

Masahiko Kobayashi · Toshiyuki Asano  
Mikio Kajiyama · Bunichiro Tomita

## Analysis on residue formation during wood liquefaction with polyhydric alcohol

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**Abstract** Liquefactions of cellulose powder, steamed lignin, alkali lignin, and their mixtures were carried out to analyze the reaction process of wood using polyhydric alcohol. The liquefaction of wood proceeded immediately and wood components were converted to *N,N*-dimethylformamide (DMF)-soluble components. After that, the condensation reaction occurred with increasing reaction time. However, none of cellulose powder, steamed lignin, and alkali lignin condensed by themselves during their liquefaction. The mixture of cellulose and lignin was also liquefied, and condensed after a long reaction time. The results of analysis showed that the behavior of the mixture resembled that of wood with respect to molecular weight distribution and the main functional groups. Lignin was converted to DMF-soluble compounds in the initial stage of wood liquefaction, followed by cellulose gradually being converted into soluble compounds. After that, condensation reactions took place among some parts of depolymerized and degraded compounds from cellulose and lignin, and were converted into DMF-insoluble compounds. It was concluded that the rate-determining step of wood liquefaction was the depolymerization of cellulose. Furthermore, it was suggested that the condensation reaction was due to the mutual reaction among depolymerized cellulose and degraded aromatic derivatives from lignin or due to the nucleophilic displacement reaction of cellulose by phenoxide ion.

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

### Introduction

The liquefaction of wood and its practical applications have been developed during the past decade. We have investigated the preparation of liquefied wood/epoxy resin and its application to wood bonding.<sup>1,2</sup> In these studies, the wood content of liquefied wood was limited to low levels, because the condensation reaction occurred concurrently among the wood components themselves during liquefaction. Therefore, it is required to illuminate the mechanism of wood liquefaction, and extensive studies have been carried out to elucidate it using model compounds. In some of the studies, cellobiose, cellulose, and starch were used as model compounds, and their liquefaction mechanisms in the presence of polyhydric alcohol or phenol, with or without sulfuric acid as catalyst, were studied.<sup>3</sup> It was reported that the liquefaction of polysaccharides in the presence of alcohols or phenol proceeds by alcoholysis or phenolysis of the glucoside linkage, initially producing the corresponding glucosides, and that the glucosides are decomposed to levulinic acid esters.<sup>4,5</sup> The liquefaction mechanism of lignin in the presence of phenol has also been investigated by using guaiacylglycerol- $\beta$ -guaiacyl ether (GG) as the model compound.<sup>6</sup> With sulfuric acid as catalyst, GG is initially transformed mainly to the benzyl cation, which rapidly reacts with phenol to give the reaction intermediates. These intermediates are quickly subjected to heterolytic cleavage of their  $\beta$ -O-4 linkages. The resulting fragments further react with phenol to form various phenolated products. On the other hand, the information about the liquefaction process of lignin with polyhydric alcohols is less extensive than that concerning reaction with phenol.

In this study, liquefactions of cellulose powder, steamed lignin, alkali lignin, and their mixture were carried out to analyze the reaction process of wood using polyhydric alcohol, such as polyethylene glycol, as solvent. The solu-

M. Kobayashi (✉) · M. Kajiyama · B. Tomita  
Institute of Agricultural and Forestry Engineering, Faculty of  
Agriculture, University of Tsukuba, Tsukuba 305-8572, Japan  
Tel. +81-29-853-4578; Fax +81-29-855-2203  
e-mail: masa3172@mx15.freecom.ne.jp

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

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bilities of liquefied wood and related compounds were determined using *N,N*-dimethylformamide (DMF), and the analyses of the soluble and insoluble constituents were performed.

## Materials and methods

### Materials

The wood meal of white birch (*Betula platyphylla* Sukatchev var. *japonica* Hara), cellulose powder (Aldrich, USA), alkali lignin (Sigma, USA), and steamed lignin were 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 and extracted with water at 60°C, followed by extraction with methanol. The methanol-soluble part was dried under vacuum after removal of the methanol, and used as steamed lignin.<sup>7</sup> All other chemicals in this study were reagent grade and they were used without further purification.

### Liquefaction of wood and related compounds

The wood and related compounds were dried at 105°C for 24h before they were used. Each dried compound was placed in a three-necked flask, equipped with condenser and mechanical stirrer, and 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 3% (w/w) of the whole polyhydric alcohols. The mixing ratio of wood materials to polyhydric alcohol was 2:3. The mixture was reacted at 150°C and small amounts of the liquefied product samples were taken several times during the process of liquefaction.

### Measurement of residual ratio

The extent of liquefaction was evaluated by determining the residual ratio. Each sample was diluted with excess DMF, and was filtered 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 24h. The residues were weighed after confirming the disappearance of the peak at 1670cm<sup>-1</sup> due to DMF by Fourier transform-infrared (FT-IR) measurement. The residual ratio was determined as the weight percentage of DMF-insoluble residue based on the starting wood raw material.

