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Almost complete dissolution of woody biomass with tetra-*n*-butylphosphonium hydroxide aqueous solution at 60 °C

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Dissolution of several kinds of woods were examined in tetra-*n*-butylphosphonium hydroxide ($[P_{4,4,4,4}]OH$) aqueous solution. Since there is a strong correlation between dissolution degree and Klason lignin content of the wood, lignin degradation and removal was found to be necessary for efficient dissolution of several woods such as cedar. It was found that moderate heating (60 °C) and addition of H_2O_2 aqueous solution to 50% $[P_{4,4,4,4}]OH$ aqueous solution are quite effective to dissolve wood. Cedar powder (final concentration of 5.0 wt%) was almost completely dissolved in this aqueous solution at 60 °C under mild stirring for 24 h. This efficient wood dissolution was caused by partial degradation of lignin.

Introduction

Woody biomass has been intimately involved in human life as useful and renewable resource for not only materials but also energy. With the inevitable depletion of petroleum-based resources, there has been an increasing interest in using natural plant biomass. Since lignocellulose is not competing against food, it could be a suitable fossil fuel substitute. Polysaccharides and/or lignin, main components of biomass, are useful materials, but the problem is its insolubility mainly attributed to both tight lignin network[1] and strong intra and inter-hydrogen bonding of cellulose.[2,3] Therefore, the effective extraction of polysaccharides has not been achieved yet. Several pre-treatment processes of woody biomass have been reported that disrupt the cellulose chains, and this makes possible to use the biomass as an renewable material.[4] However, they still require a large amount of energy, multiple steps, long-term treatment, and/or some facilities.[4] Until now, some liquids are known as solvents for cellulose, including NaOH/water mixture with or without additives,[5,6] *N*-methylmorpholine *N*-oxide monohydrate,[7] and LiCl/*N,N*-dimethylacetamide mixture.[8-10] These solvents have disadvantages such as limited ranges of conditions, toxicity, and inapplicability to lignocellulose. Recently, ionic liquids are illuminated as promising novel solvents for pure cellulose and lignocellulose.[11-14] We recently reported that polar ionic liquids dissolved polysaccharides, and we also successfully extracted them from plant biomass without heating.[15] These cellulose-dissolving ionic liquids are good solvent for cellulose, but they suffer from a drastic decrease of cellulose solubility with increasing water content.[16-18] Since polar ionic liquids are hygroscopic, they readily absorb water from the atmosphere.[19] In addition, plant biomass contains a considerable amount of water. It is therefore necessary to include a drying process for both ionic liquids and plant biomass when using ionic liquids as solvents for lignocellulose. There is a strong motivation to design a new system requiring no drying processes.

As an advanced way to solve this problem, we developed a novel solvent which dissolved cellulose at moderate condition even in the presence of water. Some alkylammonium hydroxides such as trimethylbenzylammonium hydroxide containing water was found to dissolve cellulose without heating, but they were not applied as a solvent for cellulose due to its high cost and poor recyclability.[20] Recently, we found that tetra-*n*-butylphosphonium ($[P_{4,4,4,4}]$) and tetra-*n*-butylammonium ($[N_{4,4,4,4}]$) hydroxide aqueous (aq.) solutions were excellent solvent for cellulose. They are stable throughout the cellulose dissolving process strongly suggesting that they are recyclable.[21] Regarding this, Ema *et al.* recently reported that $[N_{4,4,4,4}]OH$/crown ether mixture dissolves cellulose at room temperature.[22] In addition, quite recently, these onium hydroxide solutions were found to dissolve lignocellulosic materials such as wheat straw[23] and even woods.[24] These onium hydroxide aq. solution has a potential to partially dissolve plant biomass efficiently under mild condition. However, there were a certain amount of useful materials such as cellulose in the residue.[23,24] To maximise the potential of plant biomass, we need both complete dissolution and effective utilisation of whole components.

In this study, several woody biomasses, including soft woods and hard woods, were dissolved in $[P_{4,4,4,4}]OH$ aq. solution. We clarified what composition dominantly affects the solubility. In addition, we succeeded to almost completely dissolve obstinate woody biomass at 60 °C within 24 h.

