J Wood Sci (2005) 51:348–356
DOI 10.1007/s10086-004-0664-9

© The Japan Wood Research Society 2005

ORIGINAL ARTICLE

**Masahiko Kobayashi · Toshiyuki Asano · Mikio Kajiyama**
**Bunichiro Tomita**

# Effect of ozone treatment of wood on its liquefaction

Received: February 4, 2004 / Accepted: June 23, 2004

**Abstract** The effects of ozone treatment were investigated to improve the process of liquefaction of wood with polyhydric alcohol solvents. The liquefied wood having a high wood to polyhydric alcohol ratio (*W*/*P* ratio) could be prepared by using the wood treated with ozone in the liquid phase. The liquefied wood with a *W*/*P* ratio of 2:1 had enough fluidity to act as a raw material for chemical products. To get some information about the effects of ozone treatment toward the wood components, cellulose powder and steamed lignin were treated with ozone and liquefied. In particular, ozone treatment in the liquid phase was found to be effective for wood and cellulose powder. On the other hand, steamed lignin self-condensed during liquefaction after treatment with ozone in the liquid phase. Thus, ozone treatment provided lignin with reactive functional groups, and caused the subsequent condensation reaction. Although lignin was converted to a more condensable structure by ozone treatment, the condensation reaction was found to be suppressed for wood during its liquefaction. The wood liquefied products displayed good solubilities in *N*,*N*-dimethyl formamide (DMF) even after treatments of long duration. It was suggested that one of the main effects of ozone treatment toward wood was the decomposition of cellulose.

**Key words** Liquefied wood · Ozone treatment · Cellulose powder · Steamed lignin · Condensation reaction

M. Kobayashi (✉)
Composite Products Laboratory, Department of Wood-Based Materials, Forestry and Forest Products Research Institute, 1 Matsunosato, Tsukuba 305-8687, Japan
Tel. +81-29-873-3211 (ext. 537); Fax +81-29-874-3270
e-mail: masa7355@ffpri.affrc.go.jp

T. Asano
Ibaraki Industrial Technology Center, Ibaraki 311-3116, Japan

M. Kajiyama · B. Tomita
Institute of Agricultural and Forestry Engineering, Faculty of Agriculture, University of Tsukuba, Tsukuba 305-8572, Japan

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

## Introduction

In recent years, much efforts has been expended on the utilization of low-grade woods as a new source of raw materials for preparing resins, and new technologies and products have been developed for the liquefaction of wood.[1] Many studies have pursued the application of liquefied wood to wood adhesives and some molding materials.[2,3] We have prepared liquefied wood from Japanese cedar, which is expected to be used widely in Japan, and investigated the preparation of liquefied wood/epoxy resin and its application to wood adhesives.[4,5] One of the most important objects of the application of liquefied wood is increasing the wood contents within final products. However, to date the wood content of liquefied wood is known to be limited to low levels because condensation occurs among the degraded wood components concurrently during liquefaction. It was concluded in our previous report that lignin was solubilized in some organic solvents in the initial stage, followed by liquefaction of cellulose and gradual solubilization, followed by condensation of the liquefied cellulose and lignin to form an insoluble residue.[6]

Ozone is one of the most powerful oxidizing reagents. In this research, ozone was used for the pretreatment of wood before liquefaction so as to activate wood components. It is known that the ozonation of lignin results in derivatives of muconic acid, which have two conjugated double bonds terminated by two carboxyl groups.[7] Because many chemical reactions can be based on these structures, some effects of the liquefaction process can be expected. In particular, because the condensed residue contained a lot of aromatic compounds, it was expected that the condensation might be suppressed by cleaving of the aromatic rings of lignin with ozone. The pretreatment of wood was conducted in the gas phase or in some organic solvents. After that, each ozone-treated wood was liquefied using a mixture of ethylene glycol oligomers and glycerol as solvent. In addition, ozonized cellulose powder and steamed lignin were liquefied, and the processes of their liquefactions were compared with that of wood. The solubilities of the liquefied products in *N*,*N*-dimethyl formamide (DMF) were examined, and the

molecular weight distributions of their DMF-soluble constituents were evaluated.

## Materials and methods

### Materials

The heartwood meal of Japanese cedar (*Cryptomeria japonica* D. Don), and the meal of white birch (*Betula platyphylla* Sukatchev var. *japonica* Hara) were prepared as softwood and hardwood samples, respectively, as raw materials for liquefaction. Cellulose powder (Sigma-Aldrich, USA) and steamed lignin were used as model samples of the main wood components and were also used as raw materials for liquefaction. The steamed lignin was prepared from wood chips of white birch. The chips were steamed for 15 min at 180°C, extracted with water at 60°C, and then extracted with methanol. The methanol-soluble part was dried under vacuum after removal of the methanol, and used as the steamed lignin.[8] All other chemicals were reagent grade, and were used without further purification.

### Ozone treatments in gas phase

Each material (15 g) was placed into a 150 liter polyethylene plastic bag after drying at 105°C for 24 h. An ozone generator (DMA-10BDF, Ishimori, Japan) was used with an oxygen flow rate of 500 ml/min, and the generated ozone concentration was 3%. The gas flow was introduced into the bag with shaking for 4.08 h, and the total amount of ozone introduced was 7.7 g. The weight increases after ozone treatments were determined to be 0.065–0.073 g per gram of four kinds of samples: Japanese cedar, white birch, cellulose powder, and steamed lignin. After allowing the samples to stand at room temperature for 1 week, the samples were liquefied in a similar manner as that used for untreated materials.