### Gel permeation chromatography measurements

Gel permeation chromatography (GPC) of DMF-soluble components was performed by using a Waters 600E multisolvent delivery system with two Shodex KD-806M columns at 50°C, using DMF containing 0.01 M lithium bromide as an eluent. The detection was done with a differen-

tial refractometer (410 Differential Refractometer, Waters, USA) and an ultraviolet (UV) detector (HP-1100 Series Diode Array Detector, Hewlett-Packard, USA).

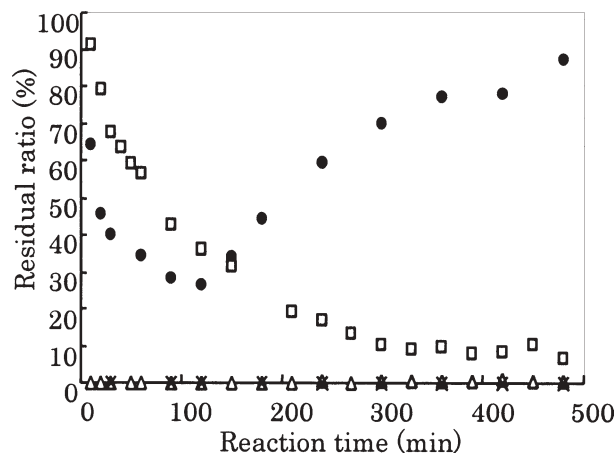
### FT-IR measurements

DMF-soluble and insoluble constituents were dried under vacuum, and analyzed by using a FT-IR spectrometer (Perkin-Elmer Paragon 1000, Perkin-Elmer, UK). The measurements were conducted using the KBr pellet method.

## Results and discussion

### Dissolution behavior of wood and major wooden components

In Figure 1, a curve corresponding to sample A (herein after expressed as Fig. 1A) shows the results of DMF solubility of liquefied wood as a function of reaction time. The liquefaction proceeded immediately at the beginning of the process. Up to 60% of the wood was converted to soluble components within 30 min. However, the condensation reaction, which produced insoluble components, took place after 120 min when the minimum value of the residual ratio was observed. The residual ratio reached 90% at the reaction time of 480 min. Figure 1B shows the results for liquefaction of cellulose powder. The rate of liquefaction was slower than that for wood. It took 270 min for 90% of the cellulose powder to convert into soluble components. After that, the residual ratio remained constant at about 10%, and the condensation reaction could not be observed within 480 min. Figure 1C shows the results for steamed lignin, which is essentially a DMF-soluble compound. Therefore,

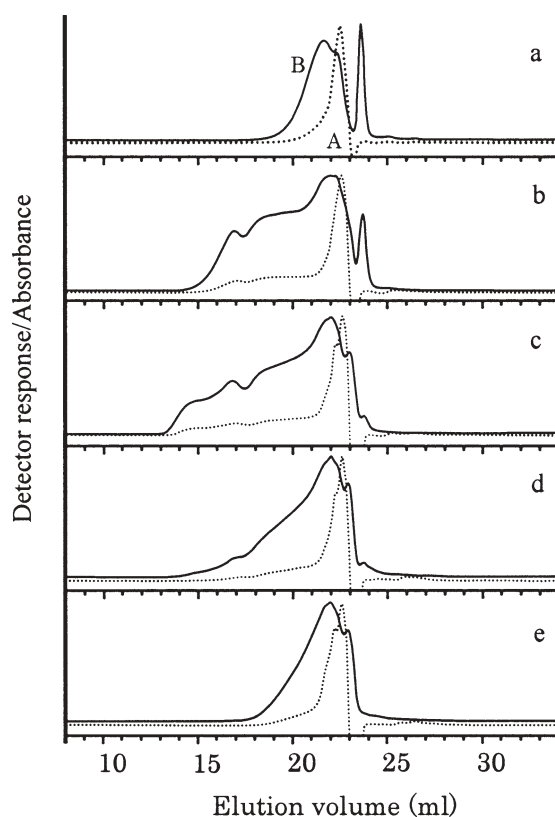


**Fig. 1.** Dimethyl formamide (DMF) solubilities of wood, cellulose powder, alkali lignin, and steamed lignin as functions of liquefaction time. All the mixing ratios of liquefaction materials to solvent were 2/3. Filled circles, reaction A: wood; shaded squares, reaction B: cellulose powder; crosses, reaction C: steamed lignin; open triangles, reaction D: alkali lignin

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 1D shows the results for alkali lignin. The alkali lignin was also completely soluble in DMF as shown in Fig. 2B. The liquefaction behaviors of lignin-related parts were clearly shown, because the UV detector did not detect the solvents.

