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ARTICLE TYPE

Dissolution of wet wood biomass without heating

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Lignocellulose biomass including wood is an abundant, natural, and renewable material, and is a promising fossil fuel substitute. However, there are still no powerful solvents to extract polysaccharides from biomass. Here we report tetra-*n*-butylphosphonium hydroxide/water mixture as a potential solvent for wood dissolution without heating. Upon gentle stirring at room temperature, this solution containing 40 wt% water extracted 37% polysaccharides after stirring for only 1 hour. This excellent dissolution ability was maintained in a wide range of water content and temperature.

Introduction

Since plants cannot escape predation by moving, many protect themselves using an armor made of high strength polymers such as cellulose which is sparingly soluble in most solvents. The only way to dissolve them is the use of enzymes such as cellulase as termites do. In spite of its insolubility, polysaccharide, which is a major component of plants, is a useful material. From the viewpoint of energy conversion, lignocellulose can be regarded as the accumulated energy from the sun. Hydrolysis of lignocelluloses yields glucose, which is also the hydrolysis product of starch. Glucose is a potential starting material for several chemicals, as well as energy. Since lignocellulose is not competing against food, it could be a suitable fossil fuel substitute.[1] The problem is its insolubility. Because of the lignin network and the strong intra- and inter-hydrogen bonding networks of cellulose,[2] effective extraction of polysaccharides has not yet been achieved. A variety of pretreatment processes of wood biomass have been reported that disrupt the cellulose structure and make it possible to use the biomass as an renewable material; these processes may be physical, biological, or chemical.[3] However, they still require a large amount of energy, multi-step, long-term treatment, and much equipment.[3]

Several solvents exist for cellulose, including NaOH/water mixture with/without additives,[4,5] *N*-methylmorpholine *N*-oxide monohydrate,[6] and a LiCl/*N*,*N*-dimethylacetamide mixture.[7-9] These solvents have disadvantages such as very limited range of conditions, toxicity, inapplicability to lignocellulose, and others. In contrast, ionic liquids are promising novel solvents for pure cellulose and lignocellulose.[10-13] Some ionic liquids have potential to dissolve cellulose. We recently reported that polar ionic liquids dissolved polysaccharides, and we also successfully extracted them from plant biomass without heating.[14] These cellulose-dissolving ionic liquids suffer from a drastic decrease of cellulose solubility with increasing water content.[15,16] Since polar ionic liquids are highly hygroscopic, like polar molecules, they readily absorb water from the atmosphere.[17] 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 lignocellulosic biomass. There is a strong request to design new system without drying processes.

Recently, hydroxide solutions that have organic cations with/without additives are illuminated as novel solvents for cellulose.[18,19] Especially, tetra-*n*-butylphosphonium hydroxide (TBPH) has a strong proton accepting ability even in the presence of water.[18] Here we report on wood biomass treatment without heating using TBPH containing water. This solvent successfully extracted polysaccharides without heating nor biomass drying.

Experimental

Materials

TBPH containing 60 wt% water was provided by Hokko Chemical Industry Co. Ltd., and TBPH/water mixtures were prepared with evaporation or addition of water. Wood disks (34 mm in diameter and 1 mm in thickness) and poplar powder (36-200 mesh) were provided from Forestry and Forest Products Research Institute. Methanol (>99.8%) was purchased from Kanto Chemical Co. Ltd.

Poplar dissolution test

Poplar powder was preliminarily dried under vacuum for 6 hours at room temperature before use (water content was about 1 %). The water content of poplar powder was measured with thermogravimetric analysis (TGA). The TGA measurements were performed using a SEIKO TG/DTA 220 instrument with a heating rate of 10 ºC min^{-1} from 25 to 110 ºC under nitrogen gas. After 30 min holding at 110 ºC, the weight loss was detected as the water content of the sample. TBPH solutions (9.5 g) that containing different amount of water were put in 30 ml vial, and the dried poplar powder (0.5 g) was added (Scheme S1 in Electronic Supplementary Information, ESI). The mixture of TBPH solution and poplar powder was gently stirred (300 rpm) at

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25 °C. After that, the residue was separated by centrifugation. The collected supernatant solution containing poplar-exctracts was stirred vigorously, and methanol was put in it to precipitate the extracted materials from poplar. After washing, the dried weight of the precipitated materials was evaluated, and the extraction rate was determined with the following equation.

$$\text{Extraction rate (\%)} = (9.5 \times Y) / \{0.5 \times (X - Y)\} \times 100$$

where X is the weight of the poplar dissolving TBPH (g) and Y is the weight of the extracted material (g), and the number 9.5 and 0.5 is the initial weight of TBPH aqueous solution and poplar powder, respectively.