### Ozone treatments in liquid phase

Each material (15 g) was placed into a three-necked 1-liter flask and immersed in a mixture of 1,4-dioxane (300 ml) and methanol (600 ml). The same gas flow as described earlier was bubbled into the solvent with stirring for 4.08 h at 0°C, and the total amount of ozone introduced was 7.7 g. The weight increases after ozone treatments were determined to be 0.229 g, 0.199 g, 0.213 g, and 0.301 g per gram for Japanese cedar, white birch, cellulose powder, and steamed lignin, respectively. After suction drying, the samples were liquefied.

### Liquefaction of wood and related compounds

Wood and related samples were dried at 105°C for 24 h before they were used. Each dried sample was placed in a two-necked flask, equipped with condenser and mechanical stirrer, after it was mixed with polyethylene glycol (average molecular weight 400), glycerol, and sulfuric acid. The weight percentage of glycerol in polyhydric alcohols was 20%. The amount of sulfuric acid used as catalyst was 3wt% on polyhydric alcohols. The mixing ratios of wood materials and polyhydric alcohol were 2:3. As for the liquefaction of ozone treated Japanese cedar, the mixing ratios were changed to 2:3, 1:1, 3:2, and 2:1. The mixture was reacted at 150°C and small amounts of liquefied product samples were taken at regular intervals during liquefaction. The viscosities of the liquefied products were measured with an Advanced Rheometric Expansion System (Reometric Scientific, USA) at a frequency of 1 Hz.

### Measurement of residue content

The extent of liquefaction was evaluated by determining the residual content. Each small sample of liquefied products was diluted with an excess amount of DMF and was filtered off on a GA-100 glass filter paper (Toyo Roshi Kaisha, Japan). Insoluble residues were rinsed with DMF and dried in an oven at 105°C for 24 h. The residue content was determined as the weight percentage of DMF-insoluble residue to the raw starting material.

### Fourier transform infrared measurements

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Paragon 1000 (PerkinElmer, UK) FT-IR spectrometer by using the KBr pellet method.

### Gel permeation chromatography analysis

Gel permeation chromatography (GPC) of DMF-soluble components was performed by using a Waters 600E multisolvent delivery system with a Shodex KD-2002 column heated at 50°C, using DMF containing 0.01 M lithium bromide as eluent. Detection was achieved with a differential refractometer (410 Differential Refractometer, Waters, USA). The molecular weights of the liquefied products were roughly estimated based on polyethylene glycol standards.

### X-ray diffraction analysis

X-ray diffraction patterns of the samples were recorded on a RINT-Ultima diffractometer (Rigaku, Japan) equipped with a reflection-type goniometer, using CuK$\alpha$ radiation. The crystallinity indexes (CI) were calculated from the ratios of peak areas due to the crystalline region to total area of the X-ray diffraction patterns.[9]

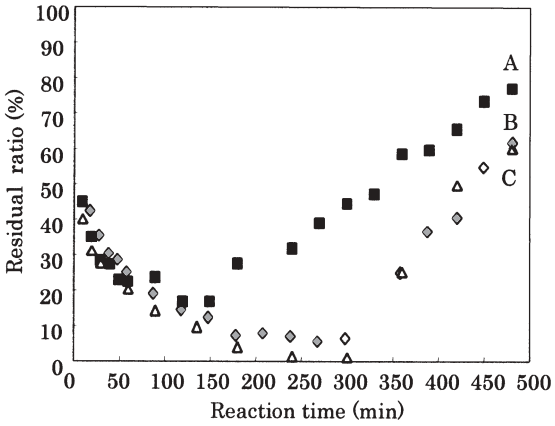


**Fig. 1.** Dimethyl formamide (DMF) solubility (expressed as residual ratio) of untreated Japanese cedar and ozone-treated Japanese cedar during liquefaction as functions of reaction time, with a wood to polyhydric alcohol ratio (*W*/*P*) of 2:3. Sample A (*squares*), untreated Japanese cedar; sample B (*diamonds*), ozone-treated Japanese cedar in the gas phase; sample C (*triangles*), ozone-treated Japanese cedar in the liquid phase

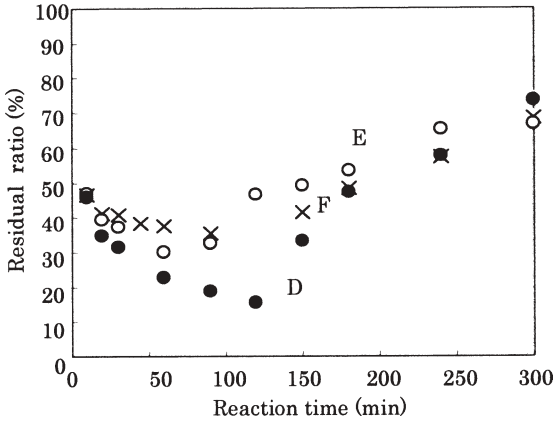


**Fig. 2.** DMF solubility of ozone-treated wood in the liquid phase during liquefaction as a function of reaction time. Sample D (*filled circles*), *W*/*P* ratio 1:1; sample E (*circles*), *W*/*P* ratio 3:2; sample F (*crosses*), *W*/*P* ratio 2:1

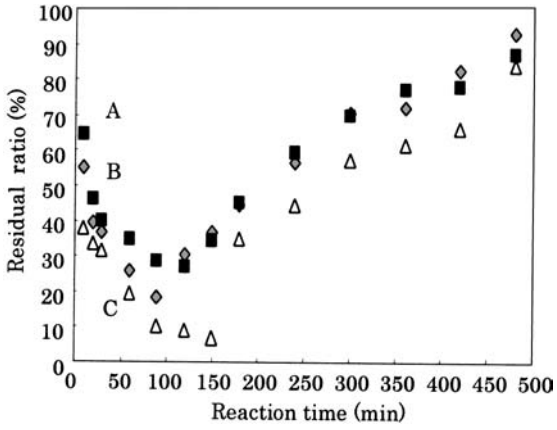


**Fig. 3.** DMF solubility of untreated white birch and ozone-treated white birch during liquefaction as functions of reaction time, with a *W*/*P* ratio of 2:3. Sample A (*squares*), untreated white birch; sample B (*diamonds*), ozone-treated white birch in the gas phase; sample C (*triangles*), ozone-treated white birch in the liquid phase