#### Progress of wood liquefaction

GPC measurement of DMF-soluble parts during the liquefaction of wood was carried out. Figure 2 shows the chromatograms recorded by a differential refractometer and a UV detector at 280 nm. Some low molecular weight peaks were observed after 10 min. As the reaction time proceeded, a broad peak began to develop in the high molecular weight region. After 120 min, when the minimum residual ratio was observed (Fig. 1A), the peaks due to high molecular weight components were detected. Subsequently, as some parts of the liquefied products were converted to insoluble compounds due to the condensation, the peaks due to high molecular weight components became small and disappeared within 480 min. However, because the peaks representing the liquefaction products overlapped with those from the unreacted solvents on the

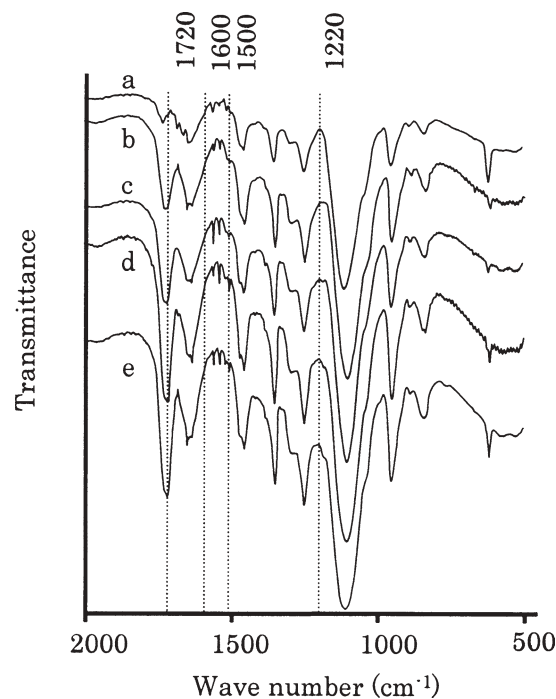


**Fig. 2a-e.** Gel permeation chromatograms of DMF-soluble part for liquefied wood during liquefaction. Detector: A (dotted lines), differential refractometer; B (solid lines), UV detector. Liquefaction time: a 10 min; b 120 min; c 150 min; d 240 min; e 480 min

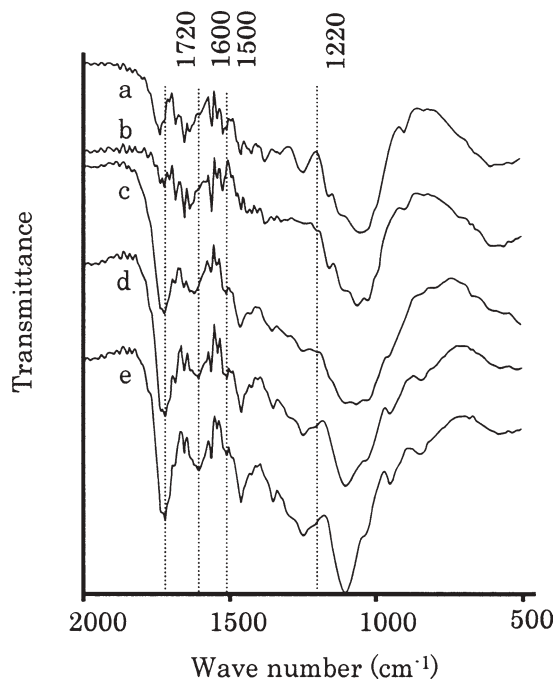
measurements with the differential refractometer, it was difficult to observe the entire molecular weight distribution of liquefaction products. The broad peak in the high molecular weight region, detected by the differential refractometer, was consistent with that obtained by the UV detector as shown in Fig. 2B. The liquefaction behaviors of lignin-related parts were clearly shown, because the UV detector did not detect the solvents.

Figure 3 shows the FT-IR spectra of the DMF-soluble parts of liquefied components of wood. Intense bands of the C—O linkage of alcohol or ether were observed at around  $1100\text{cm}^{-1}$ . These bands were mainly due to polyethylene glycol. In the early stage of the liquefaction, a small band at  $1500\text{cm}^{-1}$  and shoulder peaks at  $1220$  and  $1600\text{cm}^{-1}$  were observed, but they disappeared as the liquefaction proceeded. The bands at  $1500$  and  $1600\text{cm}^{-1}$  were derived from aromatic skeletal vibrations of lignin, and the band at  $1220\text{cm}^{-1}$  was derived from methoxyl groups of lignin.<sup>8,9</sup> The intense band at  $1720\text{cm}^{-1}$  increased as liquefaction proceeded.

Figure 4 shows the spectra of the DMF-insoluble part of liquefied wood. After 150 min, the intensities of the bands at  $1100$ – $1200$ ,  $1500$ ,  $1600$ , and  $1720\text{cm}^{-1}$  strengthened and increased with the liquefaction time. The bands at  $1100$ – $1200\text{cm}^{-1}$  were caused by the liquefaction solvent, and their existences showed that the liquefaction solvent was incorporated into the residue together with cellulose and lignin. The intense bands at  $1500$  and  $1600\text{cm}^{-1}$  were due to lignin, and that at  $1720\text{cm}^{-1}$  was due to derivatives of cellulose. It was suggested that the aromatic rings of lignin incorporated



**Fig. 3a-e.** Fourier transform-infrared (FTIR) spectra of DMF-soluble parts of liquefied wood during liquefaction. Liquefaction time: a 10 min; b 120 min; c 150 min; d 240 min; e 480 min