Experimental

Materials

An aqueous $[P_{4,4,4,4}]OH$ solution was provided by Hokko Chemical Industry Co., Ltd., and 50% $[P_{4,4,4,4}]OH$ aq. solution was prepared by evaporating the solution. Water content of $[P_{4,4,4,4}]OH$ was measured with Karl-Fischer Moisture Titrator. Quercus crispula Blume (Oak), Eucalyptus viminalis Labill

(Eucalyptus), Pinus densiflore Sieb. et Zucc. (Pine), Picea Jezoensis Carr. (Spruce), Cryptomeria Japonica D. Don (Cedar), Ginkgo biloba L. (Ginkgo) were provided by the Forestry and Forest Products Research Institute as wood powder sample (50-300 mesh). Methanol (1st grade) was purchased from Wako Pure Chemical Industries, Ltd. 35% H_2O_2 aq. solution and 1-ethyl-3-methylimidazolium methylphosphonate ([C_2mim] [(MeO)(H)PO_2]) was purchased from Kanto Chemical Industry Co., Ltd.

Wood dissolution test

Water content of each wood powder was measured using thermogravimetric analysis (TGA). The TGA measurements were performed using a SEIKO TG/DTA 220 instrument with a heating rate of 10 °C min^{-1} from 25 to 110 °C, and retain at 110 °C for 20 min. under nitrogen gas. Water content of wood powder was summarised in Table S1 (Electronic supplementary information, ESI). Aqueous solutions of 50% [$P_{4,4,4,4}$]OH (5 g) were put into 50 ml vials, and each wood powder was added (final concentration was 5 wt% as dried weight). These mixtures were stirred (300 rpm) at predefined temperature. After that, the supernatant and residue were separated by centrifugation (10400 G, 20 °C, 5 min) and the residue was collected. The collected residue was washed with 50% [$P_{4,4,4,4}$]OH aq. solution and methanol. We had already confirmed that there is no extra dissolution of the residue during the washing. After washing, the dried weight of residue was evaluated, and the degree of dissolution was determined with following equation:

$$\text{Dissolution degree (wt\%)} = (W_{\text{initial}} - W_{\text{residue}}) / W_{\text{initial}} \times 100 \quad \text{(Eq. 1)}$$

where W_{initial} represents the weight of initial wood powder, and W_{residue} is the weight of dried residue.

Composition analysis of residues

Holocellulose   The holocellulose content of residue was determined with wise method. The residues of wood powder (300 mg) after 1, 3 and 10 h treatment were put into 50 mL vials, and water (30 mL), NaClO$_2$ (0.5 g), and HCl (100 μL) were added respectively. The mixture was shaken for 1 h at 70-80 °C. After shaking, NaClO$_2$ (0.5 g) and HCl (100 μL) were added to the mixture and it was shaken again. This process was repeated 4 times. The mixture was filtrated and washed with water and acetone. The residue was weighed after drying at 110 °C, and the amount of holocellulose was determined.

α-Cellulose   The dried holocellulose was used for determination of α-cellulose content. The holocellulose was put into a 50 mL vial and NaOH (5 mL) was added. This mixture was stirred by glass rod every 5 min. After 30 min, water (6 mL) was added. This mixture was filtrated with water after 5 min stirring. The residue was washed by 10% acetate aq. solution (8 mL), water (130mL), and acetone. The residue was weighed after drying at 110 °C to determine the amount of α-cellulose.

Lignin   The residues of wood powder (300 mg) after 1, 3, and 10 h processing were put into 50 mL vials, and 72 % H_2SO_4 aq. solution (5 mL) was added to the residues. The mixture was stirred for every 15 min with glass rod at r.t. After 2 h, the mixture was transferred to 500 mL reagent bottle with water (191 mL). This bottle was heated with a pressure cooker for 20 min at 700 W, and for 5 min at 1400 W. After these steps, the bottle was heated for 1 h at 700 W. The mixture was filtrated and the residue was washed by water (130 mL) and acetone.

The washed residue was weighed after drying at 110 °C to determine the amount of Klason lignin. Acid soluble lignin was determined by the maximum UV absorbance of the supernatant at 205-210 nm using an extinction coefficient of 110 L g^{-1} cm^{-1}. Acid soluble lignin was calculated by the following formula,

$$\text{Acid soluble lignin (\%)} = (d_{\text{f}} \times V \times A) / (110 \times W) \times 100 \quad \text{(Eq. 2)}$$

where d_{f} is dilution factor, V is total volume of the supernatant, A is the absorbance, and W is the weight of initial wood powder.

