# Rapid and Complete Dissolution of Softwood Biomass in Tetra-*n*-butylphosphonium Hydroxide with Hydrogen Peroxide

Hajime Yamada,[a] Hisashi Miyafuji,[b] Hiroyuki Ohno,[c] and Tatsuhiko Yamada [a,]*

The wood dissolution properties of tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$) were investigated. Cedar wood meal was treated with several concentrations of aqueous (aq.) $[P_{4,4,4,4}]OH$ with hydrogen peroxide ($H_2O_2$) in a glass tube at 121 °C. The solution of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ at 121 °C showed the best dissolution capability for woody biomass with a high dissolution rate of 0.152 g $min^{-1}$. Under this condition, 98.5% of the woody biomass, including both lignin and holocellulose, was dissolved after 3 h of treatment. The molecular weight distribution of lignin in the soluble fraction of the $[P_{4,4,4,4}]OH$ mixtures was determined *via* size exclusion chromatography, and its weight-average molecular weight decreased from approximately 7500 g/mole after 0.5 h to 2 h of treatment to 5700 g/mole after 3 h and 2500 g/mole after 5 h of treatment. Lower molecular weight components were determined by high-performance liquid chromatography, and vanillin and vanillic acid were identified. The dissolved cellulose was precipitated, and its polymerization degree decreased significantly after 0.5 h of treatment compared to that of the original cellulose.

*Keywords: Aqueous ionic liquid; Tetra-n-butylphosphonium hydroxide; Softwood; Lignin; Cellulose; Multi-sample analysis*

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## INTRODUCTION

Ionic liquids are room temperature molten salts that have recently received increased attention because of their novel cellulosic biomass-dissolving abilities. It has been reported that imidazolium-based ionic liquids can dissolve cellulose (Swatloski *et al.* 2002a,b; Remsing *et al.* 2006) and lignocellulose (Fort *et al.* 2007; Kilpeläinen *et al.* 2007) extensively, and sustainable "green" biomass chemistry can be achieved with these ionic liquids. In particular, tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$, TBPH, an organic base, Fig. 1) presents a high biomass dissolution ability, dissolving microcrystalline cellulose even in moisture-rich or mild (*e.g.*, 60 °C) conditions (Abe *et al.* 2014).

The authors have attempted to dissolve cellulose at milder conditions compared with the previous reports, and found that cellulose could be dissolved in a series of low-polarity ionic liquids, containing methylphosphonate-anion (Abe *et al.* 2010). However, these low-polarity ionic liquids are highly hygroscopic, and a small addition of water to the ionic liquids causes a drastic decrease in their cellulose-dissolving abilities (Mazza *et al.* 2009). This means that raw plant biomass should be dried before an ionic liquid dissolving treatment, because it typically contains a considerable amount of moisture. Therefore, the authors have focused on the use of hydroxide anions in the solvent system to avoid the necessity of a drying pretreatment. Ionic pairs of hydroxide anions with onium cations, such as $[P_{4,4,4,4}]OH$ were found as novel solvents for cellulose (Abe *et al.* 2012, 2014). $[P_{4,4,4,4}]OH$ presents a strong proton-accepting ability even in the presence of water, and the necessity of drying pretreatment could be eliminated. It has been reported that 40% to 70% aq. $[P_{4,4,4,4}]OH$ solutions can readily dissolve cellulose (Abe *et al.* 2012), some woody biomasses (Abe *et al.* 2014), wheat (Hyväkkö *et al.* 2014), and rice husks (Lau *et al.* 2015) at low temperature. Furthermore, woody biomass can be almost completely dissolved in 60% $[P_{4,4,4,4}]OH$ with the addition of hydrogen peroxide ($H_2O_2$) as a dissolution accelerator (Abe *et al.* 2015).

The authors have developed a simple method for separating lignin and carbohydrates from softwood biomass (Yamada *et al.* 2016). This process can be applied using a general-purpose apparatus, such as a screw-top glass tube, and an ordinary autoclave, and was intended to be extended to the chemical analysis of multiple samples. However, this technique required 20 or more hours to achieve sufficient lignin and carbohydrate separation.

