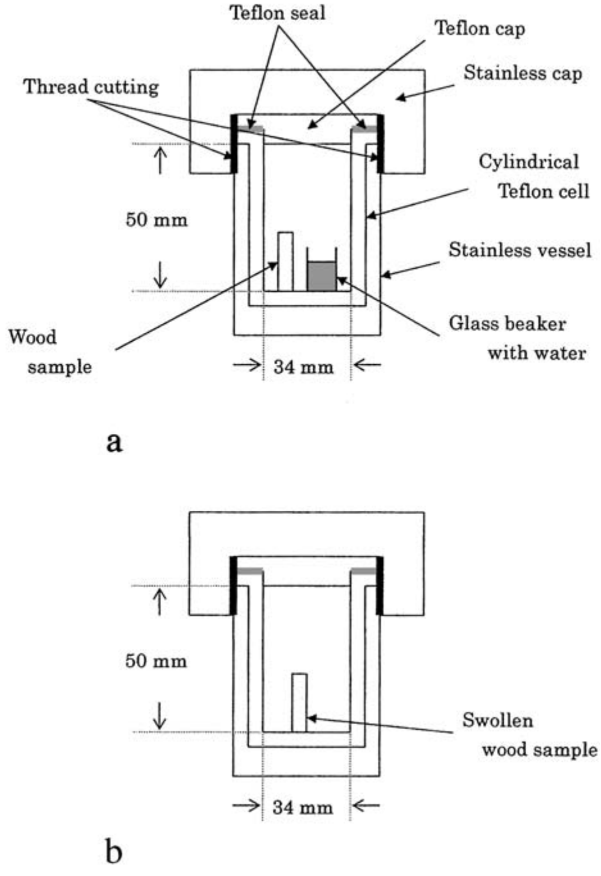


Fig. 1. Stainless steel and Teflon vessels used in heat-treatment procedures II (**a**) and III (**b**)

Raman measurements

FT-Raman spectra were recorded with a Jeol JIR 7000W spectrometer connected to an RS-RSU-200 Raman module with a backscattering configuration. Excitation of Raman spectra was carried out with irradiation of 1064.1nm from a Nd^{3+}: YAG laser. The focused spot of the laser beam was about 0.5mm in diameter and the laser power was about 200mW on the sample. 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 points were located on earlywood at the center of the transverse sectional surface of the wood blocks. Raman spectra were measured twice at the same point on the sample surface before and after heat treatment.

Difference spectra

Strong background owing to fluorescence was eliminated by calculation of the difference Raman 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.

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

where k is calculated when the intensity of an internal reference in a difference spectrum is zero.

Results and discussion

Water content of wood samples

The average water contents of Japanese larch and beech samples before heat treatment are listed in Table 1. Water in the glass beaker was scarcely reduced when heat treatment II was completed, indicating that the inside of the Teflon cell was held at a saturated-water-vapor pressure during the heat treatment. Immediately after completion of procedure III, all the heat-treated larch and beech samples had more than 60% water content. The results clearly show

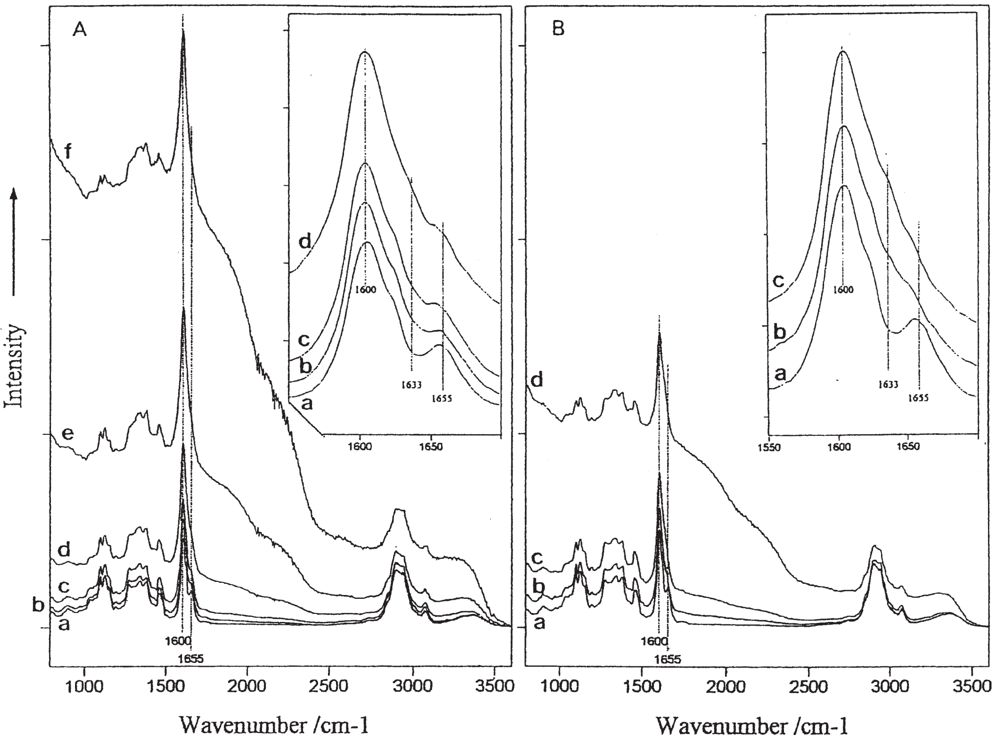


Fig. 2. Raman spectra of larch heartwood heat-treated by procedures I (**A**) and III (**B**). **A**: *a*, untreated; *b* 120°C; *c* 140°C; *d* 160°C; *e* 170°C; *f* 180°C. **B**: *a* untreated; *b* 100°C; *c* 110°C; *d* 120°C

Table 1. Average water content of the wood samples before heat treatment

	25°C, 60% RH (procedure I)	25°C, 90% RH (procedure II)	Water-swollen (procedure III)
Japanese larch	8.2%	17.7%	110%
Japanese beech	8.3%	20.0%	120%

RH, relative humidity

that the wood samples maintained free water sufficiently in the lumen and intercellular space throughout the heating run, because the fiber saturation point of wood is usually in the water content range of 22% to 35%.