Holocellulose and α-cellulose content of natural woods used in this study was cited from reference by Pettersen.[25] Lignin content was determined using sulfuric acid method.[26] Sum of β- and γ-cellulose content was determined by subtracting weight of α-Cellulose from that of holocellulose.

Molecular weight distribution measurement

The Molecular weight distribution (MWD) of cellulose before and after treatment with [$P_{4,4,4,4}$]OH/H_2O_2 aq. solution was analysed with high performance ionic liquid chromatography (HPILC). [C_2mim][(MeO)(H)PO_2] was passed through an alumina column and filtrated by PTFE membrane filter (pore size: 0.20 μm in diameter). After that, it was dried under reduced pressure until the water content turned to be less than 0.30%, and used as eluent under helium gas atmosphere.

As a model of cellulose, microcrystalline cellulose (MCC) was added in the [$P_{4,4,4,4}$]OH/H_2O_2 aq. solution to be 5.0 wt%, and the solution was stirred for 24 h at 60 °C. After that, methanol was added to precipitate the dissolved MCC followed by washing and drying steps. MCC (2.5 mg) before or after treatment with [$P_{4,4,4,4}$]OH/H_2O_2 aq. solution was added to [C_2mim][(MeO)(H)PO_2] (500 mg) and stirred under nitrogen atmosphere at room temperature until the MCC was completely dissolved. Each sample was injected into the HPILC system and the MWD of cellulose was recorded with refractive index detector. Experimental condition was the same as that in our previous reports.[27,28]

Results and discussion

Solubility of several wood species

Since there are very few reports about lignocellulose dissolution with alkyl-onium hydroxide aq. solutions,[23,24] effect of composition and structure of lignocellulosic biomass have not been clarified. Therefore, we firstly dissolved several kinds of woody biomass with [$P_{4,4,4,4}$]OH aq. solution without heating.

Hard woods (oak and eucalyptus), soft woods (pine, spruce and cedar), and ginkgo powders were individually added (5.0 wt%) to 50% [$P_{4,4,4,4}$]OH aq. solution, and the mixtures were stirred for 1 h without heating. As a result, the appearance of these mixtures were significantly changed and it strongly suggested that the 50% [$P_{4,4,4,4}$]OH aq. solution partly dissolved every woody biomass used in this study without heating (see Fig. S1). This means that the aq. solution is usable to dissolve not only herbaceous biomass and hard wood but also soft woods and other wood such as gingko. Colour and viscosity of those mixed solutions were different, thus the dissolution degree and/or dissolved components seemed to depend on the wood species.

Next, dissolution degrees of these woods were evaluated. It was obvious that the dissolution degree deeply depended on the wood species (Fig. 1). Hard woods, i.e., oak and eucalyptus
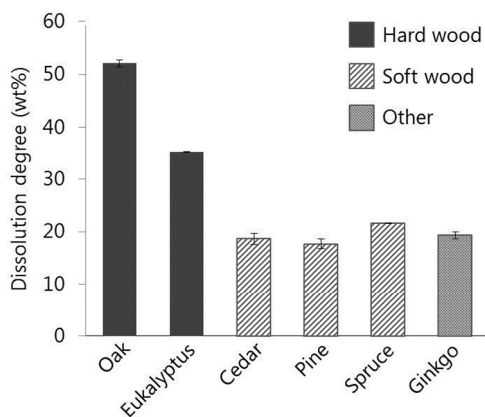
Figure 1 Dissolution degree of hard wood, soft wood, and other wood powder (5 wt%) in [$P_{4,4,4,4}$]OH (50 wt% aq. solution) for 1 h stirring at 25 °C.
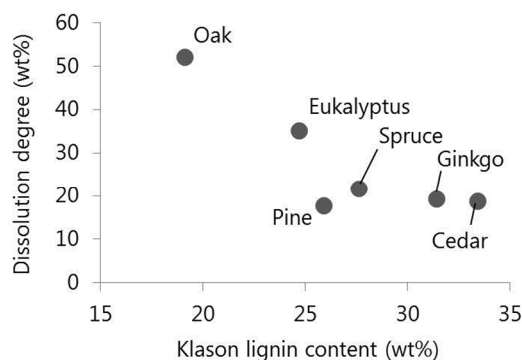

Figure 2 Correlation between dissolution degree of wood powders and their Klason lignin content.