The present study aims to dissolve wood rapidly and completely by using an aq. $[P_{4,4,4,4}]OH$ solution. Several concentrations of aq. $[P_{4,4,4,4}]OH$ with and without $H_2O_2$ were tested at high temperature conditions (*i.e.*, 121 °C), and the results were compared with the previous findings. The wood residue contents and dissolution speed were determined, and the chemical compositions of the residues were investigated to reveal the dissolution mechanism. The properties of the dissolved lignin and the polymerization degree of the dissolved cellulose were investigated.

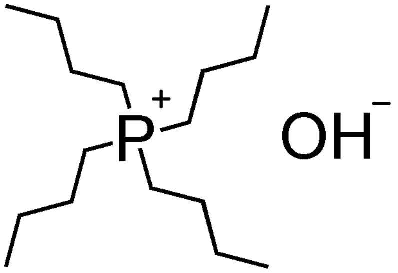


**Fig. 1.** Chemical structure of tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$)

## EXPERIMENTAL

### Materials

Japanese cedar (*Cryptomeria japonica* D. Don) (Forestry and Forest Products Research Institute, Tsukuba, Japan) was used as the woody biomass material in this work. Bark-free cedar chips were air-dried and crushed by a rotor mill (Pulverisette 14, Fritsch Japan, Yokohama, Japan). Wood meal passing through a 0.5-mm mesh sieve was collected and extracted with an ethanol:benzene solution (v/v, 1:2) in a Soxhlet extractor (Sibata, Soka, Japan). The extractive-free wood meal was vacuum-dried at 40 °C for 24 h and then used for the $[P_{4,4,4,4}]OH$ dissolution test.

A 40% aq. $[P_{4,4,4,4}]OH$ solution was purchased from Hokko Chemical Industry (Tokyo, Japan), and other concentrations of $[P_{4,4,4,4}]OH$-water mixtures were prepared from this solution by evaporation. The water content in the mixtures was determined by the Karl Fischer Method. A 30% aq. $H_2O_2$ was purchased from Wako Pure Chemical Industries (Osaka, Japan). Other chemicals used for the experiment were purchased from Tokyo Chemical Industry (Tokyo, Japan) and Junsei Chemical (Tokyo, Japan). All chemicals were used as received without further purification.

## Methods

Wood meal was treated with several aq. $[P_{4,4,4,4}]OH$ solutions under varying aq. $[P_{4,4,4,4}]OH$ concentrations (*i.e.*, 40%, 50%, 60%, or 90%), $H_2O_2$ additions (*i.e.*, with or without), and treatment durations (*i.e.*, 0.5 h, 1 h, 2 h, 3 h, or 5 h). A total of 1 g of wood meal and 20 g of aq. $[P_{4,4,4,4}]OH$ solution was placed in a glass vial equipped with a screw-cap. For the treatments with $H_2O_2$, 19 g of aq. $[P_{4,4,4,4}]OH$ and 1 g of $H_2O_2$ solution was placed in the vials. The screw-caps were closed loosely, and the treatments were performed in an autoclave (STH364FA, 50.2 L, Advantec, Tokyo, Japan) at 121 °C and 2 atm. After treatment, the insoluble residues and soluble fractions were separated by centrifugation, and the residue was filtered and washed with 40% aq. $[P_{4,4,4,4}]OH$ solution followed by methanol and water. After washing and oven-drying at 105 °C, the weights of the residues were measured, and the dissolution rates were calculated.

The properties of the residues, including their residual contents, dissolution rates, and chemical compositions (lignin and holocellulose content), were determined. The properties of the soluble fractions were also investigated. The molecular distribution of the dissolved lignin was characterized by a size exclusion chromatography (SEC) analysis, and the low-molecular weight compounds of the dissolved lignin were identified by a High-performance Liquid Chromatography (HPLC) analysis. The polymerization degree of cellulose in the soluble fractions was also determined by a viscosity analysis.

### *Compositional analysis*

The chemical compositional ratio of the insoluble wood meals was determined using the same method performed in the authors' previous report (Yamada *et al.* 2016). The wood meal samples were treated by TBPH solutions described above, and separated to soluble fractions and residues. The holocellulose content in the residue was determined by the Wise method (Dahlman *et al.* 1999), and the lignin content was determined by the Klason method (Lin and Dence 1992). The lignin content was determined as the sum of the acid-insoluble and acid-soluble lignin contents.