Raman spectra

Figure 2 demonstrates Raman spectra in the range from $800\,\mathrm{cm}^{-1}$ to $3600\,\mathrm{cm}^{-1}$ of heat-treated larch samples from procedures I (Fig. 2A) and III (Fig. 2B). For both heat-treatment methods, Raman spectral changes became greater with increasing HTT and the most remarkable change was strong background due to fluorescence in the low wavenumber region. As can be seen in Fig. 2, there were pronounced differences in fluorescence intensity between the two heat-treatment procedures. In the heating runs of procedure I, the increase in fluorescence with increasing HTT was very small up to 140°C, but became exponentially greater when HTT exceeded 160°C. In procedure III, the steep intensification of background started from 120°C. The larch samples heat-treated in procedure II also showed a prompt increase of fluorescence intensity from 120°C, although the increase was not as steep as that in procedure III. Assuming that the fluorescence is induced by laser irradiation of products of the heat treatments, these Raman spectra suggest progress of some chemical reactions in wood constituents and important roles of water in the reactions.

We next describe the vibrational Raman bands of wood samples. The most notable change in vibrational bands was a reduction of the relative intensity of the band at about $1655\,\mathrm{cm}^{-1}$ with increasing HTT. This band is mainly attributed to the C=O and C=C groups in the coniferaldehyde and coniferyl alcohol structures, respectively, in lignin molecules.[20,21] Moreover, a new band is observed around 1630–$1640\,\mathrm{cm}^{-1}$ as a shoulder as shown in the inset of Fig. 2. According to Agarwal and Atalla,[22] olefinic C=C bonds in the stilbene structure show a strong Raman band at $1635\,\mathrm{cm}^{-1}$. Therefore, this band may suggest that stilbene derivatives are produced by the heat treatments. These spectral changes resulting from the heat treatments were expected after considering the previously reported Raman spectra of artificially dried larch.[19]

Figure 3 depicts the Raman spectra of heat-treated beech from procedures I (Fig. 3A) and III (Fig. 3B). The control samples exhibit a band around $1740\,\mathrm{cm}^{-1}$ due to the C=O groups, mainly in xylan.[23,24] This is a characteristic Raman band of hardwood species and usually appears as only a trace in the Raman spectra of softwood.[24–26] Like larch heartwood, both treatments I and III led to fluorescence intensification and the reduction of band intensity at $1660\,\mathrm{cm}^{-1}$, whereas it was not clear whether the relative intensity of the bands at 1630–$1640\,\mathrm{cm}^{-1}$ and $1740\,\mathrm{cm}^{-1}$ changed during heat treatment from Fig. 3 alone.

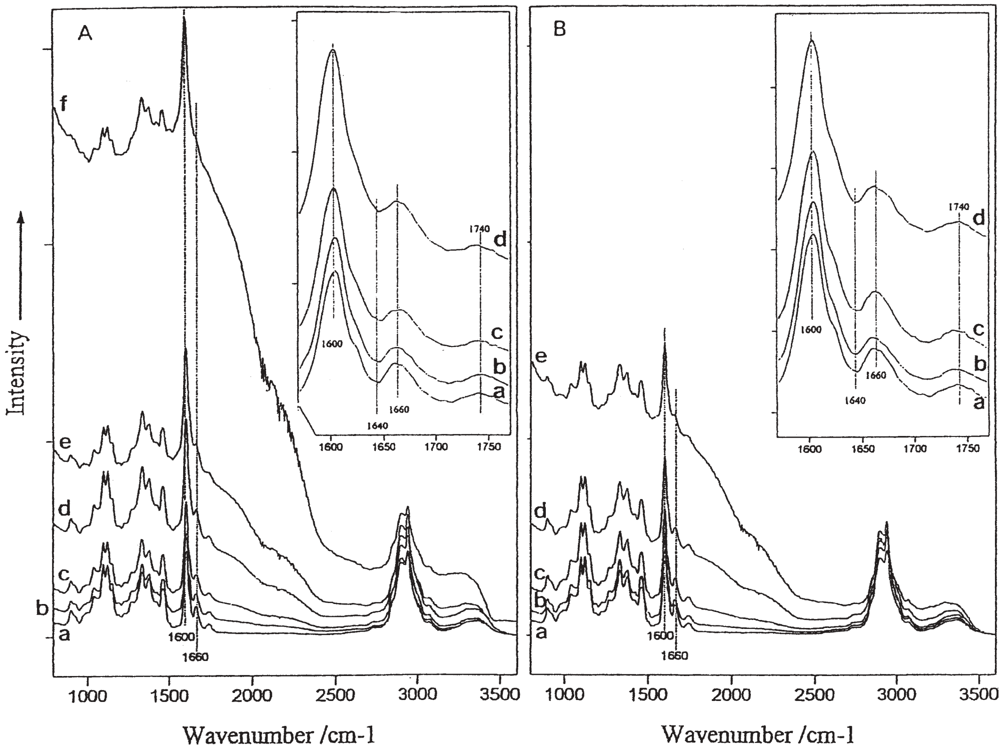


Fig. 3. Raman spectra of beech sapwood heat-treated by procedures I (**A**) and III (**B**). **A**: *a* untreated; *b* 140°C; *c* 150°C; *d* 160°C; *e* 170°C; *f* 180°C. **B**: *a* untreated; *b* 80°C; *c* 90°C; *d* 100°C; *e* 110°C

It may be expected that the fluorescence contains much information on chemical changes with heat treatments at low temperatures. However, the mechanisms of fluorescence induction by laser irradiation are very intricate, and a trace amount of the product of heat treatment can result in intense fluorescence. Hence, the chemical changes in Japanese larch and beech wood during the heat treatments were discussed based on the spectral changes in vibrational Raman bands.