Table 1. Dissolution degree of cedar (5 wt%) in 50% [$P_{4,4,4,4}$]OH aq. solution.

Entry	Temp. (°C)	Time (h)	Dissolution degree (wt%)
1	25	1	18 ±1
2	25	24	22 ±1
3	60	1	20 ±4
4	60	10	29 ±2
5	60	24	48 ±5

were easily dissolved and their dissolution degrees reached 52 and 35%, respectively. On the other hand, soft woods, i.e., cedar, pine, and spruce were relatively recalcitrant and their dissolution degree was around 20%. The dissolution degree of ginkgo was not so high.

The difference of these dissolution degrees should be a result from component ratio of these woody biomasses. Therefore, we analysed the correlation between woody biomass component ratio and degree of dissolution of woods after treating them with 50% [$P_{4,4,4,4}$]OH aq. solution.

Holocellulose and lignin content certainly affected the dissolution degree (see Figs. S2A and B). On the other hand, there was no relationship between dissolution degree and α-cellulose or β-, γ-cellulose content (see Figs. S2C and D). Woody biomass generally contains 2 types of lignin, i.e., acid soluble lignin and Klason lignin. Among them, the amount of acid soluble lignin did not affect the dissolution degree (see Fig. S2E). In contrast, the Klason lignin content of woody biomass had strong influence on the dissolution degree, they were negatively correlated (see Fig. 2). Acid soluble lignin has small molecular weight, and thus they are easily soluble to typical solvents. By contrast, it is known that Klason lignin has huge and complicated network structure, and accordingly it is difficult to dissolve it. These results obtained here suggest that [$P_{4,4,4,4}$]OH aq. solution do not dissolve Klason lignin well, in spite that it is a good solvent for polysaccharides. The Klason lignin should be an obstacle network for efficient dissolution of woody biomass.

Efficient dissolution of cedar

Since all woody biomasses contain a certain amount of Klason lignin, an efficient dissolving method for lignin rich wood is strongly desired. Here, we targeted cedar because of more amount of Klason lignin than others used in this study (see Fig. 2). To get protocol to dissolve cedar efficiently, we have investigated effect of (i) optimising stirring condition, (ii) additive, and (iii) their combined utilisation.

(i) Effect of stirring time and temperature First, cedar powder was added (5 wt%) in the 50% [$P_{4,4,4,4}$]OH aq. solution, and stirred gently at 25 °C. After 1 h stirring, the dissolution degree reached 18 wt% (see Table 1, entry **1**). It reached 22 wt% after 24 h stirring (see Table 1, entry **2**). This suggested that the wood dissolution was progressed in early time, and therefore stirring for longer time at 25 °C seemed to have little

effect.

Next, similar experiments were conducted at 60 °C, which is easily obtained as an exhaust heat from most factories. As a result, dissolution degree reached 20 wt% with 1h at 60 °C (see Table 1, entry **3**). The dissolution degree increased by longer stirring time and reached 29 and 48 wt% after 10 and 24 h stirring (see Table 1, entry **4**, **5**). Moderate heating (60 °C) was found to increase the dissolution degree of cedar in 50% [$P_{4,4,4,4}$]OH aq. solution. Li *et al*. reported that heating at 170 °C is needed to remove lignin layers of woody biomass with cellulose-dissolving ILs.[29] This heating is a good way to dissolve lignin and woody biomass. However, decomposition of ILs under such heating should be avoided. On the other hand, Hyväkkö *et al*. reported that 50% [$P_{4,4,4,4}$]OH aq. solution is stable at 90 °C,[30] and there is no fear of degradation at 60 °C. These results clarify that a moderate heating is effective to enhance the dissolution of wood powder. However, there are 50 wt% residues still remained even after 24 h stirring at 60 °C.