Results and discussion

Dissolution of wood disks without heating

Pine, cedar, and poplar were used as typical types of wood. Samples were cut into disks with diameter of 34 mm and thickness of 1 mm. TBPH containing 40 wt% water was used as a solvent because this water content is the best for dissolving pure cellulose.[18] These disks were put in the TBPH solution (15 g), and changes in their shape were observed visually without stirring at room temperature. Every wood disk became swollen and distorted, and gradually broken up; in particular, the pine disk was fragmented easier than other disks (Figure 1). These results indicate that TBPH solution is powerful to extract constituents in wood biomass by simply soaking without heating. The changes of shape in the small scale were tracked by using wood powder and optical microscopy. The results are summarised in ESI (Figure S1).

Effect of water content on the dissolution of wood powder

Dissolution tests of wood samples were conducted in TBPH solutions containing different amount of water. As poplar is a typical hard wood and is often used as a standard wood sample, the poplar wood powder was used as a standard biomass sample below. The material extracted from poplar powder is a mixture of polysaccharides. Precise analysis of the ratio of components is set out in a latter section. Table 1 summarises the extraction degree of wood components after stirring for 1 hour. The degree of extraction increased with increasing water content in the TBPH from 30 to 50 wt%, but that with 70 wt% water could extract only 4.9% of the polysaccharides, since the solubility of cellulose had dropped at that water content. TBPH containing 40-50 wt% water successfully extracted 36-37% polysaccharides

Table 1 Effect of water content of TBPH on the degree of polysaccharide extraction after 1 hour stirring

Water content of TBPH (wt%)	Extraction degree (%)[a]
70	4.9
60	28
50	36
40	37
30	24

[a] Weight percent relative to added poplar and the poplar powder was added at a final concentration of 5 wt% relative to TBPH solution.

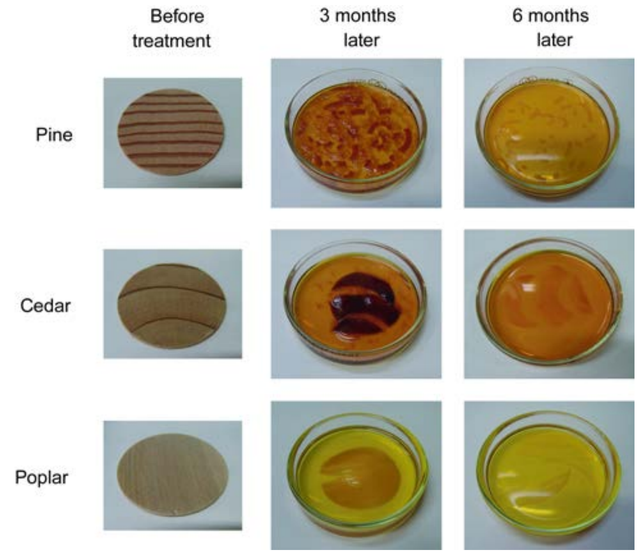

Fig. 1 Changes in shape of wood disks in TBPH containing 40 wt% water. Wood disks (diameter 34 mm, thickness 1 mm, about 0.5 g) were soaked in TBPH containing 40 wt% water (15 g) without heating or stirring.

from the poplar powder. TBPH containing 30 wt% water extracted 24% polysaccharides within 1 hour. TBPH containing 40-50 wt% water was concluded to be the best for extracting polysaccharides from wood powder at room temperature.