### *Size exclusion chromatography analysis*

The SEC analysis was performed to determine the weight distributions and average weights of the lignin molecules (Takata *et al.* 2016). The soluble fractions obtained from the mixtures of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ and treatment times of 0.5 h, 1 h, 2 h, 3 h, and 5 h were used as sample solutions. A total of 1 mL of the sample solutions was mixed with 9 mL of 5% aq. $H_2SO_4$, and the precipitates were collected by centrifugation. The precipitates were then washed several times with water and dried by evaporation. Precipitation yields were 54.2% at 0.5 h, and the yields decreased as the treatment time increased. The precipitates were extracted with *N*,*N*-dimethylformamide (DMF), and the extractive solutions were collected and dried completely by evaporation for the SEC analysis. These samples were prepared in DMF containing 10 mmol/L of LiBr and filtered through a 0.45-µm syringe filter. An SEC system (Prominence GPC System, Shimadzu, Kyoto, Japan) equipped with a UV detector and an RI detector on a two-column (Shodex KD 804 and KD 802-5) sequence was used. The DMF containing 10 mmol/L LiBr was used as the eluent, the flow rate was 1.0 mL/min, and the column temperature was 40 °C. An absorbance at 280 nm was used to determine the lignin concentrations. The molecular weight of the samples was calculated based on polyethylene oxide (PEO) type of analytical standards (ReadyCal Set Mp 200-1200000, FLUKA polyethylene glycol/polyethylene oxide, Sigma-Aldrich, St. Louis, MO, USA).

### *High-performance liquid chromatography*

The HPLC analysis was performed to identify the degraded substances in the soluble fractions. The soluble fractions obtained from the mixtures of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ and treatment times of 0.5 h to 5 h were used as the sample solutions. Sample preparation was performed using the steps identical to those in a previous report (Kubo *et al.* 2008). The soluble fractions were neutralized to a pH of 5.0 by aq. $H_2SO_4$, and a liquid-liquid extraction was performed using diethyl ether. The diethyl ether fraction was collected and evaporated completely. The HPLC samples were prepared in a mixed solvent of acetonitrile:$H_2O$ at a ratio of 45:55, and 3,4,5-trimethoxybenzaldehyde solution was added as the internal standard. The sample was filtered through a 0.45-µm syringe filter. An HPLC analysis was performed using a HP 1100 Series (Agilent Technologies, Santa Clara, CA, USA) instrument with a Supelco Discovery C18 column (Sigma-Aldrich, St. Louis, MO, USA). A mixed solvent of acetonitrile:$H_2O$ at a ratio of 45:55 was used as the eluent, and the absorbance was recorded at 210 nm and 280 nm.

### *Degree of cellulose polymerization*

The degree of cellulose polymerization in soluble fractions was determined by the conventional viscosity method according to TAPPI T230 om-08 (2013). Because the lignin content of the sample should be under 5% in this method, delignified cedar wood was prepared. Delignification was performed to obtain cedar wood holocellulose *via* the Wise method (Dahlman *et al.* 1999). Holocellulose was treated with 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$, at 121 °C for 0.5 h, 1 h, or 3 h. The treated mixture was then centrifuged, and the soluble fraction was collected. The soluble fraction was mixed with methanol and 0.1 mol/L aq. NaOH and then subjected to centrifugation to collect its precipitates. Precipitation samples were washed several times with water and dried in a vacuum oven VO-42D (Advantec, Tokyo, Japan) at 40 °C for 24 h. Precipitation yields were 33.6%, and they decreased as the treatment time increased. Samples were prepared from 40 mg of the precipitates and 20 mL of 0.5 M aq. cupriethylenediamine. As a control, alpha-cellulose was prepared *via* the condensed NaOH conventional method (Dahlman *et al.* 1999). The efflux times were determined by Cannon-Fenske viscometers (Shibata, Tokyo, JAPAN), and the viscosity-average degree of polymerization (DPw) was calculated from the efflux time by applying Mark-Houwink-Sakurada Formulas according to Eqs. 1 through 3 (Evans and Wallis 1989),

$$\eta_r = t / t_0 \tag{1}$$

$$\eta_{sp} = \eta_r - 1 \tag{2}$$

$$DPw = 175 \times \eta_{sp} / (100 \times c(1 + 0.28\eta_{sp})) \tag{3}$$

where, $\eta_r$ is the relative viscosity, $t$ is the efflux time of cellulose sample solution (s), $t_0$ is the efflux time of blank solution (s), $\eta_{sp}$ is the specific viscosity, $DPw$ is the viscosity-average degree of polymerization (cellulose unit), and $c$ is the cellulose concentration (g/mL).