Difference spectra

Although the results in Figs. 2 and 3 show the important spectral changes in the Raman bands, it was difficult to evaluate precisely all of the spectral changes from the raw Raman spectra alone. Thus, the difference spectrum method is adopted as an arithmetical analysis of Raman spectra to understand the spectral changes in more detail and to find other small spectral changes.

Japanese larch heartwood

The difference spectra calculated from the Raman spectra of larch samples before and after heat treatments I, II, and III are demonstrated in Figs. 4, 5, and 6, respectively. In each heat-treated sample, two kinds of difference spectra were calculated individually by using two internal references. One reference is the strong band at about 1600 cm^{-1} that does not shift significantly even though chemical changes occur at the side chains of an aromatic ring. The other is a band group at around 1100 cm^{-1}. The Raman bands of wood in the range 1050–1150 cm^{-1} are due mainly to stretching vibrations of C—C and C—O bonds in cellulose and hemicellulose.[20,27] The former is expressed as internal reference A, and the latter as B.

As can be seen in Fig. 4A, the first spectral changes with the rise of HTT appear at 120°C as a decrease of the band at 1655 cm^{-1} and an increase of that at about 1633 cm^{-1}. These changes become greater as HTT is increased. These spectral changes are also observable in Fig 4B, although they are not as clear as those in Fig. 4A. A peak at 1612 cm^{-1} appears above 150°C and develops with HTT by using the internal reference A, while this band is undetectable when the internal reference B is adopted. The same band appears as a small peak or shoulder above about 100°C in Figs. 5A and 6A.

In these spectral changes, the reduction of the band at 1655 cm^{-1} will be the most informative one, and is likely explained in terms of the condensation reaction of lignin molecules. As mentioned earlier, the band at 1655 cm^{-1} is due mainly to C=O and C=C groups in coniferaldehyde and coniferyl alcohol structures of lignin, and hence it is likely that the reduction of band intensity is attributable mainly to condensation reactions of lignin molecules. The band at 1612 cm^{-1} may be due to the vibrational mode of benzene rings having side chains that change chemically with the condensation, that is, part of the strong band at 1600 cm^{-1} shifting to slightly higher wavenumbers. A possible explanation for the intensification of the band at 1633 cm^{-1} is the formation of stilbene derivatives.

As shown in Figs. 5 and 6, similar spectral changes occur during heat treatments II and III, but become observable at much lower temperatures in comparison with procedure I,

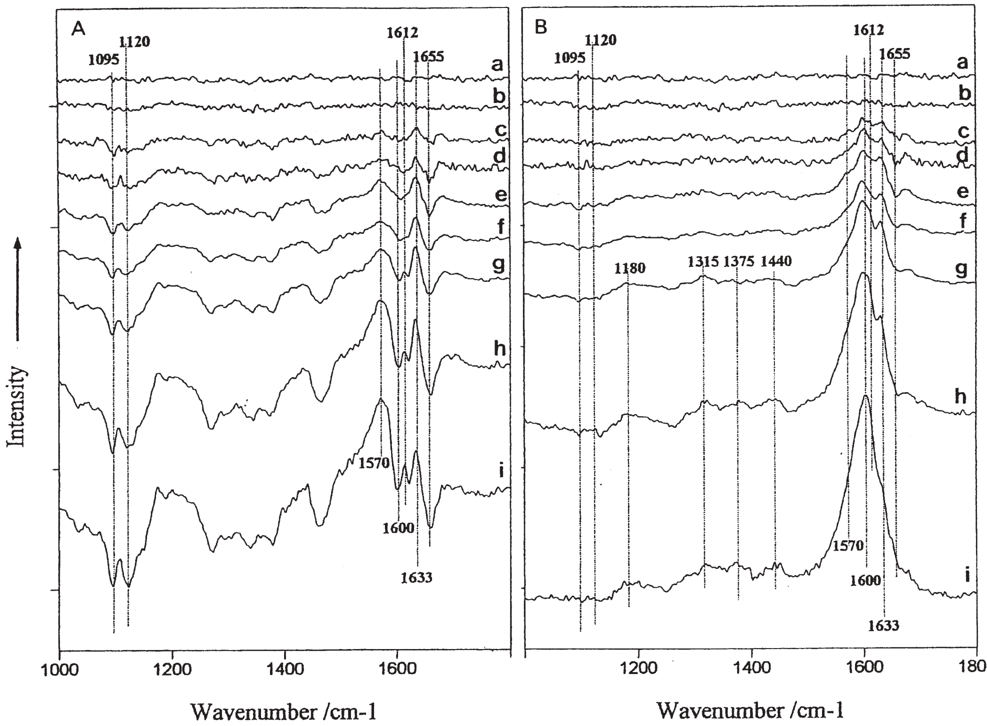


Fig. 4A,B. Difference spectra calculated from the Raman spectra of larch heartwood before and after heat-treatment procedure I. **A** Calculation method using internal reference A: *a* 100°C; *b* 110°C; *c* 120°C; *d* 130°C; *e* 140°C; *f* 150°C; *g* 160°C; *h* 170°C; *i* 180°C. **B** Calculation method using internal reference B: *a* 100°C; *b* 110°C; *c* 120°C; *d* 130°C; *e* 140°C; *f* 150°C; *g* 160°C; *h* 170°C; *i* 180°C