## Results and discussion

### Dissolution behavior of wood and ozone-treated wood

Wood and ozone-treated wood were liquefied, and their dissolution behaviors into DMF were compared. The wood to polyhydric alcohol ratios (*W*/*P* ratio) were 2:3. In Fig. 1, the curve labeled as sample A (hereinafter expressed as Fig. 1A) shows the dissolution behavior for untreated Japanese cedar as a function of reaction time. The liquefaction proceeded rapidly at the beginning. The residual ratio reached about 20% within 60 min. However, the condensation reaction, which produced insoluble components, took place after 150 min when the minimum residual ratio was observed. It reached 80% at the reaction time of 480 min. Figure 1B shows the results of ozone treatment in the gas phase. The rate of liquefaction was similar to that of untreated wood up to 150 min. However, the residual ratio continued to decrease after 180 min when the condensation reaction started in the case of untreated wood. Subsequently, the residual ratio remained constant at about 5% for the additional 150 min. After 330 min, the condensation progressed abruptly and the residual ratio exceeded 60% at the reaction time of 480 min. Figure 1C shows the results of ozone treatment in the liquid phase. The results were almost the same as those for treatment in the gas phase. However, the minimum residual ratio was further decreased and wood components were completely liquefied within 240 min. It was shown that the condensation could be suppressed to a large extent by ozone treatment. Consequently, the ozone-treated wood was completely liquefied, and its good solubility was maintained for longer than that of the untreated wood. These results suggest that the wood content within the liquefied wood could be increased by using ozone-treated wood. Therefore, preparations of liquefied woods with a higher wood content were attempted by using ozone treatment in the liquid phase. Figure 2 shows the comparison of the residual ratio during liquefaction with three different *W*/*P* ratios. In Fig. 2D (*W*/*P* ratio = 1:1), the residual ratio reached 15% at the liquefaction time of 120 min. Although the liquefied wood contained this amount of residue, it had enough fluidity ($1.40 \times 10^3$ Pa·s at 25°C) to act as a raw material for chemical products. It should be noted that the liquefied wood with a *W*/*P* ratio of 1:1 could be prepared by using the ozone treatment without applying other special methods, such as those reported in our previous works.[4,5] Figure 2E and 2F show the results of the cases with *W*/*P* ratios of 3:2 and 2:1, respectively. The higher wood content caused the decrease of liquefaction rate. The minimum residual ratios for E and F of Fig. 2 were 30% and 35%, respectively. However, even the liquefied wood which contained more than 66% of wood (*W*/*P* = 2:1) had enough fluidity ($5.48 \times 10^5$ Pa·s at 25°C) to be used as raw material for chemical products.

Figure 3A shows the liquefaction result for untreated white birch as the function of reaction time. The liquefac-

tion proceeded promptly at the beginning and the residual ratio reached 27% at the reaction time of 120 min. However, the condensation reaction took place at that time, and the residual ratio increased to 90% at 480 min. Figure 3B shows the results of ozone treatment in the gas phase. The liquefaction proceeded faster than in the case of untreated white birch, and the minimum residual ratio was shown at the reaction time of 90 min. After that, the condensation reaction took place and the process proceeded to resemble the case of the untreated sample. Figure 3C shows the results of ozone treatment in the liquid phase. The liquefaction proceeded faster than the untreated and gaseous ozone-treated samples, and the residual ratio reached 6% after 150 min. However, the condensed residue suddenly increased at that point and the residual ratio increased to 35%. Once the residue was formed, the residual ratio increased in a fashion similar to the other two cases. It was shown that the condensation reaction of the liquefied wood for white birch could be suppressed by ozone treatment as in the case of the softwood, and the remarkable effect was observed for the ozonation in the liquid phase.

The ozone-treated hardwood was liquefied faster than the untreated one as mentioned above. However, because the condensation reaction was also enhanced by ozone treatment, complete liquefaction was not achieved. On the other hand, ozone-treated softwood was completely liquefied, and its good solubility was maintained for a wider range of liquefaction periods as shown in Fig. 1. Therefore, it could be said that the ozone treatment was more effective toward the softwood than toward the hardwood.

## Influence of ozone treatment on wood raw material

In Fig. 4, A, B, and C show the IR spectra of untreated Japanese cedar, and ozone-treated Japanese cedar in gas and liquid phases, respectively. There was no difference between A and B. This fact suggests that the main functional groups of wood did not change greatly as a result of ozone treatment in the gas phase. Figure 4C displayed the increase of intensities of the band at around 1730 $cm^{-1}$, showing that carbonyl groups were produced during ozonation. However, further differences were not observed.

In Fig. 5, A, B, and C show the IR spectra of untreated white birch, and ozone-treated samples in gas and liquid phases, respectively. Figure 5B displays a decrease of the intensity of the band at 1609 $cm^{-1}$, showing that the aromatic rings of lignin were cleaved during ozonation. In Fig. 5C, it was observed that the intensity of the band at around 1730 $cm^{-1}$ increased in a similar manner as observed for Japanese cedar.