Wet biomass treatment

TBPH solution has advantage in the presence of some water, unlike other cellulose-dissolving ionic liquids. In this section, we evaluated the ability of the TBPH solution to extract polysaccharides from wet wood biomass. In the previous section, the poplar was dried in advance under vacuum, and the water content of the wood was reduced to about 1%. Of course, natural wood contains more water. Consequently, we have challenged to extract polysaccharides from air-dried wood. The poplar powder was dried naturally by standing at room temperature, and the water content of the wood fell down to 7.5% (7.5 g of water against 100 g of dried wood, details are described in ESI). Water was added to the poplar powder (20% relative to the weight of the dried poplar) and the mixture was stirred to make it homogeneous. It was then left at room temperature for 3 days. The extraction degree of polysaccharides from the air-dried poplar using TBPH containing 40 wt% water was then determined. The added poplar was 5 wt% at a final concentration (as a dried weight). The TBPH solution extracted 41% polysaccharides from the air-dried poplar, even though only 37% was extracted from well dried poplar. This difference was considered not just an experimental error, because the value of experimental error of the extraction degrees was about 2-3%. Spinu *et al*. reported that wet biomass was hydrated easier than dried biomass in an aqueous salt solution.[20] Similar hydration might occur in the case of TBPH solution with air-dried poplar (not the vacuum-dried specimen). This finding shows that it is not necessary to dry wood to extract

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polysaccharides. Air-drying is sufficient in the case of treatment with TBPH solutions.

Air-drying is an easy pre-treatment. However, natural plant biomass contains considerable amount of water in it, the air-drying needs time. We therefore evaluated the capability of TBPH solution to treat "wet" biomass without any pre-treatment even air-drying. Water was added to the poplar powder (200% relative to the weight of the dried poplar, i.e., 20 g of water was added to 10 g of dried wood powder) and the mixture was stirred to make it homogeneous. Thus prepared wet wood was then added to TBPH containing 40 wt% water so as to make 5 wt% relative to the TBPH solution (at final concentration, as a dried weight). After 1 hour stirring, TBPH containing 40 wt% water was found to extract 32% polysaccharides from the added wet poplar.

In spite of ion penetration effect in the wet wood biomass, the extraction degree of polysaccharide decreased. It might be caused by (i) the decrease of basicity of the solution.

The water content of TBPH solution was changed by the addition of wet wood biomass, and it might decrease the hydrogen bonding basicity of the TBPH solution. Since there was the water content dependence of the polysaccharide extraction as mentioned above, we calculated the water content of TBPH solution after addition of wet wood biomass. In this paper, 1.5 g of wet poplar (mixture of 0.5 g poplar and 1.0 g water) was added to 9.5 g of TBPH solution (5.7 g TBPH and 3.8 g water). Therefore the water content of the TBPH solution should be changed from 40 wt% to 45.7 wt% after addition of the wet poplar. This TBPH solution was expected to have ability to extract polysaccharides, because TBPH solutions containing both 40 and 50 wt% water have potential as summarised in Table 1. Accordingly, it should be mentioned here that this water-containing TBPH is effective to extract polysaccharides from wood powder unless adding large excess amount of wet powder.

In this experiment, we evaluated the polysaccharide extraction degree with only 1 hour stirring. Thus the difference of the dispersibility may also affect the extraction degree. Extraction degree will be improved with time.

Auto recovery of water content

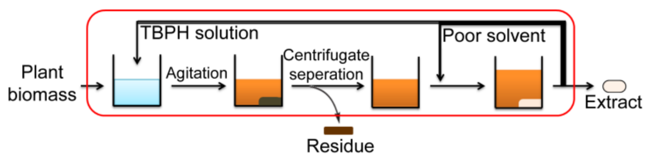
TBPH containing water dissolves and extracts polysaccharides even from wet wood biomass. However, this wet biomass treatment may lead to increasing water content in the TBPH solution. As the ability of TBPH solution to treat biomass was weakened by increasing water content above 70 wt%, the TBPH solution should be concentrated to recover extraction ability of polysaccharides from wet biomass. The process of concentration, by heating or decompression, for example, requires energy and therefore increases the energy cost of the overall process of wood biomass treatment. An energy-saving concentrating process of TBPH solution would therefore be helpful.

Fresh TBPH solution used in this paper contains 60 wt% water. This solution was left open to the atmosphere without heating or stirring, and the change in water concentration was traced with time (25 ºC, humidity: 45%). The water content was found to fell down to about 45 wt% after a week (Figure S2). This result suggests that TBPH solution can easily be concentrated again automatically without any energy consumption. Although ionic liquids are potential solvents for biomass treatment, their polysaccharide-extracting ability is significantly dropped by water addition and they also easily absorb water from air,[17] the polysaccharide-extraction requires drying of both themselves and biomass. In contrast, TBPH solution is automatically concentrated even under open air.