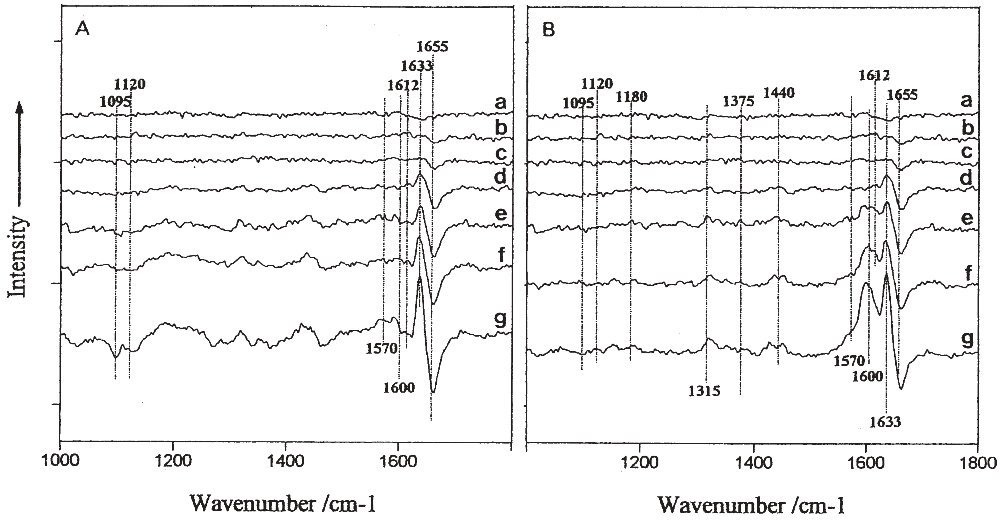


Fig. 5A,B. Difference spectra calculated from the Raman spectra of larch heartwood before and after heat-treatment procedure II. **A** Calculation method using internal reference A: *a* 60°C; *b* 70°C; *c* 80°C; *d* 90°C; *e* 100°C; *f* 110°C; *g* 120°C. **B** Calculation method using internal reference B: *a* 60°C; *b* 70°C; *c* 80°C; *d* 90°C; *e* 100°C; *f* 110°C; *g* 120°C

indicating that the presence of water accelerates the chemical reactions shown by the changes of Raman band intensity. However, there are only small differences in the progress of the chemical changes between heat treatments II and III despite large differences in water content. This suggests that free water in the lumen or intercellular space has little effect on facilitating the reactions. Moreover, the increase in the band intensity at 1633 cm^{-1} is detected at about 20°C higher than the decrease in the band at 1655 cm^{-1}. This is an important result that indicates that the chemical changes corresponding to the increase and those to the decrease in band intensity will not always occur at the same time.

We next describe the differences between the series of difference spectra A and B. The differences between them common to Figs. 4, 5, and 6 appear at the band at 1600 cm^{-1} and in the range from 1000 to 1500 cm^{-1}. For each heat-treatment procedure, it is obvious that the band intensity at 1600 cm^{-1} in B increases steeply when HTT is above a certain temperature. The benzene ring is, however, very unlikely to be produced in larch wood during heat treatment. A possible explanation for the growth of the band at 1600 cm^{-1} is the pre-resonance Raman scattering occasionally observed in Raman spectra, although we have obtained no experimental evidence. The intensification of the band at 1600 cm^{-1} is not unreasonable if any compounds that have

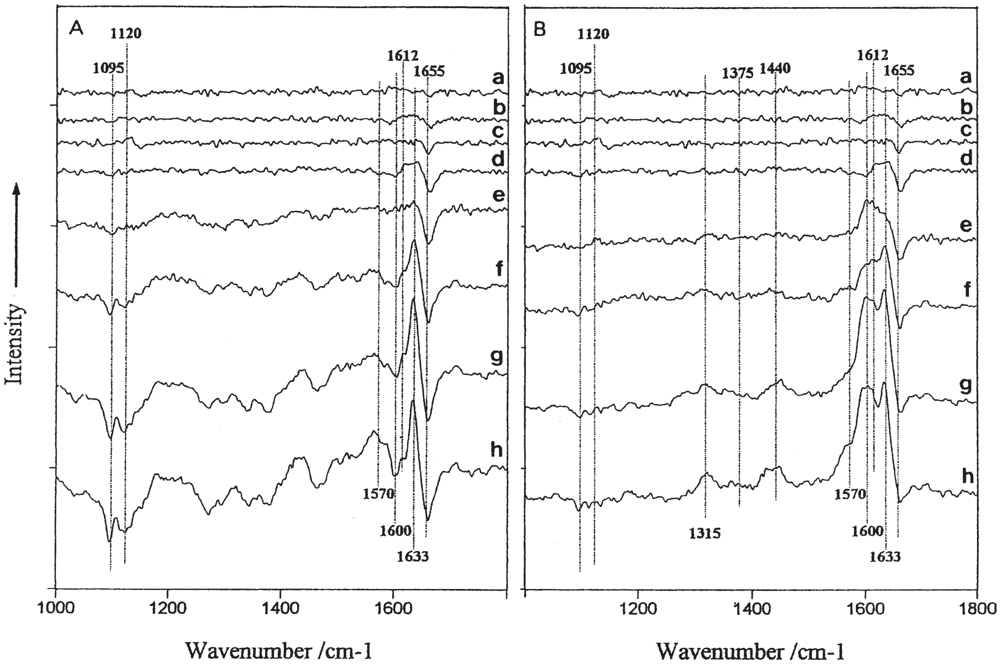


Fig. 6A,B. Difference spectra calculated from the Raman spectra of larch heartwood before and after heat-treatment procedure III. **A** Calculation method using internal reference A: *a* 50°C; *b* 60°C; *c* 70°C; *d* 80°C; *e* 90°C; *f* 100°C; *g* 110°C; *h* 120°C. **B** Calculation method using internal reference B: *a* 50°C; *b* 60°C; *c* 70°C; *d* 80°C; *e* 90°C; *f* 100°C; *g* 110°C; *h* 120°C