(ii) Effect of an additive   To improve the dissolution power, we have evaluated the effect of an additive. Recently, Wu *et al*. reported that hydrogen peroxide was found to be effective to decompose lignin model compound under alkaline conditions.[31] Based on this report, hydrogen peroxide aq. solution (35% H_2O_2 aq. solution) was selected as an additive. Several amount of 35% H_2O_2 aq. solution was added to 50% [$P_{4,4,4,4}$]OH aq. solution, and the mixture was examined to dissolve cedar powder at room temperature for 24 h (see Table 2, entry **6-9**). As a result, the dissolution degree reached 34 wt% when 35% H_2O_2 aq. solution was added (1.0 wt%) (see Table 2, entry **7**). Without H_2O_2, dissolution degree remained 22 wt% (see Table

Table 2 Dissolution degree of cedar in 50% [P$_{4,4,4,4}$]OH aq. solution at 25 °C with different amount of 35% H$_2$O$_2$ aq. solution.

Entry	Added 35% H$_2$O$_2$ aq. solution (wt%)	Temp. (°C)	Time (h)	Dissolution degree (wt%)
6	0.1	25	24	23 ±1
7	1	25	24	34 ±1
8	10	25	24	20 ±3
9	20	25	24	21 ±2
10	1	25	1	18 ±0.5

Table 3. Dissolution degree of cedar in 50% [P$_{4,4,4,4}$]OH aq. solution at 60 °C with different amount of 35% H$_2$O$_2$ aq. solution.

Entry	Added 35% H$_2$O$_2$ aq. solution (wt%)	Temp. (°C)	Time (h)	Dissolution degree (wt%)
11	1	60	1	25 ±3
12	5	60	1	33 ±1
13	10	60	1	25 ±2
14	15	60	1	19 ±2
15	20	60	1	19 ±1

1, entry **2**). Therefore, it was clarified that the addition of 35% H$_2$O$_2$ aq. solution facilitates the cedar dissolution without heating. However, the dissolution degree remained at 18 wt% after 1 h stirring (see Table 2, entry **10**), in other words, the effect of H$_2$O$_2$ addition was not found (see Table 1, entry **1**). Therefore, we have to conclude that the addition of 35% H$_2$O$_2$ aq. solution is not effective at 25 °C.

(iii) Optimisation of stirring condition with additive

Different amount of 35% H$_2$O$_2$ aq. solution was added to [P$_{4,4,4,4}$]OH aq. solution to examine the dissolution of cedar powder at 60 °C (see Table 3). When the added amount of 35% H$_2$O$_2$ aq. solution was small (1, 5, or 10 wt%), the dissolution degrees were relatively high (see Table 3, entry **11-13**). In spite of the use of more amount of H$_2$O$_2$ aq. solution (15 or 20 wt%), the dissolution degree remained 19 wt% (see Table 3, entry **14** and **15**). This decrease might be caused by the decrease of [P$_{4,4,4,4}$]OH concentration. When the 35% H$_2$O$_2$ aq. solution was added to 50% [P$_{4,4,4,4}$]OH aq. solution at the final concentration of 15 and 20 wt%, the final concentration of [P$_{4,4,4,4}$]OH became 42.5 and 40.0%, respectively. It is known that the polysaccharides dissolution ability in [P$_{4,4,4,4}$]OH aq. solution deeply depends on the water content, in other words, [P$_{4,4,4,4}$]OH concentration.[21]

Next, we changed the stirring time of the mixture at 60 °C. When a small amount of 35% H$_2$O$_2$ aq. solution was added to 50% [P$_{4,4,4,4}$]OH aq. solution, cedar powder was gradually dissolved in it (see Fig. 3, purple squares). Since there was a small amount of H$_2$O$_2$, lignin degradation might be the rate-determining process for cedar dissolution. On the other hand, when 35% H$_2$O$_2$ aq. solution was added to [P$_{4,4,4,4}$]OH aq. solution to become 10%, cedar was significantly dissolved (see Fig. 3, red circles). The dissolution degree reached ca. 90 wt% after 10 h stirring. After 24 h stirring, the added cedar powder was almost completely dissolved (97±0.6 wt%). This is the first report of the almost complete dissolution of wood powder at 60 °C under air pressure within 24 h without any other treatment such as microwave irradiation, ultrasound sonication, or delignification pre-treatments.