## RESULTS AND DISCUSSION

### Effects of aq. [$P_{4,4,4,4}$]OH Concentration and Addition of $H_2O_2$

The residual contents obtained from various concentrations of [$P_{4,4,4,4}$]OH aq. with and without the addition of $H_2O_2$ are shown in Fig. 2. Here, mixtures of 40%, 50%, 60%, and 90% aq. [$P_{4,4,4,4}$]OH were treated at 121 °C for 1 h. In summary, the mixture containing 60% aq. [$P_{4,4,4,4}$]OH showed the lowest residual content, while the mixture containing 90% aq. [$P_{4,4,4,4}$]OH showed the highest residual content. As the aq. [$P_{4,4,4,4}$]OH concentration increased from 40% to 60%, the residual contents consistently decreased. The addition of $H_2O_2$ lowered the residual contents in the mixtures of 40% to 60% aq. [$P_{4,4,4,4}$]OH but showed little effect on the residual contents of the mixture containing 90% aq. [$P_{4,4,4,4}$]OH.

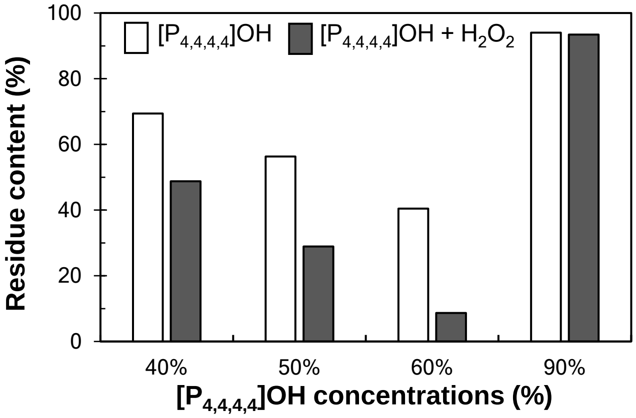


**Fig. 2.** Residual contents obtained after treatment at 121 °C for 1 h using various concentrations of aq. [$P_{4,4,4,4}$]OH, with and without $H_2O_2$

Among the investigated conditions, the mixture of 60% aq. [$P_{4,4,4,4}$]OH with $H_2O_2$ showed the best wood dissolution capability. After 1 h of treatment at 121 °C, the residual content decreased to 8.7%, which was the lowest among the contents observed and translated to a dissolution rate of 0.152 g $min^{-1}$ (Fig. 3). Thus, this mixture allowed considerable and rapid dissolution compared to the findings in previous reports on [$P_{4,4,4,4}$]OH (Abe *et al.* 2015). The concentration of aq. [$P_{4,4,4,4}$]OH in a mixture is known to present a strong relation with its cellulose-dissolving capability (Abe *et al.* 2012). For example, 60% aq. [$P_{4,4,4,4}$]OH could dissolve microcrystalline cellulose, whereas 40% aq. [$P_{4,4,4,4}$]OH could only dissolve hemicellulose and hardly dissolves cellulose.

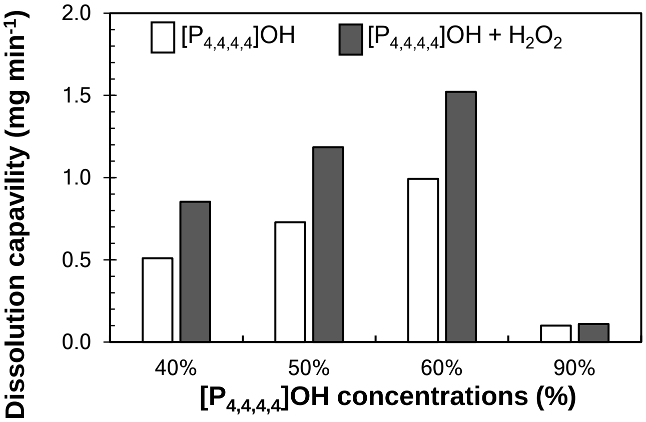
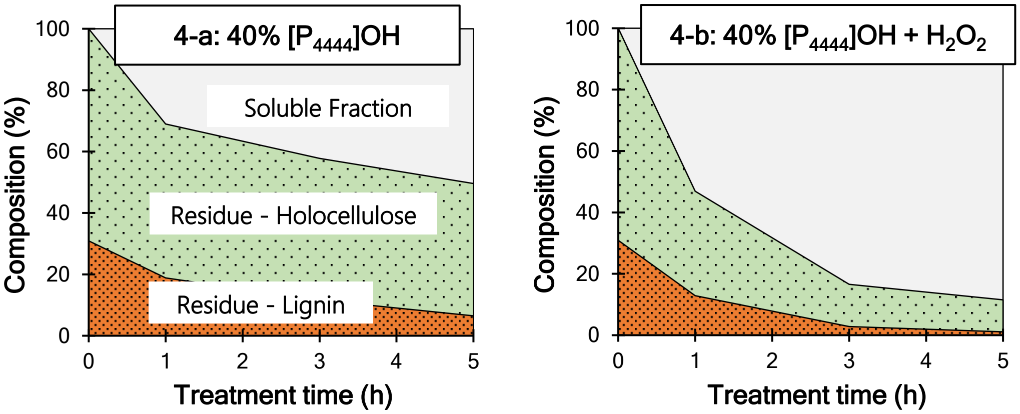