absorption near 1064.1 nm are generated from lignin molecules during the heat treatment and the absorption is ascribed to the benzene ring or groups directly bonded to the benzene ring.

In Figs. 4A, 5A, and 6A, a number of valleys appear in the range from 1000 to 1500 cm^{-1} at the same HTT that the band at 1600 cm^{-1} begins to increase in B. These valleys become deeper as HTT is increased. The spectral contours in this region are very similar to those of the Raman spectra of Japanese larch (see Fig. 2) when the vertical axis is reversed. On the other hand, quite different spectral changes are observed in the 1000–1500 cm^{-1} region with HTT when reference B is used. Several peaks that are not observed in the Raman spectra of non-heat-treated samples appear above 160°C, 110°C, and 100°C, in procedures I, II, and III, respectively, and hence they are likely due to components decomposed by heat treatment. It was reported that the major components of wood, cellulose, lignin, and hemicellulose start to decompose or depolymerize thermally at remarkably low temperatures.[2,28,29] Thus, these spectral changes in Figs. 4B, 5B, and 6B allow us to postulate partial decomposition of the wood constituents, especially hemicellulose which is considered to begin pyrolysis at the lowest temperatures.[2]

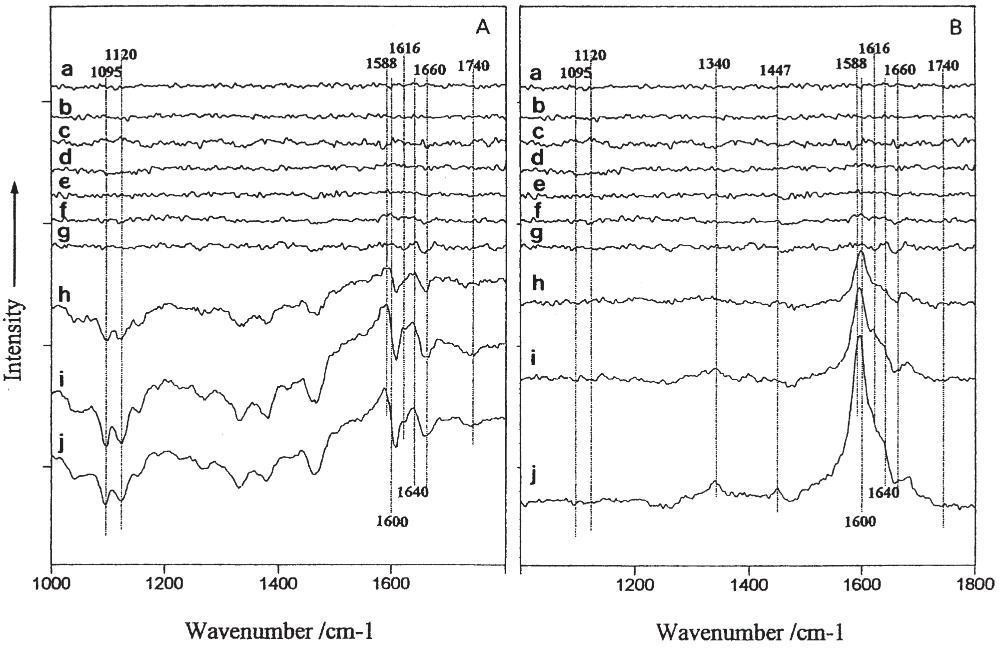
Japanese beech sapwood

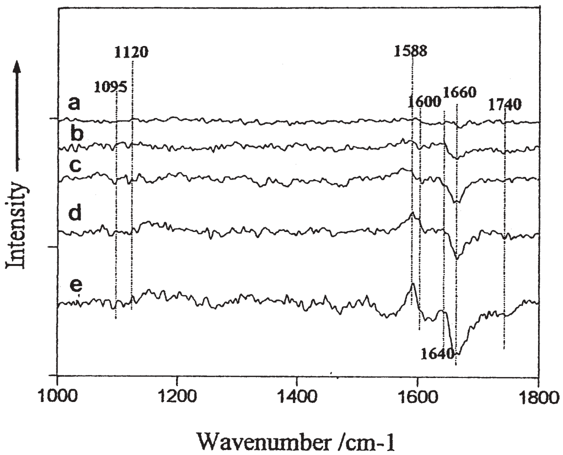
Figures 7, 8, and 9 depict the difference spectra of the heat-treated Japanese beech sapwood from procedures I, II, and III, respectively. A number of spectral changes similar to larch are observed with the rise of HTT. As can be seen in Fig. 7B, the intensification of the band at 1600 cm^{-1} caused by heat treatment I appears rapidly from 150°C, which is about 30°C higher than larch. For procedures II and III, the most prominent difference from larch was that intensification of the band at 1600 cm^{-1} during heat treatment was not observed at all up to 120°C. In other words, there is no difference between the results obtained from the calculation methods A and B in the HTT range in this study, and hence we show only the difference spectra calculated by method B of the beech sapwood heat-treated through procedures II and III.