## Influence of ozone treatment on molecular weight distribution of liquefied wood during liquefaction

GPC analysis of DMF-soluble material from the liquefaction of untreated Japanese cedar was carried out, and the results are shown in Fig. 6A. Some peaks were observed at the low molecular weight region (Mw = 400–1000) after 10 min of liquefaction. As the reaction proceeded, a peak began to develop in the high molecular weight region (Mw = 10000–20000). After 150 min, when the minimum residual ratio was observed as shown in Fig. 1A, the peaks due to high molecular weight components were clearly detected. Subsequently, as the liquefied products converted to insoluble compounds due to condensation, the peaks became smaller and disappeared by 480 min. Figure 6B shows the results of ozone treatment in the gas phase. It was observed that some peaks were spread over wide ranges toward the lower molecular weight region and more so than in the case of untreated wood. After 90 min, the peak due to high molecular weight components became clearer than in the case of untreated wood. Subsequently, the liquefaction proceeded slowly and the peaks were clearly detected after 300 min when the residual ratio was 5%. Soon afterward, because the condensation reaction took place, the peaks in

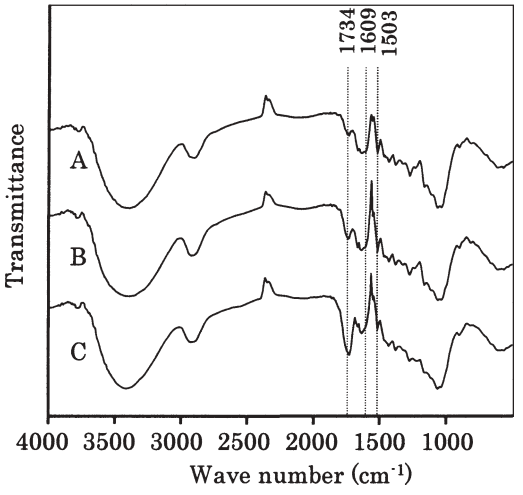


**Fig. 4.** Infrared (IR) spectra of untreated Japanese cedar and ozone-treated Japanese cedar. Samples A, B, and C as for Fig. 1

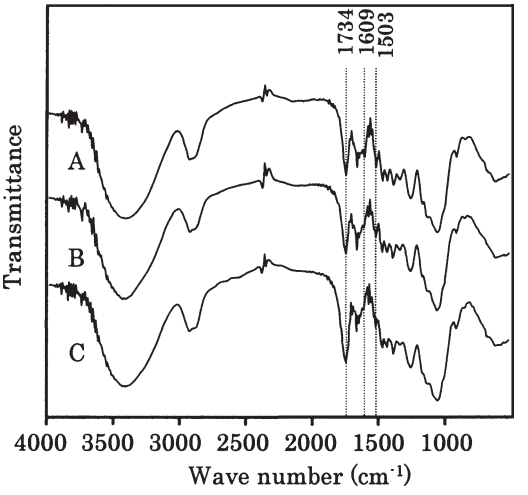


**Fig. 5.** IR spectra of untreated white birch and ozone-treated white birch. Samples A, B, and C as for Fig. 3

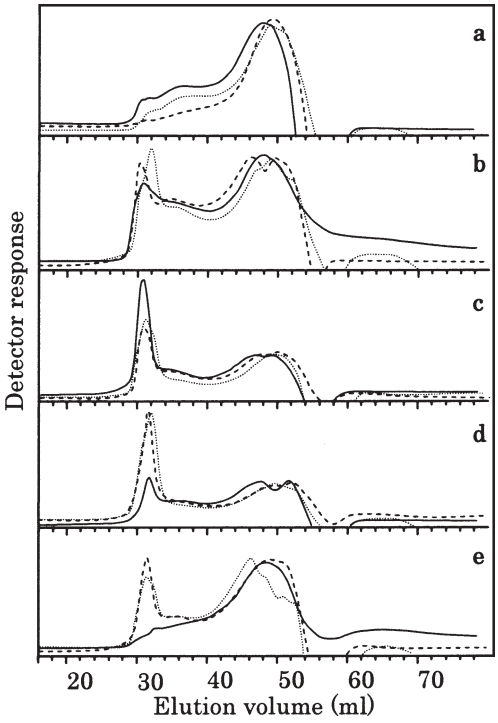


**Fig. 6a–e.** Gel permeation chromatograms of the DMF-soluble part of liquefied untreated Japanese cedar, ozone-treated Japanese cedar in the gas phase, and ozone-treated Japanese cedar in the liquid phase during liquefaction. Sample A (*solid line*), untreated Japanese cedar; sample B (*long-dashed line*), ozone-treated Japanese cedar in the gas phase; sample C (*short-dashed line*), ozone-treated Japanese cedar in the liquid phase. Liquefaction time: **a** 10 min, **b** 90 min, **c** 150 min, **d** 300 min, **e** 480 min

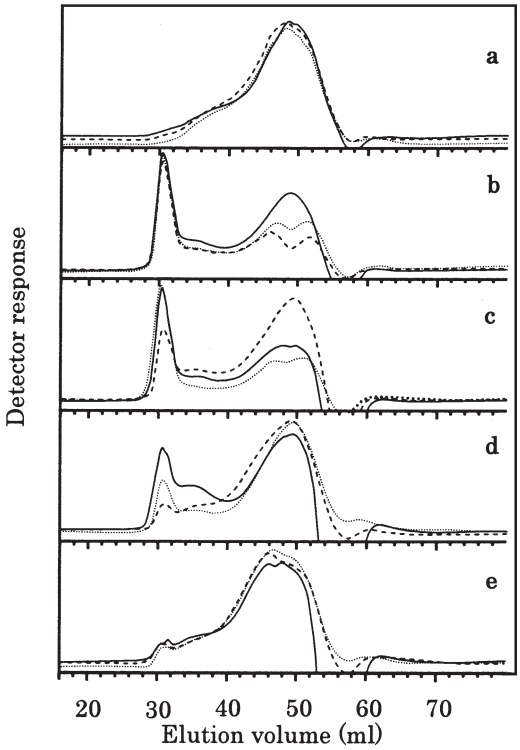


**Fig. 7a–e.** Gel permeation chromatograms of the DMF-soluble part of liquefied untreated white birch, ozone-treated white birch in the gas phase, and ozone-treated white birch in the liquid phase during liquefaction. Sample A (*solid line*), untreated white birch; sample B (*long-dashed line*), ozone-treated white birch in the gas phase; sample C (*short-dashed line*), ozone-treated white birch in the liquid phase. Liquefaction time: **a** 10 min, **b** 90 min, **c** 150 min, **d** 300 min, **e** 480 min