**Fig. 3.** Dissolution capabilities obtained after treatment at 121 °C for 1 h using various concentrations of aq. $[P_{4,4,4,4}]OH$, with and without $H_2O_2$

The mixture of 90% aq. $[P_{4,4,4,4}]OH$ showed the poorest wood dissolution capability among the mixtures studied, and the addition of $H_2O_2$ did not enhance this capability. This result may have been explained by the decomposition of $[P_{4,4,4,4}]OH$ molecules at a 90% concentration. Those results were obtained because $[P_{4,4,4,4}]OH$ would be weakened due to heat and decompose more easily (Hyväkkö *et al.* 2014), when $[P_{4,4,4,4}]OH$ was mixed with a minimal amount of water.

## Changes in Chemical Compositional Ratio

Compositional changes during treatment were determined in four aq. $[P_{4,4,4,4}]OH$ solutions. Figures 4-a through 4-d show the relations between treatment time and compositional ratios under four conditions of 40% aq. $[P_{4,4,4,4}]OH$, 40% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$, 60% $[P_{4,4,4,4}]OH$, and 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$, respectively.



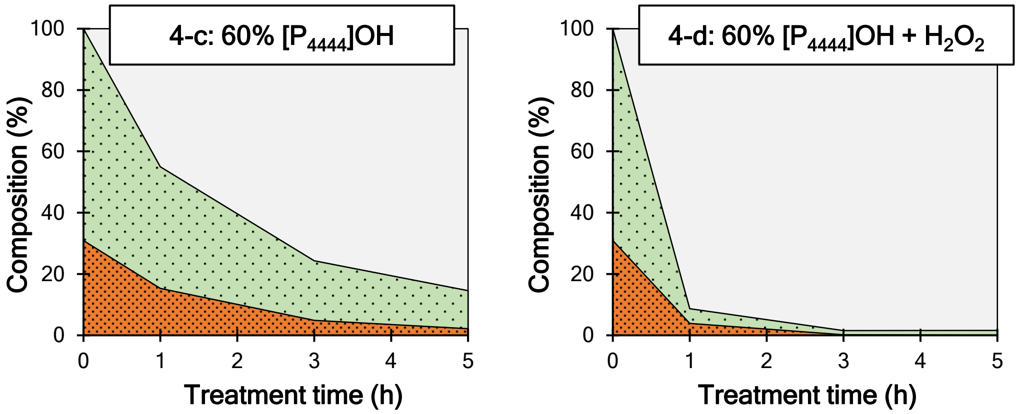


**Fig. 4.** Relationships between treatment time and compositional ratios of the soluble fraction, residual holocellulose, and residual lignin. The woody flour was treated with 40% and 60% aq. $[P_{4,4,4,4}]OH$ with and without $H_2O_2$

Under all of the treatment conditions, the residual ratios (holocellulose + lignin) decreased with increased treatment time. After 5 h of treatment, residual ratios of 49.6%, 11.5%, 14.6%, and 1.6% could be seen in Figs. 4-a through 4-d, respectively. The residual ratios decreased sharply in the early stages of treatment and then decreased gradually at around 5 h. Treatment with 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ (Fig. 4-d) yielded the minimum residual ratio within 3 h, which was fairly rapid. The wood meal was dissolved effectively in 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$, and only 8.7% and 1.5% residue remained after 1 and 3 h of treatment, respectively.