Both H$_2$O$_2$ addition and moderate heating are also effective to dissolve other biomass with lower Klason lignin content. The dissolution of oak was further accelerated by the addition of H$_2$O$_2$, and the dissolution degree reached 82±1 wt% under mild stirring for only 1 h at 60 °C.

Since lifetime of H$_2$O$_2$ is not so long, intermittent addition of H$_2$O$_2$ was considered to be effective. So the H$_2$O$_2$ aq. solution
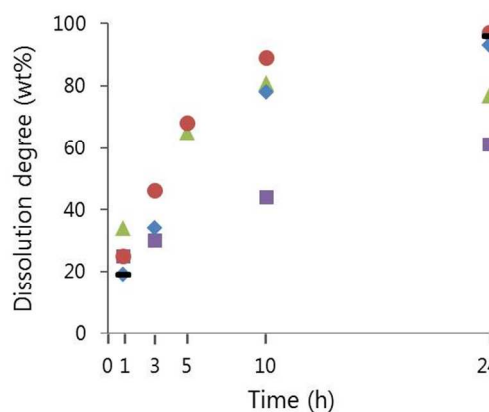

Figure 3 Dissolution degree of cedar powder in [P$_{4,4,4,4}$]OH/H$_2$O$_2$ aq. solutions at 60 °C. The added amount of 35% H$_2$O$_2$ aq. solution was 1 wt% (purple square), 5 wt% (green triangle), 10 wt% (red circle), 15 wt% (blue diamond), and 20 wt% (black bar).

was then added to 50% [P$_{4,4,4,4}$]OH aq. solution in a step-by-step manner, 1% per hour. After 10 h, the dissolution degree of cedar was evaluated (added amount of 35% H$_2$O$_2$ aq. solution was 10% in total). As a result, the dissolution degree of the added cedar was 91±0.4 wt% which is similar performance as that with 10% addition at a time. The step-by-step addition of fresh H$_2$O$_2$ did not affect the dissolution degree of cedar powder, and H$_2$O$_2$ aq. solution was considered to be consumed slowly.

Dissolution mechanism

To discuss the dissolution process, holocellulose, α-cellulose, and lignin content of the insoluble residues was analysed. Content of components were calculated based on the whole wood weight before treatment (see Fig. 4A). With treatment for a few hours, cellulose fraction was significantly decreased (see Fig. 4A, green with/without diagonal lines). In contrast, the decrease rate of Klason lignin content was not high. The amount of Klason lignin gradually decreased. The lignin component ratio decreased to about 7% on the initial whole wood basis after treatment for 10 h. The cellulose component also gradually decreased. This suggests that lignin dissolution is the rate-limiting process to dissolve cedar almost completely
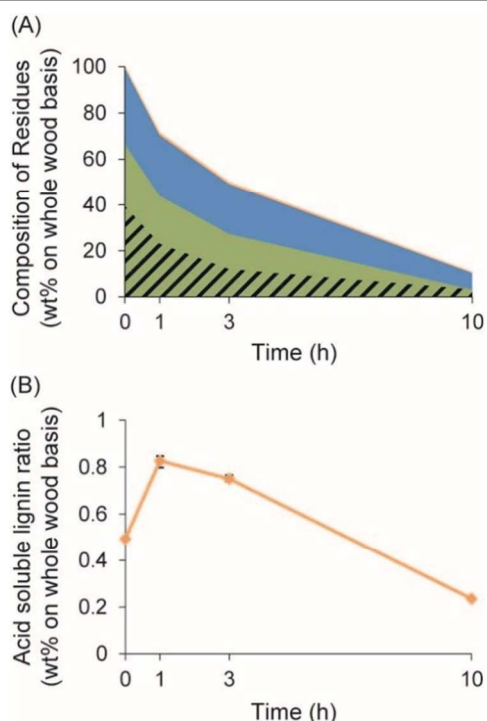
Figure 4 (A) Correlation between the composition of insoluble residues (wt% on whole wood basis) and stirring time with $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution: α-Cellulose (green with diagonal lines); β- and γ-cellulose (green without diagonal lines); Klason lignin (blue); acid soluble lignin (orange). (B) An enlarged figure of acid soluble lignin ratio (wt% on whole wood basis).