the high molecular weight region became smaller. However, some of the high molecular weight components remained soluble in DMF. Figure 6C shows the results of ozone treatment in the liquid phase. The change of molecular weight distribution was similar to those found in the treatment in the gas phase.

The results of GPC analysis of untreated white birch are shown in Fig. 7A. The changes of molecular weight distribution were similar to those found for untreated Japanese cedar. Figure 7B shows the results of ozone treatment in the gas phase. After 150 min, although the value of the residual ratio was almost the same as that for untreated sample (Fig. 2), the low molecular weight peaks appeared larger when compared with those of untreated wood. Thus, it can be said that the soluble part of the sample treated with ozone in the gas phase and then liquefied contained larger amounts of low molecular weight constituents than those found for the untreated samples. Figure 7C shows the results of ozone treatment in the liquid phase. After 150 min, when the minimum residual ratio (6.6%) was observed as shown in Fig. 3C, the molecular weight distribution was similar to that of untreated wood (Fig. 7A) in spite of the fact that the residual ratio of untreated wood was 34%. After 300 min, the chromatogram was very similar to that observed for treatment in the gas phase at 150 min (Fig. 7B). These results indicate that the start of the condensation reaction was delayed by ozone treatment in the liquid phase. After that, the peaks in the high molecular weight region (Mw = 10 000–20 000) became smaller and disappeared within 480 min.

## Dissolution behavior of untreated and ozone-treated cellulose

Figure 8A shows the DMF solubility of untreated cellulose powder as a function of liquefaction time. Because cellulose powder contains a significant crystalline portion, the rate of liquefaction seemed to be slower than that of wood. After 90 min, 50% of the material remained as insoluble residue. It took 270 min for most of the cellulose powder to dissolve. After that, the residual ratio remained constant at about 10%, and the condensation could not be observed within 480 min. Figure 8B shows the results of ozone treatment in the gas phase. The results are quite similar to those of untreated cellulose. Figure 8C shows the results of ozone treatment in the liquid phase. After 10 min, the residual ratio reached 65%, while it was 90% and 80% for A and B, respectively. The rate of liquefaction was concluded to be faster than A and B, and 80% of the wood components were solubilized within 120 min. Subsequently, the residual ratio decreased as the reaction proceeded, and the residue

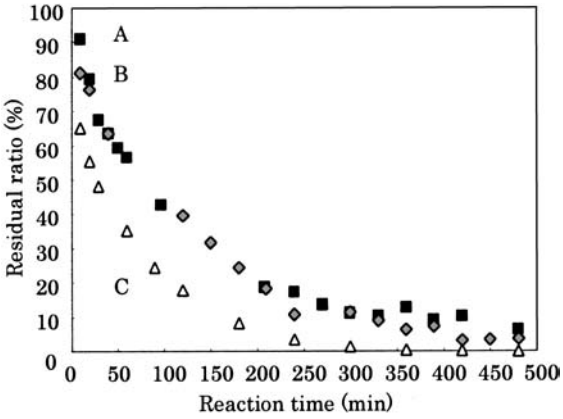


**Fig. 8.** DMF solubility of untreated cellulose powder and ozone-treated cellulose powder during liquefaction as functions of reaction time. The cellulose powder to polyhydric alcohol ratio was 2:3. Sample A (*squares*), untreated cellulose powder; sample B (*diamonds*), ozone-treated cellulose powder in the gas phase, sample C (*triangles*), ozone-treated cellulose powder in the liquid phase

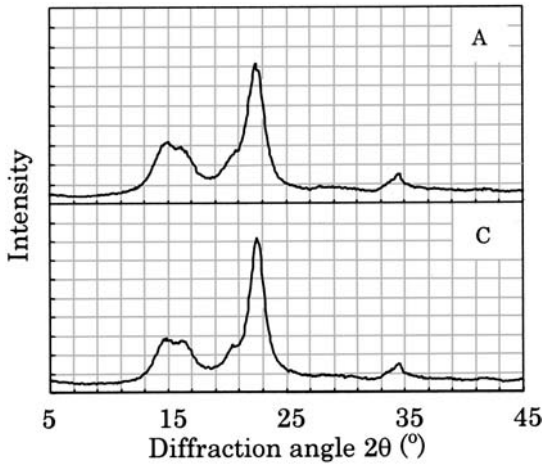


**Fig. 10.** X-ray diffraction patterns of untreated cellulose powder and ozone-treated cellulose powder. Samples A and C as for Fig. 8