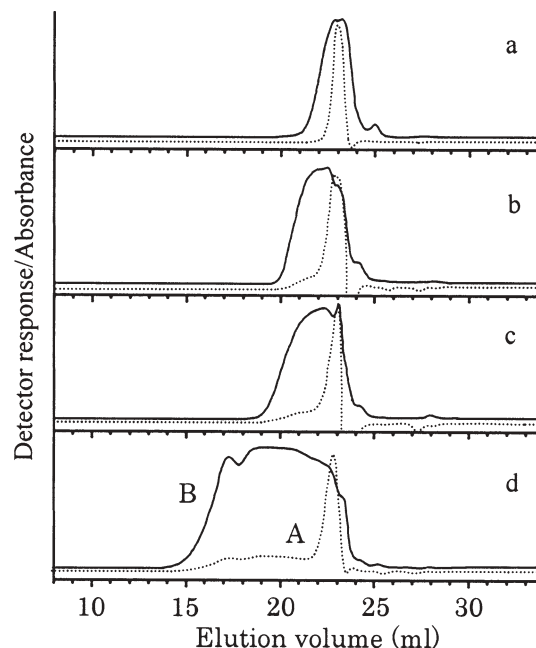
**Fig. 4a-e.** FT-IR spectra of DMF-insoluble parts of liquefied wood during liquefaction. Liquefaction time: **a** 10 min; **b** 120 min; **c** 150 min; **d** 240 min; **e** 480 min

in DMF-insoluble residue did not cleave, because the spectrum of the residue reflected the strong band derived from aromatic skeletal vibrations of lignin.

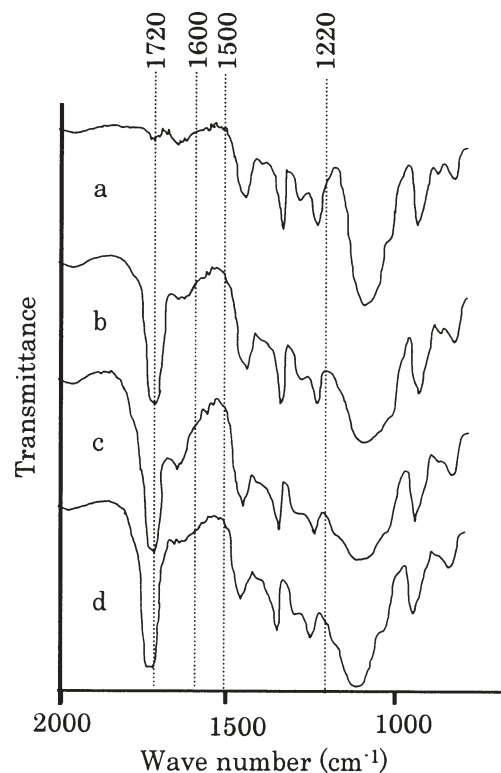
#### Progress of cellulose powder liquefaction

Figure 5 shows the gel permeation chromatograms of the DMF-soluble part of cellulose powder during the liquefaction. The pattern of the chromatograms detected by the UV detector was consistent with the high molecular weight peak detected by the differential refractometer. In the early stage of the liquefaction, a single peak was observed in the low molecular weight region. It was considered that the low molecular weight compounds of cellulose were liquefied immediately and converted to DMF-soluble components. The peaks of liquefied products began to spread over the high molecular weight region with reaction time. The chromatogram obtained after 480 min roughly showed all the components of liquefied products, because they were almost soluble in DMF, as shown in Fig. 1B. It was concluded that the molecular weights of the liquefied products of cellulose were distributed over a wide molecular weight range.

Figure 6 shows the FT-IR spectra of the same samples shown in Fig. 5. After 10 min, only the bands derived from liquefaction solvent were observed because the liquefaction had barely proceeded as shown in Fig. 1B. After that, it was observed that the band at  $1720\text{ cm}^{-1}$  increased in intensity as liquefaction proceeded in a similar manner to wood. It has been reported that levulinic acid ester is produced by solvolysis of cellulose through cleavage of the pyranose linkage, and that levulinic acid has a strong absorption at



**Fig. 5a-d.** Gel permeation chromatograms of DMF-soluble part for liquefied cellulose powder during liquefaction. Detector: *A* (dotted lines), differential refractometer; *B* (solid line), UV detector. Liquefaction time: **a** 10 min; **b** 150 min; **c** 210 min; **d** 480 min



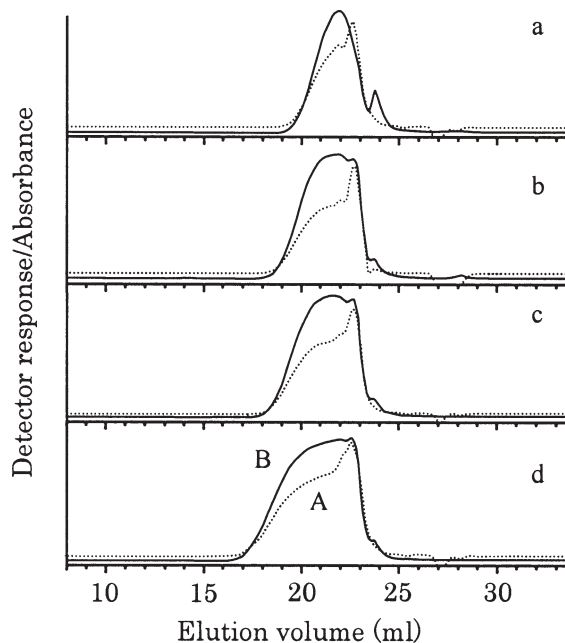
**Fig. 6a-d.** FT-IR spectra of DMF-soluble parts of liquefied cellulose powder during liquefaction. Liquefaction time: **a** 10 min; **b** 150 min; **c** 330 min; **d** 480 min

$1724\text{cm}^{-1}$  due to a ketone group.<sup>10</sup> The information indicated that the intense band at  $1720\text{cm}^{-1}$  observed in this experiment is due to the derivatives of levulinic acids. The spectra showed that more derivatives of levulinic acids formed in the early stage of the reaction than in the case of wood liquefaction. The derivatives of levulinic acids remained after a long reaction time without condensing.