with $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution. As shown in Fig. 4B, the amount of acid soluble lignin increased unexpectedly at the first stirring process for 1 h. This should be attributed to the degradation of Klason lignin by the added H_2O_2. Wu *et al.* reported that H_2O_2 generated OH radicals in alkali aq. solutions at 60 °C, and lignin model compounds were found to be decomposed.[31] Also in $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution, OH radicals should be generated and Klason lignin was partly decomposed by the radicals, and thus degraded Klason lignin was considered to be changed into acid-soluble lignin. The unexpected increase of the amount of acid-soluble lignin was explained by this hypothesis. This lignin degradation made it easier to solubilise cellulose in this solution. Consequently, it was suggested that cedar powder was efficiently and almost completely dissolved in $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution through the partial degradation of lignin.

The OH radicals generated from H_2O_2 might also degrade the dissolved cellulose. To confirm this, molecular weight distribution (MWD) of microcrystalline cellulose (MCC) before and after treatment with $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution was evaluated as a simple model. As a result, the molecular weight of MCC was found to decrease after treatment with $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution (see Fig. 5). There was no specific peaks in the chromatogram of the treated MCC, suggesting that a random degradation of cellulose occurred in $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution at 60 °C.

This dissolution method is a promising one to dissolve woody biomass almost completely regardless of wood species. Chemical conversion and use of the dissolved component materials are the next important issues, and they are now under investigation.
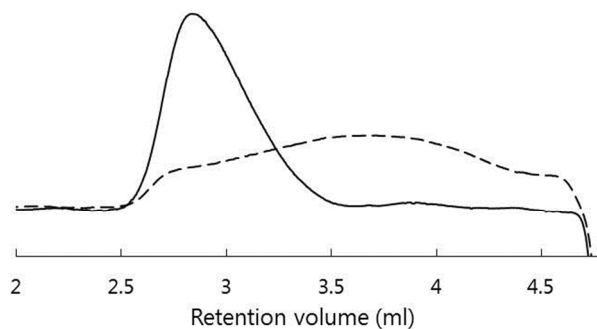

Figure 5. Molecular weight distribution of microcrystalline cellulose before (solid line) and after (dashed line) treatment with $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution at 60 °C for 24 h.

Conclusions

In this paper, several kinds of wood powders were examined to be dissolved in $[P_{4,4,4,4}]OH$ aq. solution. Since there was a negative correlation between dissolution degree and Klason lignin content of the wood samples, lignin removal is necessary to dissolve woody biomass efficiently. Moderate heating (60 °C) and addition of H_2O_2 to 50% $[P_{4,4,4,4}]OH$ aq. solution were found to be a powerful strategy to dissolve cedar which contains more amount of lignin than other wood samples examined. $[P_{4,4,4,4}]OH/H_2O_2$ aq. solution certainly dissolved 89 and 97 wt% cedar after stirring at 60 °C for 10 and 24 h, respectively.

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Notes and references

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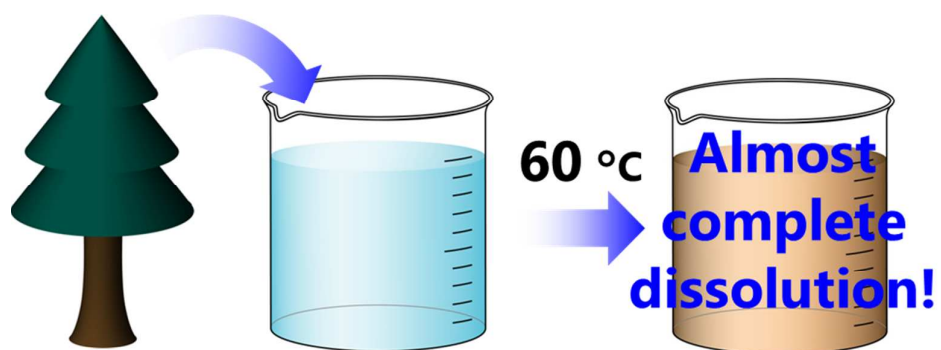
Tetra-n-butylphosphonium hydroxide aqueous solution containing hydrogen peroxide dissolved wood powder almost completely under mild stirring for 24 h at 60 °C without any pretreatment.