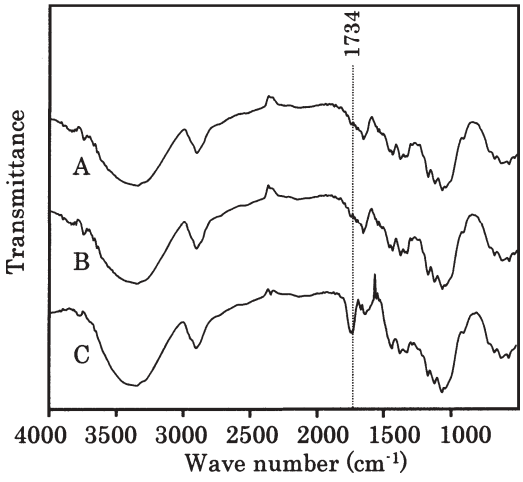


**Fig. 9.** IR spectra of untreated cellulose powder and ozone-treated cellulose powder. Samples A, B, and C as for Fig. 8

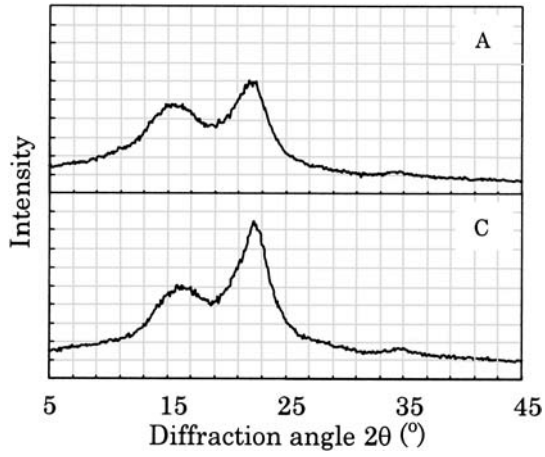


**Fig. 11.** X-ray diffraction patterns of untreated Japanese cedar and ozone-treated Japanese cedar. Samples A and C as for Fig. 1

disappeared after 300 min. It was indicated that complete liquefaction was achieved and the ozone treatment effectively acted on cellulose in the liquid phase.

## Influence of ozone treatment on cellulose

Figure 9 shows the IR spectra of untreated cellulose (A) and ozone-treated cellulose in the gas (B) and liquid (C) phases, respectively. No difference was observed between A and B. This suggests that the main functional groups of cellulose did not change by the ozone treatment in the gas phase as was recognized in the case of wood. However, the absorption bands appeared at around 1730 $cm^{-1}$ in Fig. 9C. It was reported that when ozone was applied to cellulose, it induced the formation of carbonyl groups and carboxyl groups to a minor extent.[10] Furthermore, it was reported that gluconic acid was the major product in the first stages of ozonation for the model compounds of cellulose.[11] This information suggests that the absorption bands at around 1730 $cm^{-1}$ are derived from carboxyl groups which were produced by cleavage of the glycosidic linkage.

To obtain some information about the crystallinity of cellulose, X-ray diffraction of cellulose and wood was carried out. Figure 10 shows the X-ray diffraction patterns of untreated cellulose powder (A) and ozone-treated cellulose powder in the liquid phase (C). It was observed that the peak intensity due to cellulose I increased after ozone treatment.[9] The CI increased from 35.11% to 37.95%. This suggests that the amorphous cellulose was decomposed by ozone. Figure 11 shows the X-ray diffraction patterns of untreated Japanese cedar (A) and ozone-treated Japanese cedar in the liquid phase (C). The peak area of untreated wood was smaller than that of the ozone-treated material as in the case of cellulose. The CI increased from 17.17% to 18.49% by ozone treatment. Thus, it appears that the amorphous cellulose contained in wood seemed to be influenced

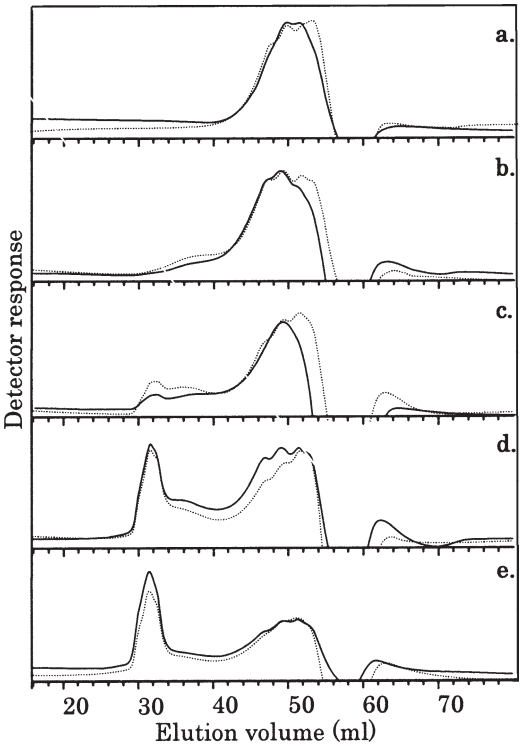


**Fig. 12a–e.** Gel permeation chromatograms of the DMF-soluble part of liquefied untreated cellulose powder and ozone-treated cellulose powder in the liquid phase during liquefaction. Sample A (*solid line*), untreated cellulose powder; sample C (*short-dashed line*), ozone-treated cellulose powder in the liquid phase. Liquefaction time: **a** 10 min, **b** 90 min, **c** 180 min, **d** 300 min, **e** 480 min