#### Progress of steamed lignin liquefaction

Figure 7 shows the gel permeation chromatograms of the DMF-soluble fraction for steamed lignin during the liquefaction. Steamed lignin is not modified by any chemicals in the process of preparation. Therefore, the analysis of liquefaction behavior of steamed lignin is more suitable than that of alkali lignin in obtaining information about the behavior of wood during liquefaction. Because lignin is soluble in DMF, as described previously, the chromatogram reflected the behavior of all the components during the liquefaction. The peak profiles shifted to the high molecular weight region with increasing reaction time. It has been suggested that the lignin condenses with itself under acidic conditions.<sup>11</sup>

Figure 8 shows the FT-IR spectra of the same samples as Fig. 7. Except for the bands derived from the liquefaction solvent, intense bands were observed at  $1500$ ,  $1600$ , and  $1220\text{cm}^{-1}$ . Because these bands were not observed in the spectra obtained during the cellulose liquefaction, they are indices for the existence of lignin. The relative intensities of the bands at  $1500$  and  $1600\text{cm}^{-1}$  due to the aromatic skeletal vibrations did not change, even after long reaction time.



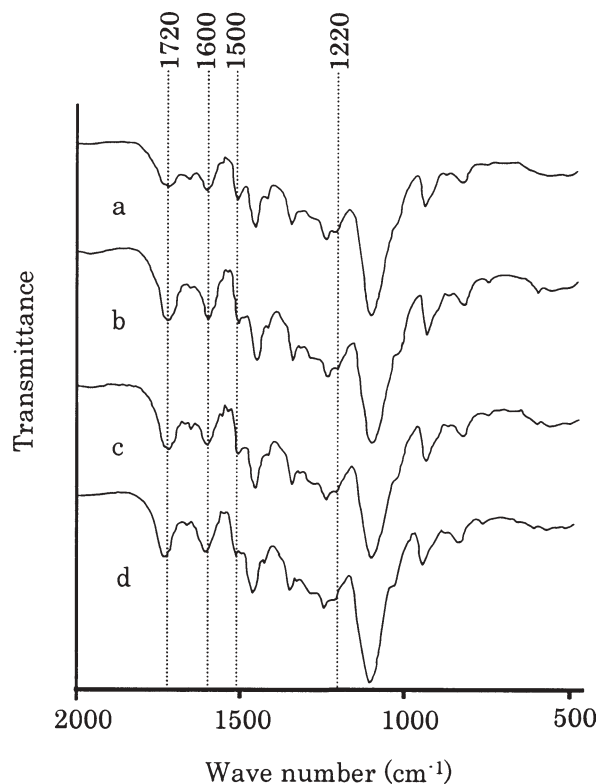
**Fig. 7a–d.** Gel permeation chromatograms of DMF-soluble parts for liquefied steamed lignin during liquefaction. Detector: A (dotted lines): differential refractometer, B (solid lines): UV detector. Liquefaction time: **a** 10 min; **b** 150 min; **c** 210 min; **d** 480 min

The band at  $1220\text{cm}^{-1}$  derived from methoxyl groups of lignin also did not change. It was concluded that no major functional groups of steamed lignin repolymerized during the liquefaction.

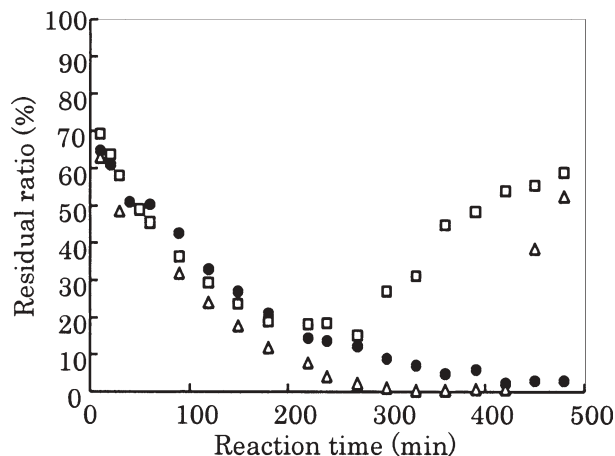
As the results of cellulose or lignin liquefaction were compared with that of wood, it was shown that the DMF-soluble part of wood began to contain the levulinic acid derivatives from about 150 min, when the minimum residual ratio was observed. Traces of lignin were slight in the DMF-soluble fraction at the beginning of the wood liquefaction; however, when the recondensation reaction occurred, the lignin traces disappeared. It was shown that the DMF-insoluble parts of wood contained a lot of the aromatic derivatives from lignin after the recondensation reaction began. At the same time, levulinic acid derivatives were observed in them. These facts suggest that the aromatic derivatives gradually eluted from the beginning of the wood liquefaction, and then, as soon as cellulose degraded to the levulinic acid derivatives, the aromatic derivatives react with them. As a result, the residue was produced.