The difference spectra of beech show decreases in band intensity at about 1660 cm^{-1} with increasing HTT for all heat-treatment procedures, like those of larch. These results indicate that the primary chemical reactions in beech sapwood are analogous to those in larch heartwood and suggest the same effects of water on the reactions. However, the lowest temperatures yielding a decrease in band intensity at 1660 cm^{-1} are 140°C, 100°C, and 90°C in procedures I, II, and III, respectively, and are higher than those for larch.

The changes in the decreasing rates of band intensity at 1660 cm^{-1} are discussed for the HTT range free from interference of the band intensification at 1600 cm^{-1}. As shown in Fig. 10, the Raman spectrum after heat treatment was normalized by the use of internal reference B in the Raman spectrum before heat treatment, and the ratio of peak height at 1660 cm^{-1} after heat treatment to that before heat treatment, h'/h, was determined. The value of $h'/h \times 100$ (%) is plotted against HTT in Fig. 11. As expected from the difference spectra, the decreasing rate of the band intensity at 1660 cm^{-1} in Fig. 7 is much smaller than those in Figs. 8 and 9. Moreover, it can be seen that the decrease rate in Fig. 8 is smaller than that in Fig. 9, although the differences between them are not large. This confirmed that water, especially water absorbed in the cell wall, plays an important part in the chemical reactions of lignin molecules caused by heat treatment at low temperatures.

Fig. 7A,B. Difference spectra calculated from the Raman spectra of beech sapwood before and after heat-treatment procedure I. **A** Calculation method using internal reference A: *a* 80°C; *b* 90°C; *c* 100°C; *d* 110°C; *e* 120°C; *f* 130°C; *g* 140°C; *h* 150°C; *i* 160°C; *j* 170°C. **B** Calculation method using internal reference B; *a* 80°C; *b* 90°C; *c* 100°C; *d* 110°C; *e* 120°C; *f* 130°C; *g* 140°C; *h* 150°C; *i* 160°C; *j* 170°C





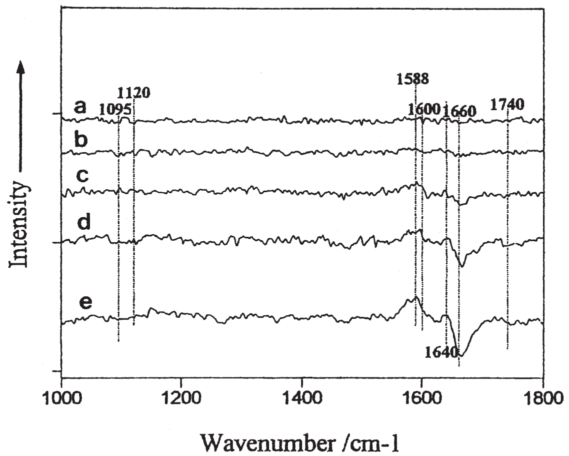


Fig. 8. Difference spectra calculated from the Raman spectra of beech sapwood before and after heat-treatment procedure II. *a* 80°C; *b* 90°C; *c* 100°C; *d* 110°C; *e* 120°C

Fig. 9. Difference spectra calculated from the Raman spectra of beech sapwood before and after heat-treatment procedure III. *a* 80°C; *b* 90°C; *c* 100°C; *d* 110°C; *e* 120°C

The difference spectra of heat-treated beech in Figs. 7, 8, and 9 show that the intensity at about 1640 cm^{-1} rises with increasing HTT and a shoulder appears at 1616 cm^{-1} above 150°C. These spectral changes probably indicate that chemical changes similar to those in larch occur in beech during the heat treatments, although the wavenumbers are slightly higher than those of larch.

In heat treatment I (Fig. 7), like Japanese larch, several small peaks appear in the 1200–1500 cm^{-1} region above 160°C when reference B is used, suggesting the thermal decomposition of wood constituents. Consequently, chemical changes similar to those in larch occur throughout the heat treatments, but higher HTT is necessary for prompt progress of the changes as compared with larch.

From the measurements and analysis of Raman spectra of Japanese larch and beech heat-treated at low temperatures, it is likely that water content has a considerable effect on the reaction rate of lignin molecules. It is expected that water absorbed in the cell wall contributes to progress of the condensation and other reactions much more considerably than free water in the lumen. In other words, water as a solvent or reactant would have only a small effect on the chemical reactions. A likely explanation for the role of water in the chemical reactions during heat treatment is that it is a driving force for a reduction in the softening temperature of wood.

In general, wood shows softening temperatures due to cellulose (T_C), lignin (T_L), and hemicellulose (T_H), and they

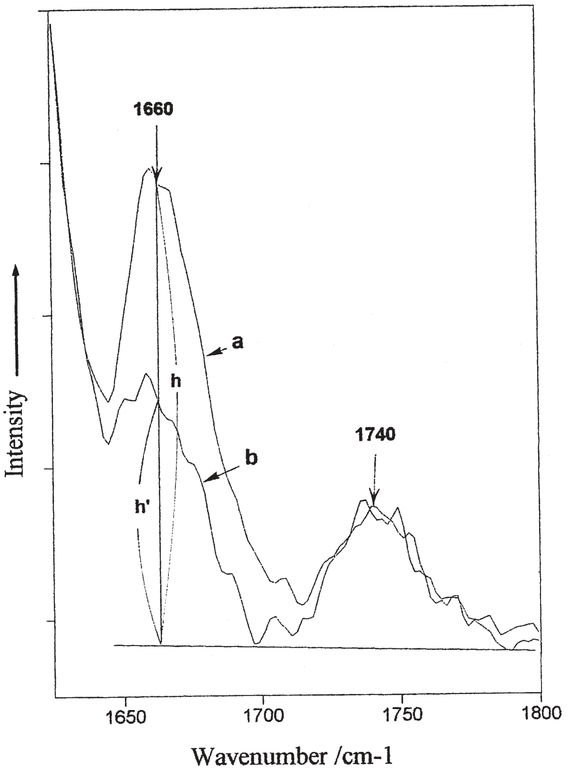


Fig. 10. Determination of *h* and *h′* in Raman spectra of beech sapwood before (*a*) and after (*b*) heat treatment