These findings for wet biomass treatment and auto recovery suggest a save energy recycling system for treating biomass as depicted in Scheme 1. The plant biomass will be separated into residues and extracted by adding poor solvent. After that, the filtrate will be re-concentrated with time when water was used as a poor solvent. However, there are a few more steps to realize recycling because of fear of effect of impurities and others

Effect of time on the degree of extraction

It is empirically comprehensible that the stirring time is another important factor for the extraction degree. Poplar powder containing 1% water was added to TBPH containing 30-70 wt% water, and the mixture was stirred for up to 24 hours at room temperature. The results are summarised in Figure 2. When the TBPH contained a large amount of water, the extraction degree of polysaccharide was low (see Table 1. TBPH containing 70 wt% water could extract only 5.7% of polysaccharides even after 24 hours stirring. On the other hand, TBPH containing 40 wt% water extracted polysaccharides more than 50 wt% after mixing them for 24 hours. The extent of polysaccharide extraction with TBPH containing 40 or 50 wt% water and 24 hours stirring reached 59% or 44%, respectively. Furthermore, the value with TBPH containing 30 wt% water reached 62% after 24 hours stirring. This should be due to high concentration of hydroxide



Scheme 1 A proposed procedure for plant biomass treatment with TBPH solution.

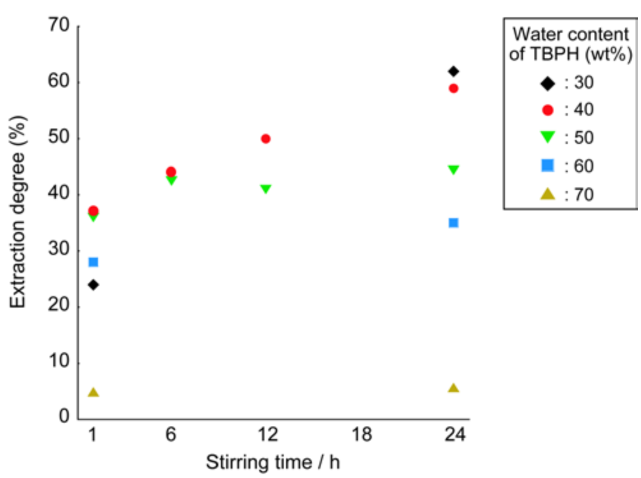


Fig. 2 Effect of stirring time for polysaccharide extraction. The extraction degree is in wt% relative to the added poplar.

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anions. A certain amount of water is known to be needed to suppress decomposition of TBPH.[18] On the other hand, more amount of water than 70% lowered the extraction ability of the TBPH solution. Considering both the stability of the TBPH aqueous solution and the extraction performance, TBPH containing 40 wt% water is proposed to be the best medium for treating wood biomass.

Selective extraction of polysaccharides

Here we have analysed the component ratio of the extracted material. After 1 hour treatment of poplar powder with TBPH containing 40 wt% water, the extracted material was analysed by a standard sugar analysis (Figure 3 and Table S1).[21] The extract was found to be consisted mainly of polysaccharides such as cellulose (glucan) and xylan. Acordingly, lignin was found in mostly in the residue than the extract. It was confirmed that cellulose was extracted easier than xylan when TBPH solution containing 40 wt% water was used as a solvent.

However, solubility of these components should not be the same in the TBPH with different amount of water. Then, selective extraction of polysaccharides was examined by changing water content of the TBPH.

We found that the power of TBPH solutions to dissolve xylan was the function of the water content of the TBPH. Commercially available xylan from beechwood was added to several TBPH solutions with different water content and stirred at 25 °C. The best concentration of TBPH for dissolving xylan was not the same as that for cellulose (Table S2). TBPH containing 30 wt% water did not dissolve xylan powder. That with 40 wt% water dissolved only a small amount of xylan. On the other hand, xylan was rapidly dissolved in TBPH containing 50 wt% or more amount of water. TBPH containing larger amounts of water should therefore dissolve xylan more efficiently than cellulose. These results suggested that xylan-rich materials should be extracted from lignocellulose simply by controlling the water content of the TBPH solutions. This should be useful to design not only extraction solvent but also poor solvent.