#### Dissolution behavior of the mixture of lignin and cellulose

The mixture of cellulose powder and steamed lignin was liquefied, and its behavior was compared with that of wood. The mixing ratio of cellulose to lignin was 7:3. This repre-

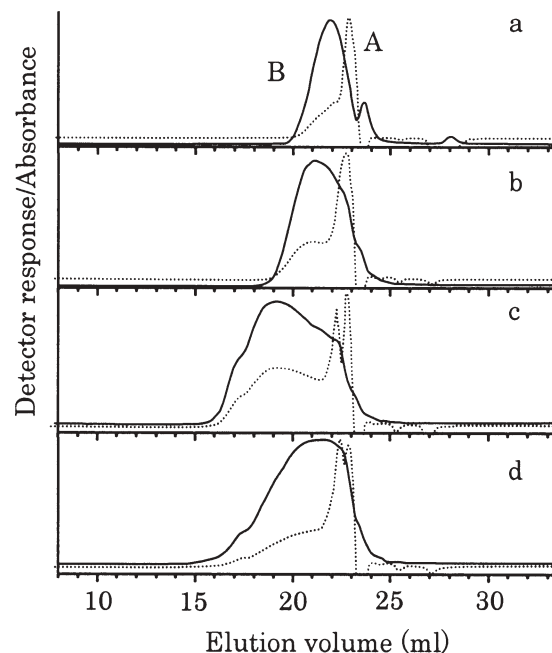


**Fig. 8a–d.** FT-IR spectra of DMF-soluble parts of liquefied steamed lignin during liquefaction. Liquefaction time: **a** 10 min; **b** 150 min; **c** 330 min; **d** 480 min



**Fig. 9.** DMF solubility of cellulose powder and alkali lignin mixture, and cellulose powder and steamed lignin mixture in comparison with calculated value as function of liquefaction time. All the mixing ratios of cellulose components to lignin components were 7/3. All the mixing ratios of liquefaction materials to solvent were 2/3. *E* (triangles), cellulose powder and steamed lignin mixture; *F* (squares), cellulose powder and alkali lignin mixture; *G* (circles), calculated value

sents the rough composition of polysaccharides and lignin in wood. The result of the residual ratio of the mixture, as a function of reaction time, is shown in Fig. 9E. After 10 min, the residual ratio remained at 70%. This fact suggests that most of the cellulose was not liquefied. It was clearly shown that the rate-determining step of liquefaction of the mixture was depolymerization of cellulose. The residual rate reached 0% after 250 min of reaction, and it remained at the same level for a long time afterward. Although the condensation reaction was not observed in each of the independent cases of cellulose and lignin (Fig. 1B–D), the condensation reaction took place after 400 min, and the residual ratio reached 50% after 480 min. Figure 9F also shows the result of the same experiment, in which alkali lignin was used instead of steamed lignin. In this case, the mixture was liquefied slower than that observed with the steamed lignin and cellulose mixture, and then after 270 min, the residual ratio reached a minimum of 16%. After that, the amount of residue increased steeply and the residual ratio reached 76% after 480 min. The reaction rates of both of the model experiments were slower than that of wood. Because wood has amorphous cellulose and hemicellulose, these parts can be easily liquefied. On the other hand, the liquefaction of the mixture is difficult because it contains crystalline cellulose. Moreover, because wood contains a chemically linked lignin–carbohydrate complex (LCC), its liquefaction seems to be easier than that of the mixture. A calculation was conducted to obtain the calculated value *G* assuming that there is no interaction between cellulose powder and alkali lignin. The calculated values were determined by the residue contents of Fig. 1B and Fig. 1C. The values were calculated by adding 70% of each value due to cellulose in Fig. 1B to 30% of lignin in Fig. 1C at each reaction time. The result of the calculation is shown in Fig. 9G which reflected only the liquefaction behavior of cellulose because the share of lignin was zero at every reaction time in this calcu-



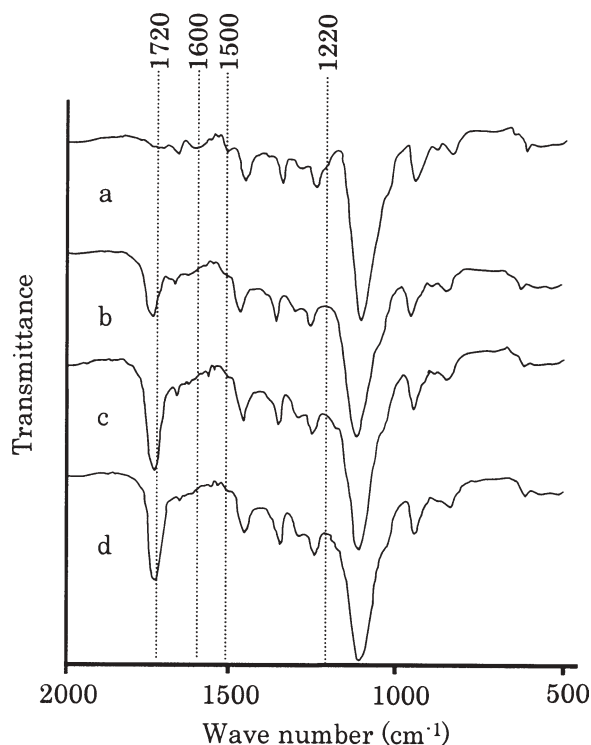
**Fig. 10a–d.** Gel permeation chromatograms of DMF-soluble parts for liquefied mixture of cellulose powder and steamed lignin during liquefaction. Detector: *A* (dotted lines), differential refractometer; *B* (solid lines), UV detector. Liquefaction time: **a** 10 min; **b** 150 min; **c** 210 min; **d** 480 min