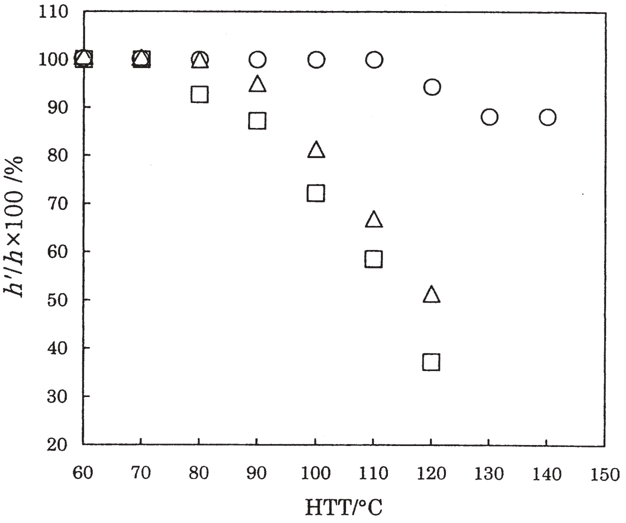


Fig. 11. Relationship between decreasing rate of band intensity at 1660 cm^{-1} in Raman spectra of beech and HTT. *Circles*, heat-treatment procedure I; *triangles*, heat-treatment procedure II; *squares*, heat-treatment procedure III

decrease in the order $T_C > T_L > T_H$.[1,30] An increase in water content reduces T_L and T_H drastically, whereas T_C is almost independent of water content. Kelley et al.[31] reported that the glass transition temperatures (T_g) of lignin and hemicellulose decrease with increasing water content, steeply at first and then gradually. From the measurements of modulus of elasticity in bending of more than 20 wood species planted in Japan, Iida[32] showed that all species had two softening points in the regions of 39°–54°C and 67°–80°C. In addition, a recent study of dynamic viscoelasticity[33] confirmed the softening point of water-swollen lignin near 80°C. These softening phenomena in wood have been interpreted in terms of micro-Brownian motion of lignin and hemicellulose molecules. Therefore, it is considered that the reactivity of functional groups in lignin molecules is raised because of micro-Brownian motion caused by heating so that condensation and other reactions are considerably facilitated.

Concluding remarks

The measurements and analysis of Raman spectra have given us important information about chemical changes in wood during heat treatment at low temperatures from 50°C to 180°C. The reduction of the band at 1655–1660 cm^{-1} due to the C=O and C=C groups is probably explained by chemical reaction of lignin molecules due mainly to condensation. The lowest HTT yielding a decrease in the band at 1655–1660 cm^{-1} was markedly reduced by the presence of water: the effect of water in the cell wall on the lowest HTT was much larger than that of water in the lumen and intercellular space. Water would have little or no contribution to the chemical reactions of lignin as a reactant or ordinary solvent. Thus, the reduction of the lowest HTT with increasing water content allowed us to postulate that the softening phenomenon of wood is closely associated with the beginning of the lignin condensation, and water acts as a driving force for the reduction of softening temperature. Moreover, it is suggested that the primary chemical reactions in larch during heat treatment are very similar to those in beech and occur at lower temperatures than in beech.

The heat treatments would lead to other chemical changes as well as the condensation of lignin molecules. From the spectral changes of both the wood species in the 1000–1500 cm^{-1} region, it was inferred that the thermal decomposition of wood constituent molecules begins at temperatures lower than 160°C.

References

1. Goring DAI (1963) Thermal softening of lignin, hemicellulose and cellulose. Pulp Pap Canada 64:T517–T527
2. Ramiah MV, Goring DAI (1967) Some dilatomeric measurements of the thermal decomposition of cellulose, hemicellulose and lignin. Cell Chem Technol 1:277–285
3. Hatakeyama H, Nakano J, Hatano A, Migita N (1969) Variation of infrared spectra with temperature for lignin and lignin model compounds. TAPPI 52:1724–1728
4. Haw JF, Schultz TP (1985) Carbon-13 CP/MAS NMR and FT-IR study of low-temperature lignin pyrolysis. Holzforschung 39:289–296
5. Pakdel H, Grandmaison JL, Roy C (1989) Analysis of wood vacuum pyrolysis solid residues by diffuse reflectance infrared Fourier transform spectroscopy. Can J Chem 67:310–314
6. Shukry N, Girgis BS, Sefain MZ (1991) Pyrolysis stage of hemicellulose determined by thermogravimetry. Bull Soc Chim Fr 127:515–519