The lignin/holocellulose ratio in the residue decreased as the treatment time increased in all four conditions investigated (Figs.4-a through 4-d). The authors' previous report also noted the tendency of lignin to dissolve faster than holocellulose (Yamada *et al.* 2016). In that report, the holocellulose ratio decreased and reached saturation at 39% after 20 h of treatment with 40% aq. $[P_{4,4,4,4}]OH$; thus, 40% aq. $[P_{4,4,4,4}]OH$ was not considered to dissolve cellulose adequately. The present study showed that the addition of $H_2O_2$ to the mixture could overcome this limitation, *i.e.*, 40% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ dissolved the cellulose. Mixtures of 60% aq. $[P_{4,4,4,4}]OH$ aq. are also known to dissolve microcrystalline cellulose at ambient temperature (Abe *et al.* 2012). In this study, the authors applied a temperature of 121 °C for treatment and observed that the wood meal was nearly completely dissolved within 3 h. From these results, $H_2O_2$ could be considered to rapidly accelerate the dissolution of both holocellulose and lignin.

The mechanism of wood meal dissolution should be considered from the aspects of lignin dissolution and cellulose dissolution. The use of 40% aq. $[P_{4,4,4,4}]OH$ was previously considered to enable nearly complete lignin dissolution (Yamada *et al.* 2016). An addition of $H_2O_2$ and concentration of 40% aq. to 60% aq. of $[P_{4,4,4,4}]OH$ could accelerate lignin dissolution. A strong nucleophile regent, perhydroxyanion ($[OOH^-]$), would be formed from $H_2O_2$ in an alkaline condition (Gierer 1990). The $H_2O_2$ and $[OOH^-]$ works as a nucleophile regent, and these attack the alpha or gamma position of the lignin side chain, which caused lignin decomposition and fragmentation. Active oxygen species', such as hydroxyl radical ([*OH]) and superoxide anion radical ([*O2-]), are also formed by $H_2O_2$ in the presence of some types of metallic ions (Gierer 1997). These active oxygen species lead to radical reactions that can decompose lignin *via* several pathways and cause a peeling reaction or fragmentation of carbohydrate chains (Ek *et al.* 1989).

The dissolution ability of aq. $[P_{4,4,4,4}]OH$ for both lignin and holocellulose clearly increased as the aq. $[P_{4,4,4,4}]OH$ concentration increased. Previous reports have determined that 40% aq. $[P_{4,4,4,4}]OH$ could dissolve hemicellulose but not alpha-cellulose at 40 °C and 121 °C. In the present study, 40% aq. $[P_{4,4,4,4}]OH$ showed a slight holocellulose dissolution ability and could not dissolve cellulose, which was similar to previous findings. Holocellulose and lignin rapidly dissolved and their dissolution ratios increased, as the $[P_{4,4,4,4}]OH$ concentration increased from 40% to 60%. This change could have been explained by the hydrotropic effect of high-density salt solutions (Suguri and Kondo 1971). A molecular aspect of $[P_{4,4,4,4}]OH:H_2O$ could be calculated as 1:10 in 60% $[P_{4,4,4,4}]OH$ aq., and 1:20 in 40% $[P_{4,4,4,4}]OH$ aq., respectively. This difference in molecular aspect could make the different solution state of holocellulose and lignin macromolecular.

The $[P_{4,4,4,4}]OH$ was able to decompose lignin and holocellulose. The addition of $H_2O_2$ produced synergistic effects and accelerated the dissolution of these macromolecules. In particular, 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ showed a rapid and complete dissolution capability for woody biomass. The dissolution mechanism of this solution is described in the following section.

## Lignin Properties in the $[P_{4,4,4,4}]OH$ Soluble Fraction

Figure 5 shows the SEC-UV chromatograms of the lignin prepared from the soluble fractions of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$. As the treatment time increased, the total areas of the chromatograms appeared to increase; in addition, the top peaks of the chromatograms moved backwards. These results indicated that the total amount of dissolved lignin increased and that the lignin molecules became smaller in size as the treatment time increased. Three peaks with retention times of 20.3 min, 21.1 min, and 22.0 min that corresponded to compounds with PEO based molecular weights of 220, 170, and 150, respectively, were observed. The areas of these peaks increased as the treatment time increased, and an HPLC analysis was applied to identify these compounds.