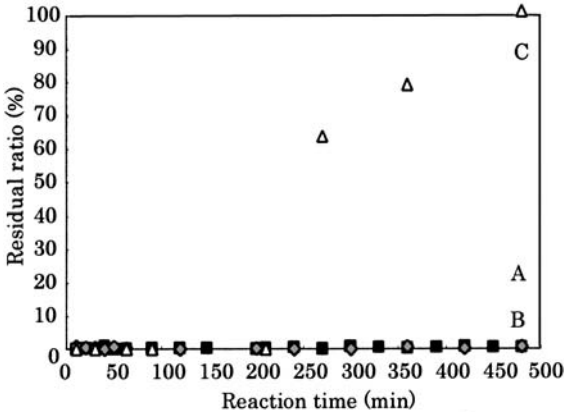


**Fig. 13.** DMF solubility of untreated steamed lignin and ozone-treated steamed lignin during liquefaction as functions of reaction time. The steamed lignin to polyhydric ratio was 2:3. Sample A (*squares*), untreated steamed lignin, sample B (*diamonds*), ozone-treated steamed lignin in the gas phase, sample C (*triangles*), ozone-treated steamed lignin in the liquid phase

by ozone, although it is covered with hemicellulose and lignin, the latter of which is more easily ozonized than cellulose.[12]

## Influence of ozone treatment on molecular weight distribution of liquefied cellulose during liquefaction

Figure 12A shows the gel permeation chromatograms of the DMF-soluble part of untreated cellulose powder during liquefaction. In the initial stage of the liquefaction, some peaks were observed in the low molecular weight region (Mw = 200–1000). Only the low molecular weight parts of cellulose were liquefied in this stage and converted to DMF-soluble components. The peaks of liquefied products began to develop in the high molecular weight region (Mw = 10000–20000) with increased reaction time. The chromatogram obtained after 480 min roughly showed all components of liquefied products, because they were almost all soluble in DMF as shown in Fig. 8A. Figure 12C shows the result of ozone treatment in the liquid phase. The results showed a tendency similar to those of untreated wood from the beginning to the end of the reaction. However, in the initial stages of the liquefaction, the peaks derived from cellulose spread toward the lower molecular weight region (Mw = 200–400) than those of untreated cellulose. It was suggested that cellulose was partially decomposed during these processes. Consequently, ozone-treated cellulose was completely liquefied. After 300 min, large peaks were observed in the high molecular weight region as observed in the case of untreated cellulose powder. However, this result indicated that more cellulose could be converted to soluble components by ozone treatment, because the residual ratio was 0% at 300 min, while in the case of untreated cellulose it was 15% at this reaction time. Similarly, the chromatogram showed almost the same pattern as that of untreated cellulose at 480 min, but it was observed that the relative intensity of the peak in the high molecular weight region was a little smaller than that for untreated cellulose.

## Dissolution behavior of untreated and ozone-treated lignin

DMF solubilities of untreated steamed lignin and ozone-treated lignin were compared during liquefactions. It was difficult to prepare steamed lignin from softwood such as Japanese cedar. Therefore, white birch was used as raw material. Figure 13A shows the results for untreated steamed lignin as a function of liquefaction time. Untreated steamed lignin is essentially a DMF-soluble compound. Therefore, due to total solubility, the residual ratio was 0% from the beginning of the liquefaction. Although the viscosity of the liquefaction product increased to some extent as the reaction proceeded, the lignin remained completely soluble even after 480 min. Figure 13B shows the results of ozone treatment in the gas phase. Because the lignin was soluble just like untreated lignin, the residual ratio was 0% from the beginning to the end of the liquefaction. Figure 13C shows the results of ozone treatment in the liquid phase and shows an obvious distinction from Fig. 13A or B. The residual ratio was 0% at the beginning, but condensation suddenly took place after 200 min. The residual ratio then increased rapidly and reached 100% at the reaction time of 480 min. Although most wood and cellulose was not soluble

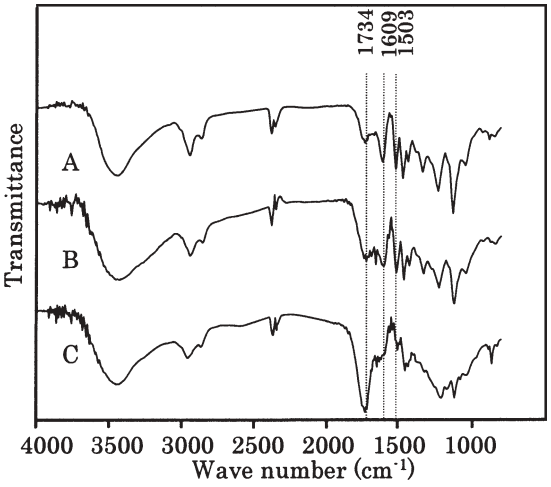


**Fig. 14.** IR spectra of untreated steamed lignin and ozone-treated steamed lignin. Samples A, B, and C as for Fig. 13

in 1,4-dioxane–methanol after ozone treatment, lignin was completely soluble in this mixture. Consequently, it can be said that ozone reacted with lignin effectively and reactive components were formed.

### Influence of ozone treatment on lignin

Figure 14 shows the IR spectra of untreated steamed lignin (A) and ozone-treated lignin in the gas (B) and liquid (C) phases. It was observed that the spectrum pattern of B was similar to that of A. On the other hand, ozone treatment in the liquid phase effected some changes in the main functional groups of lignin, as shown in Fig. 12C. The most visible difference between Fig. 14C and Fig. 14A,B are the presence of strong bands observed at 1720–1740 $cm^{-1}$ derived from C=O double bonds. Similarly, the intensities of absorptions at 1503 $cm^{-1}$ and 1609 $cm^{-1}$ due to the aromatic skeletal vibrations decreased. These facts suggest that the effective ozonation of lignin produced derivatives of muconic acid, which have two conjugated C=O double bonds.[7] It could be said that these conversions of lignin structure by ozone treatment trigger the condensation reaction.