7. Ponder GR, Richards GN (1991) Thermal synthesis and pyrolysis of a xylan. Carbohydr Res 218:143–155
8. Masuku CP (1992) Thermolytic decomposition of coniferyl alcohol. J Anal Appl Pyrolysis 23:195–208
9. Scholze B, Meier D (2001) Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin). Part I. PY-GC/MS, FT-IR, and functional groups. J Anal Appl Pyrolysis 60:40–54
10. Thompson WS (1969) Effect of steaming and kiln drying on the properties of southern pine poles. Forest Prod J 19:21–28
11. Yoshida T, Hashizume T, Nakashima Y, Takeda T (1999) Effects of high-temperature kiln-drying on mechanical properties in square-sawn Japanese larch timber I. Bending strength (in Japanese). Mokuzai Kogyo 54:122–125
12. Nakashima Y, Takeda T, Yoshida T, Hashizume T (1999) Effects of high-temperature kiln-drying on mechanical properties in square-sawn Japanese larch timber II. Compressive strength (in Japanese). Mokuzai Kogyo 54:265–268
13. Doi S , Takahashi M, Yoshimura T, Kubota M, Adachi A (1998) Attraction of steamed Japanese larch (*Larix leptolepis* (Sieb et Zucc.) Gord.) heartwood to a subterranean termite *Coptotermes formosanus* Shiraki (Isoptera: Rhinotermitidae). Holzforschung 52:7–12
14. Doi S, Kurimoto Y, Omura W, Ohara S, Aoyama M, Yoshimura T (1999) Effects of heat treatments of wood on the feeding behaviour of two subterranean termites. Holzforschung 53:225–227
15. Sumi H (1978) High temperature drying of wood II. Effect of heating condition on some mechanical properties and color of western hemlock (in Japanese). Mokuzai Gakkaishi 24:391–399
16. Yamauchi S, Koizumi A, Kurimoto Y, Tamura Y (1997) Vibrational spectroscopic studies on wood and wood-based materials. II. Infrared and Raman spectroscopic investigation for MDI penetration behavior in wood (in Japanese). J Adhes Soc Jpn 33:95–102
17. Yamauchi S, Tamura Y, Kurimoto Y, Koizumi A (1999) Vibrational spectroscopic studies on wood and wood-based materials. IV. Solvent effects of diluent on MDI penetration behavior in wood (in Japanese). J Adhes Soc Jpn 35:300–308
18. Yamauchi S, Doi S (2003) Raman spectroscopic study on the behavior of boric acid in wood. J Wood Sci 49:227–234
19. Yamauchi S, Horisawa S, Koizumi A, Iijima Y, Doi S (2004) Chemical changes of Japanese larch heartwood during high-temperature drying. A Raman spectroscopic study. Eurasian J Forest Res 7:53–57
20. Agarwal UP, Atalla RH (1993) Raman spectroscopic evidence for coniferyl alcohol structures in bleached and sulfonated mechanical pulps. In: Heintner C, Scaiano JC (eds) Photochemistry of lignocellulosic materials (ASC symposium series 531). American Chemical Society, Washington DC, pp 26–44
21. Agarwal UP, Atalla RH, Forsskahl I (1995) Sequential treatment of mechanical and chemimechanical pulps with light and heat. A Raman spectroscopic study. Holzforschung 49:300–312
22. Agarwal UP, Atalla RH (2000) Using Raman spectroscopy to identify chromophores in lignin-lignocellulosics. In: Glasser WG, Northey RA, Schultz TP (eds) Lignin: historical, biological, and materials in perspectives (ASC symposium series 742). American Chemical Society, Washington DC, pp 250–264
23. Harrinton KJ, Higgins HG, Michell AJ (1964) Infrared spectra of *Eucalyptus regnans* F. Muell and *Pinus radiate* D. Don. Horzforschung 18:108–113
24. Lewis IR, Daniel NW Jr, Chaffin NC, Griffiths PR (1994) Raman spectrometry and neural networks for the classification of wood types-1. Spectrochim Acta 50A:1943–1958
25. Yamauchi S, Tamura Y, Kurimoto Y, Koizumi A (1997) Vibrational spectroscopic studies on wood and wood-based materials. III. Identification of adhesives in wood by using FT-Raman spectroscopy as a nondestructive analytical method. J Adhes Soc Jpn 33:380–388
26. Yang H, Lewis IR, Griffiths PR (1999) Raman spectrometry and neural networks for the classification of wood types. 2. Kohonen self-organizing maps. Spectrochim Acta 55A:2783–2791
27. Agarwal UP, Ralph SA (1997) FT-Raman spectroscopy of wood. Identifying contributions of lignin and carbohydrate polymers in the spectrum of black spruce (*Picea mariana*). Appl Spectrosc 51:1648–1655
28. Kosik M, Herain J, Domansky R (1968) Pyrolyse des Buchenholzes bei niedrigen Temperaturen. IV. Grundlegende Angaben über die Bildung flüchtiger Produkte. Holzforsch Holzverw 20:56–59
29. Shimizu K, Teratani F, Hashi M, Miyazaki K (1972) Effect of the thermal treatment on wood hemicelluloses. VI. Studies on the thermal analysis of arabinogalactan, and *O*-acetyl- and deacetylated-galactoglucomannans (in Japanese). Mokuzai Gakkaishi 18:79–84
30. Hillis WE, Rozsa AN (1978) The softening temperatures of wood. Holzforschung 32:68–73
31. Kelley SS, Rials TG, Glasser WG (1987) Relaxation behavior of the amorphous component of wood. J Mater Sci 22:118–121
32. Iida I (1986) The thermal softening of green wood evaluated by its Young's modulus in bending (in Japanese). Mokuzai Gakkaishi 32:472–477
33. Furuta Y, Imanishi H, Kohara M, Yokoyama M, Obata Y, Kanayama K (2000) Thermal-softening properties of water-swollen wood. VII. The effect of lignin (in Japanese). Mokuzai Gakkaishi 46:132–136