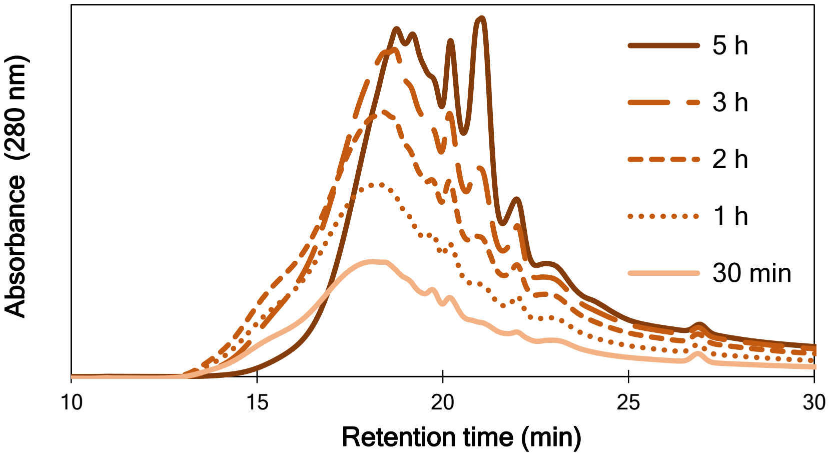


**Fig. 5.** SEC-UV chromatograms of the lignin in soluble fractions obtained at various treatment times; the soluble fractions were obtained from mixtures of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$

Table 1 shows the weight-average molecular weight ($M_w$), number-average molecular weight ($M_n$), and molecular weight distributions ($M_w/M_n$) of lignin prepared from the soluble fractions of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ mixtures. The lignin samples obtained at the treatment times ranging from 0.5 h to 2 h did not show substantial differences in the $M_w$, and values of 7400 to 7600 were determined. However, as the treatment time increased to 3 h, the $M_w$ decreased to 5700; after 5 h of treatment, the $M_w$ decreased to 2500. These results revealed that degraded lignin at a $M_w$ of around 7500 would be dissolved smoothly in 60% aq. [$P_{4,4,4,4}$]OH. When the treatment time was more than 3 h, a greater fragmentation of the dissolved lignin could be produced. The molecular weight distributions were kept almost stable during the treatment time of 0.5 h to 3 h, and then they sharply decreased at 5 h. This could have been explained because the lignin molecules were extensively degraded, and the variety of lignin molecular distribution was lost.

**Table 1.** Weight-average Molecular Weight ($M_w$), Number-average Molecular weight ($M_n$), and Molecular Weight Distributions ($M_w/M_n$) of the Lignin in Soluble Fractions of aq. [$P_{4,4,4,4}$]OH and $H_2SO_4$ Mixtures Obtained at Various Treatment Times

| Treatment Time | $M_w$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| 30 min | 7,400 | 2,500 | 2.9 |
| 1 h | 7,600 | 2,600 | 3.0 |
| 2 h | 7,700 | 2,500 | 3.0 |
| 3 h | 5,700 | 1,800 | 3.1 |
| 5 h | 2,500 | 1,000 | 2.4 |

Figure 6 shows the HPLC chromatograms of the solutions prepared from 60% aq. [$P_{4,4,4,4}$]OH with $H_2O_2$. The vanillin ($M$ = 152) and vanillic acid ($M$ = 168) were identified by their retention times of 7.7 min and 8.5 min, respectively. These retention times were confirmed by a comparison with the chromatograms of the authentic preparations. Vanillin and vanillic acid are generated from many lignin decomposition pathways (Gierer 1982a,b), including some types of ionic liquid treatments (Kubo *et al.* 2008). The concentrations of vanillin and vanillic acid increased as the treatment time increased, and the former was the main component dissolved in the aq. [$P_{4,4,4,4}$]OH soluble fraction. The compound with a molecular weight of 220, which was detected during SEC analysis, could not be identified by an HPLC analysis.