We then examined the extraction of xylan-rich materials from wood. Poplar was treated with TBPH containing 70 wt% water, and the components of the extracted material were investigated with sugar analysis. When TBPH containing 40 wt% water was used to treat poplar material, the main component of the extract was cellulose (Figure 4A, based on the same data as shown in Figure 3; the width of each bar related to the amount of the material extracted). In contrast, TBPH containing 70 wt% water successfully extracted xylan-rich materials from poplar, and the xylan content exceeds 50% (Figure 4B; again the width of the bar

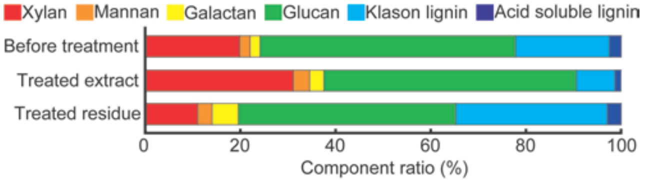

Fig. 3 Component ratio of intact poplar, extract, and residues treated with TBPH containing 40 wt% water for 1 hour. The value of the glucan ratio essentially indicates the amount of cellulose.

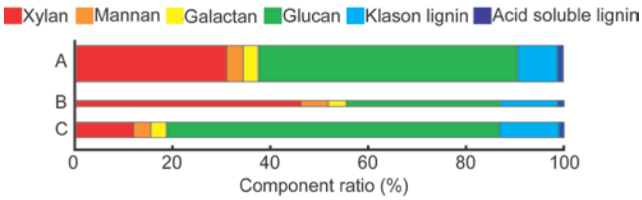

Fig. 4 Component ratio of extracts. The materials were extracted from poplar that had been treated with TBPH containing 40 wt% water (A) or 70 wt% water (B) with 1 hour stirring, and the precipitated materials which was precipitated by adding excess water to the TBPH solution containing both 40 wt% water and extracts from poplar (C).

indicates the amount of material extracted (4.24%), Table S3). We also made FT-IR and ^{13}C-NMR measurements to analyse the components of the extracted materials. These results also suggested that the extract was the xylan-rich material (Figure S3). The amount of extracted material was 4.24% and it is less than that using TBPH containing 40 wt% water (37.0%), but it was clarified that TBPH containing 70 wt% water dissolves and extracts xylan-rich materials easily.

We also proposed a simple process for obtaining cellulose-rich materials selectively with the effective use of water. We have studied the precipitation characteristics of cellulose and xylan from TBPH solutions. When water was added to TBPH solutions containing both cellulose and xylan, cellulose was selectively precipitated from the solution (Table S4). Based on these results, we have studied the selective precipitation capability of cellulose from poplar-dissolving TBPH solution. After dissolution of poplar in the TBPH containing 40 wt% water, an excess amount of water was added to the solution. The precipitated materials were collected after washing, and the component ratio was analysed using sugar analysis method (Figure 4C; the width of the bar indicates the amount of material extracted (14.4%) and Table S3), as well as FT-IR and ^{13}C-NMR measurements (Figure S4). The results indicated that the precipitated material comprises cellulose-rich polysaccharides. This tells us that cellulose-rich compounds are collected as precipitates selectively from TBPH solution which has dissolved poplar, simply by using water as a poor solvent.

Component ratio of extracts from poplar has been found to be controlled easily by the aid of water. Cellulose-rich materials and xylan-rich materials can be extracted preferentially from wood by using both TBPH solution and suitable poor solvent, such as water. Since these selective collection processes do not require any complex or energy-dependent processes such as heating, cooling, or explosions, they may become important methods to get polysaccharides in diverse fields.

Conclusions

We have proposed a novel treatment process for wood using TBPH solution. Using this solvent, much polysaccharide is extracted from poplar within a short period of time without heating or cooling. This solvent extracts a certain quantity of polysaccharides from wood biomass even in the wet condition (e.g., containing 200% water). Component ratio of extracts from poplar is controlled easily by the amount of water.

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† Electronic Supplementary Information (ESI) available: Oprical micrographs of poplar in TBPH solution, poplar powder dissolution test, auto recovery of water content, xylan dissolution test, xylan rich material extraction from wood, polysaccharides precipitation test, and cellulose rich material extraction from wood, including FT-IR and ^{13}C-NMR spectra. See DOI: 10.1039/b000000x/

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