lation. It is clearly shown that the condensation reaction took place by the mutual interaction between cellulose and lignin.

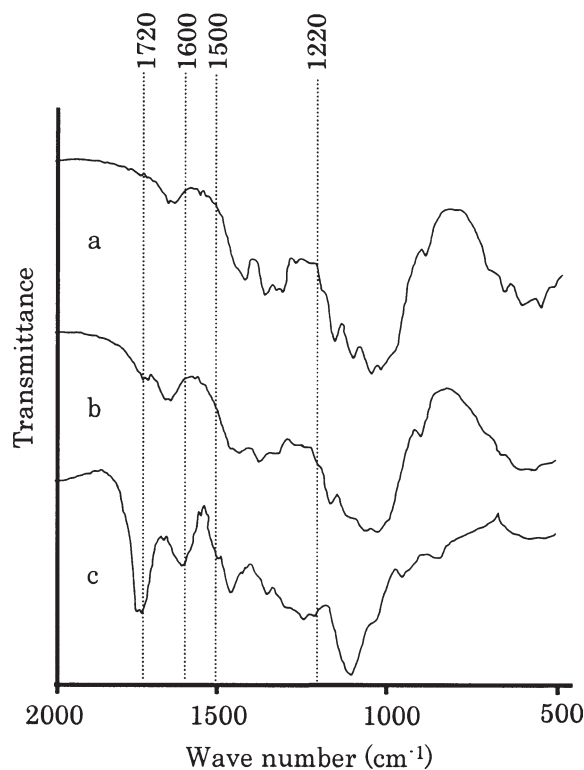
#### Comparison of the liquefaction behavior between wood and the mixture

Figure 10 shows the gel permeation chromatograms of DMF-soluble parts of the mixture of cellulose powder and steamed lignin during the liquefaction. The results are quite similar to those of wood as shown in Fig. 2 for the entire reaction time. After 10 min, the lignin peaks, as shown in Fig. 7, were observed. After that, the peaks of liquefied products began to spread over the low molecular weight region as reaction time proceeded. The mixture was almost converted into DMF-soluble components within 210 min, and the widest molecular weight distribution was observed at this time. The peaks of the high molecular weight region diminished after 480 min. The liquefaction behavior of the mixture was different from the behaviors of cellulose and lignin themselves as shown in Figs. 5 and 7, respectively.

Figure 11 shows the FT-IR spectra of the DMF-soluble fraction for the mixture of cellulose powder and steamed lignin during the liquefaction. After 10 min, although lignin was completely soluble in DMF, only the small bands due to lignin were observed at 1220, 1500, and 1600  $\text{cm}^{-1}$ . The absorption at 1720  $\text{cm}^{-1}$  appeared and the traces of lignin disappeared after 150 min of liquefaction. The spectra clearly showed that the absorption at 1720  $\text{cm}^{-1}$  became more intense during the process of liquefaction. Its intensity was relatively small when compared with the cellulose case



**Fig. 11a–d.** FT-IR spectra of DMF-soluble parts of liquefied cellulose powder and steamed lignin mixture during liquefaction. Liquefaction time: **a** 10 min; **b** 150 min; **c** 210 min; **d** 480 min



**Fig. 12a–c.** FT-IR spectra of DMF-insoluble parts of liquefied cellulose powder and steamed lignin mixture during liquefaction. Liquefaction time: **a** 10 min; **b** 150 min; **c** 480 min

shown in Fig. 6. It suggests that carbonyl groups were consumed for the condensation reaction. However, no further difference was observed during liquefaction, because of the presence of a large amount of liquefaction solvent. When these results were compared with those of wood, the intense bands at around  $1660\text{cm}^{-1}$  due to compounds that had conjugated  $\text{C}=\text{C}$  double bonds were not observed during the liquefaction of the mixture. However, these compounds did not relate to wood liquefaction or the condensation reaction, because the bands were observed from the beginning to the end of wood liquefaction.

Figure 12 shows the FT-IR spectra of the DMF-insoluble part of the mixture of cellulose powder and steamed lignin. The spectrum after 10 min was almost the same as that of cellulose. However, the band at  $1720\text{cm}^{-1}$  appeared as a trace after and was 150 min strong after 480 min of liquefaction. The bands at  $1500$  and  $1600\text{cm}^{-1}$  appeared the same way. These observations suggest that carbonyl derivatives were consumed during the condensation reaction and the residue contained a lot of aromatic compounds. When these results are compared with those of wood, both of the liquefaction systems behaved the same way.