### Influence of ozone treatment on molecular weight distribution of liquefied lignin during liquefaction

Figure 15A shows the gel permeation chromatograms of the DMF-soluble part of untreated lignin. Because lignin was soluble in DMF as described previously, the chromatogram reflected the behavior of all the components during the liquefaction. The peaks gradually shifted to the high molecular weight region with increasing reaction time. It has been suggested that the lignin self-condenses under acidic conditions.[13] Figure 15C shows the results for ozone treatment in the liquid phase. The molecular weight distributions were in the lower molecular weight region when

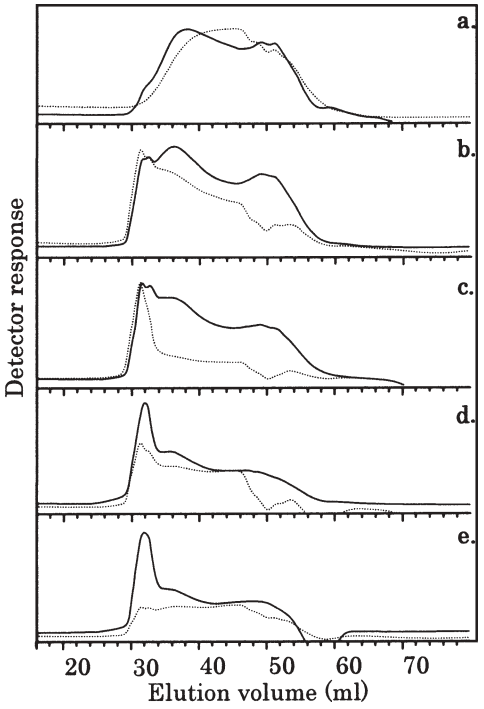


**Fig. 15a–e.** Gel permeation chromatograms of the DMF-soluble part of liquefied untreated steamed lignin and ozone-treated steamed lignin in the gas phase during liquefaction. Sample A (*solid line*), untreated steamed lignin; sample C (*short-dashed line*), ozone-treated steamed lignin in the liquid phase. Liquefaction time: **a** 10 min, **b** 90 min, **c** 180 min, **d** 300 min, **e** 480 min

compared with those of untreated lignin at the reaction time of 10 min. However, the distribution shifted much faster to the high molecular weight region than in the case of untreated lignin. After 180 min, the peaks due to high molecular weight components were quite evident. Because the liquefied products were converted to insoluble compounds due to condensation, the high molecular weight peaks became small after 480 min.

## Conclusions

In this study, it was found that wood treated with ozone in gas and liquid phases could be liquefied more easily than untreated wood. The liquefied wood with a high *W*/*P* ratio of 2:1 could be prepared by using the wood treated with ozone in the liquid phase, and it had enough fluidity to be used as the raw material for chemical products. These results suggest that it was possible to increase the wood contents of final products by using ozone-treated woods. To get some information about the effects of ozone treatment toward the wood components, ozonized cellulose and lignin were also liquefied, and their liquefaction behaviors were observed. Ozone treatment in the liquid phase was effective for wood and cellulose. It was suggested that the amorphous cellulose was decomposed by the treatment. On the other hand, the lignin condensed together during liquefaction when it was ozonized in the liquid phase. This indicated

that the ozone treatment gave lignin reactive functional groups, followed by the condensation reaction. Although lignin converted to a more condensable structure by ozone treatment, the condensation reaction could be suppressed during liquefaction. It was suggested that one of the main effects of ozone treatment toward wood was the decomposition of cellulose.

## References


1. Shiraishi N (1986) Plasticization of wood (in Japanese). Mokuzai Gakkaishi 32:755–762
2. Lin L, Yoshioka M, Yao Y, Shiraishi N (1995) Preparation and properties of phenolated wood/phenol/formaldehyde cocondensed resin. J Appl Polym Sci 58:1297–1304
3. Yao Y, Yoshioka M, Shiraishi N (1995) Rigid polyurethane foams from combined liquefaction mixtures of wood and starch (in Japanese). Mokuzai Gakkaishi 41:659–668
4. Kobayashi M, Tsukamoto K, Tomita B (2000) Application of liquefied wood to a new resin system – synthesis and properties of liquefied wood/epoxy resin. Holzforschung 54:93–97
5. Kobayashi M, Hatano Y, Tomita B (2001) Viscoelastic properties of liquefied wood/epoxy resin and its bond strength. Holzforschung 55:667–671
6. Kobayashi M, Asano T, Kajiyama M, Tomita B (2004) Analysis on process of wood liquefaction with polyhydric alcohol. J Wood Sci 50:407–414
7. Kaneko H, Hosoya S, Nakano J (1980) Degradation of lignin with ozone (in Japanese). Mokuzai Gakkaishi 26:752–758
8. Yoshida Y, Kajiyama M, Tomita B, Hosoya S (1990) Synthesis of ozonized lignin/aminomaleimide resins using the Diels–Alder reaction and their viscoelastic properties (in Japanese). Mokuzai Gakkaishi 36:440–447
9. Isogai A, Usada M (1990) Crystallinity index of cellulosic materials (in Japanese). Sen-i Gakkaishi 46:324–329
10. Chirat C, Lachenal D (1994) Effect of ozone on pulp components application to bleaching of kraft pulps. Holzforschung 48 Suppl.:133–139
11. Olkkonen C, Tylli H, Forsskahl I, Fuhrmann A, Hausalo T, Tamminen T, Hortling B, Janson J (2000) Degradation of model compounds for cellulose and lignocellulosic pulp during ozonation in aqueous solution. Holzforschung 54:397–406
12. Ek M, Gierer J, Jansbo K (1989) Study on the selectivity of bleaching with oxygen-containing species. Holzforschung 43:391–396
13. Yasuda S, Terashima N, Ito T (1980) Chemical structures of sulfuric acid lignin I. Chemical structures of condensation products from monolignols (in Japanese). Mokuzai Gakkaishi 26:552–557