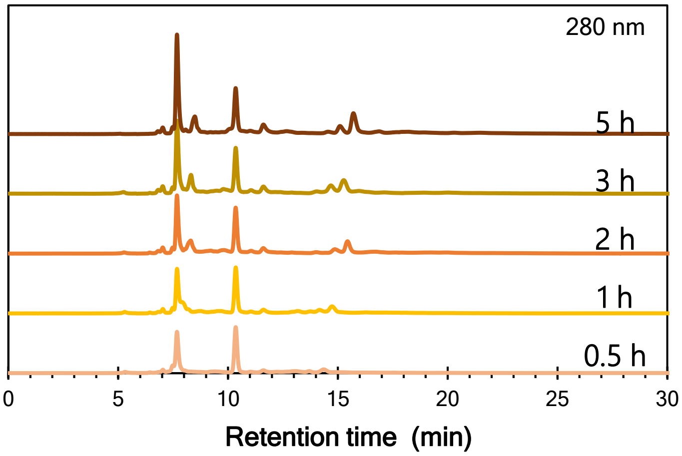


**Fig. 6.** HPLC chromatographs of lignin in the soluble fractions of aq. [$P_{4,4,4,4}$]OH and $H_2SO_4$ mixtures obtained after treatment at 121 °C and various treatment times

### Cellulose Properties in the $[P_{4,4,4,4}]OH$ Soluble Fraction

Figure 7 shows the DPws of the precipitated cellulose obtained from the soluble fractions of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$. As the treatment time increased, the DPw decreased. The DPws of 105, 55, and 47 were obtained after treatment for 0.5 h, 1 h, and 3 h, respectively. The $[P_{4,4,4,4}]OH$-dissolved cellulose was extensively depolymerized compared with the untreated materials. The DPw of holocellulose from cedar wood meal was 631, while that of alpha-cellulose was 860. The DPw of alpha-cellulose was higher than that of holocellulose. This was because hemicellulose, which presented a relatively low polymerization degree, could be eliminated by a high-density aq. NaOH treatment. These results demonstrated that the dissolved cellulose obtained from a solution of 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ presented a very low polymerization degree and suggested that the heating treatment promoted deeper depolymerization.

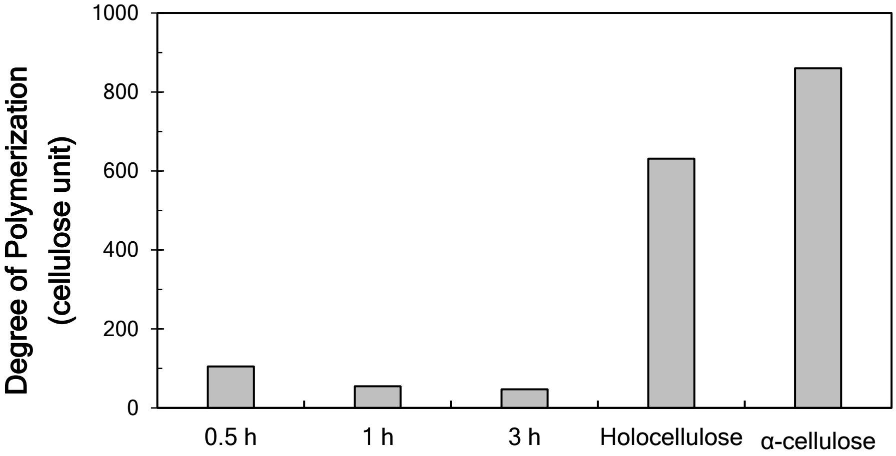


**Fig. 7.** Viscosity-average polymerization degree (DPw) of the precipitations obtained from soluble fractions of aq. $[P_{4,4,4,4}]OH$; Japanese cedar holocellulose was treated with 60% aq. $[P_{4,4,4,4}]OH$ with $H_2O_2$ at 121 °C, and precipitates were obtained from mixtures of NaOH + aq. methanol and the soluble fractions

## CONCLUSIONS

1. The rapid and complete dissolution of woody biomass was performed with 60% aq. $[P_{4,4,4,4}]OH$ with the addition of $H_2O_2$.
2. Approximately 98.5% of the wood meal, including both lignin and holocellulose, was completely dissolved after 3 h of treatment. An addition of $H_2O_2$ to 60% aq. of $[P_{4,4,4,4}]OH$ promoted wood biomass dissolution.
3. The molecular weight of the dissolved lignin was approximately 7500 and remained stable until around 2 h of treatment. Treatment for longer than 3 h caused a rapid decrease in molecular weight. Vanillin and vanillic acid were identified from the dissolved fraction by HPLC analysis.
4. The dissolved cellulose was collected by an addition of mixtures of NaOH + aq. methanol, and its polymerization degree was quite low compared with that of untreated cellulose.

## ACKNOWLEDGMENTS

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