Analysis of the mixture showed that its behavior resembled that of wood in changes of molecular weight distribution and the main functional groups. The liquefied products of lignin existed in the DMF-soluble part before those from cellulose were observed in the cases of wood and the mixture. It was suggested that cellulose gradually converted to levulinic acid derivatives, following the conversion of lignin into DMF-soluble compounds in the early stage of

wood liquefaction. Then, the mixture of levulinic acid derivatives and aromatic compounds reacted and converted to the DMF-insoluble residue, simultaneously. In other words, the DMF-insoluble residue was formed when cellulose and lignin coexisted. The carboxylic acids such as levulinic acid or aromatic compounds are difficult to react by themselves in acidic conditions, so that none of the cellulose model or lignin model condensed by themselves as described above. At the same time, the carbonic acid is usually difficult to react with aromatic compounds in acidic conditions. It was reported that cellulose was degraded by solvolysis with polyhydric alcohol.<sup>5,12,13</sup> When cellulose existing in wood was liquefied in the presence of lignin solution which resembles the case of the mechanical mixture, cellulose was considered to degrade via the phenolic hydroxyl groups of lignin, because they were more reactive than the hydroxyl groups of polyhydric alcohol solvent. In brief, it was estimated that the C1 position of the pyranose structure was attacked by phenoxide ion as a nucleophile, and that a kind of nucleophilic displacement reaction occurred. As the result, composite compounds of cellulose and lignin would be produced. When the resulting compound led the condensation reaction, cellulose and lignin would condense together.

## Conclusions

The liquefaction of cellulose powder, steamed lignin, alkali lignin, and their mixture was carried out to estimate the

liquefaction process of wood in the system using polyethylene glycol as a coexisting medium. Wood started to liquefy immediately at the beginning of the process and the wood components converted to DMF-soluble products. After that, the recondensation reaction occurred. It was clearly shown that none of the cellulose powder, steamed lignin, or alkali lignin condensed by itself. The mixture of cellulose and lignin was liquefied as well as wood. The mixtures also showed condensation after prolonged treatment, being similar to the case of wood. Analysis of the mixture of cellulose powder and steamed lignin showed that its behavior resembled that of wood in respect to changes in molecular weight distribution and the main functional groups. These results suggested that wood was liquefied by similar reaction to that of the mixture. DMF-insoluble residue was formed when the cellulose and lignin coexisted as in the cases of wood and the mixture described above. During the liquefaction of wood, lignin was converted to DMF-soluble compounds in the early stage, followed by cellulose dissolution into DMF by gradually changing its molecular structure. After that, recondensation took place and degraded compounds from cellulose and lignin were converted to DMF-insoluble compounds. It was concluded that the rate-determining step of wood liquefaction was depolymerization of cellulose. Furthermore, it was suggested that the condensation reaction was due to the mutual reaction between depolymerized cellulose and aromatic derivatives of lignin, or due to the nucleophilic displacement reaction of cellulose by the phenoxide ion. The issue hereafter is to obtain particular information about the behavior of cellulose and lignin during wood liquefaction by analyzing the liquefaction process of mixtures of simple models of cellulose and lignin.

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## References

1. 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

2. Kobayashi M, Hatano Y, Tomita B (2001) Viscoelastic properties of liquefied wood/epoxy resin and its bond strength. *Holzforschung* 55:667–671
3. Shiraishi N (1986) Plasticization of wood (in Japanese). *Mokuzai Gakkaishi* 32:755–762
4. Yamada T, Ono H, Ohara S, Yamaguchi A (1996) Characterization of the products resulting from direct liquefaction of cellulose I. Identification of intermediates and the relevant mechanism in direct phenol liquefaction of cellulose in the presence of water (in Japanese). *Mokuzai Gakkaishi* 42:1098–1104
5. Yamada T, Ono H (2001) Characterization of the products resulting from ethylene glycol liquefaction of cellulose. *J Wood Sci* 47:458–464
6. Lin L, Yao Y, Yoshioka M, Shiraishi N (1997) Liquefaction mechanism of lignin in the presence of phenol at elevated temperature without catalysts. Studies on  $\beta$ -O-4 lignin compound. I. Structural characterization of the reaction products. *Holzforschung* 51:316–324
7. 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
8. Faix O (1991) Classification of lignins from different botanical origins by FT-IR spectroscopy. *Holzforschung* 45:21–27
9. Collier W, Schultz T, Kalasinsky V (1992) Infrared study of lignin: reexamination of aryl-alkyl ether C-O stretching peak assignments. *Holzforschung* 46:523–528
10. Yamada T, Ono H (1999) Rapid liquefaction of lignocellulosic waste by using ethylene carbonate. *Bioresource Technol* 70:61–67
11. 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
12. Shiraishi N, Tani Y, Kubo K, Fukuda K (2000) Practical development of biodegradable plastics. *Kogyo Chosakai, Tokyo* pp 173–176
13. Yamada T, Hu Y, Ono H (2001) Condensation reaction of degraded lignocellulose during wood liquefaction in the process of polyhydric alcohols. *J Adhes Soc Jpn* 37:471–478