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Electronic Supplementary Information

# Dissolution of wet wood biomass without heating

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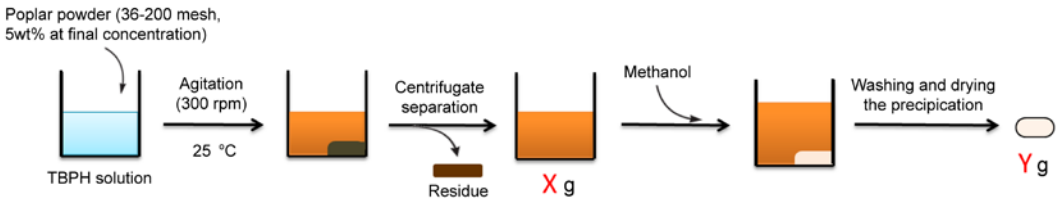
**Poplar dissolution test**

Extraction rate was calculated by

Extraction rate (%) = (9.5 × Y) / {0.5 × (X – Y)} × 100

where X is the weight of the poplar dissolving TBPH solution (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. The dried weight was determined after drying under vacuum for 6 hours at 25 ºC. The water content of the extracted materials was measured with thermogravimetric analysis (TGA). 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 water content of the sample. As a result, extracts contained about 0.5-1 wt% water in it.




**Scheme S1** Procedure of the poplar dissolution test. The weights of the poplar dissolving TBPH (X g) and the extracted material (Y g) were used to determine the extraction rate.

**Optical micrographs of poplar in TBPH solution**

Shape changing of the added poplar was observed through an optical microscope. These micrographs show that the complicated and recalcitrant fibrils were gradually unbraided in TBPH solution without heating. Although the poplar particles and TBPH solution are difficult to diffuse between the slide- and cover-glass, the solution sank into the wood particles within 10 minutes. In addition, after 24 hours, the recalcitrant particles were significantly swelled without stirring or heating. This suggests that TBPH solution has an excellent ability to treat wood biomass with only soaking at room temperature.


**Fig. S1** Optical micrographs of poplar in TBPH containing 40 wt% water. Each picture shows a poplar particle of 30 seconds (A), 10 minutes (B), or 24 hours (C) after the addition of TBPH solution.

**Water content of wood biomass**

In this paper, two types of water content are used for solutions (A) and wood biomass (B). These "water content" have different meanings. On solutions (A), 100 wt% represent overall weight of the solution, therefore "the water content of the solution is 100 wt%" means that "It is pure water." On the other hand, on wood biomass (B), 100 wt% represent the weight of the dried biomass. Hence, "the biomass contains 100 wt% water" means that the biomass has the equal amount of water as dried weight of the biomass (dried biomass/water = 1). Although it is very confusable, they are popular representation in each area.

**Auto recovery of water content**

TBPH containing 60 wt% water (20 ml) was put in a 50 ml beaker, and it was placed in laboratory at 25 °C without cap. The humidity of the room was kept at 45%. The water content of the TBPH solution was measured at specified time intervals by using Karl-Fischer titration method.

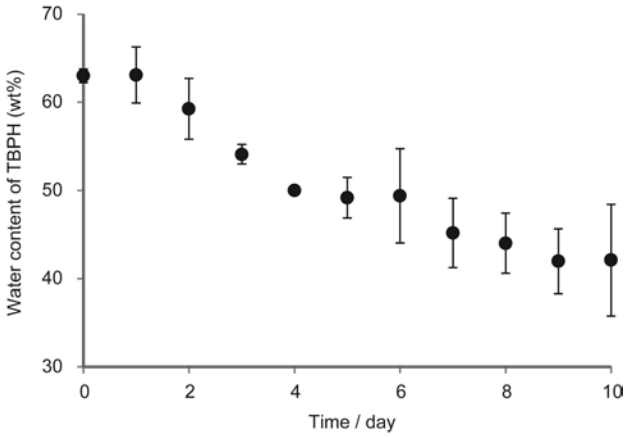



**Fig. S2** Water content transition of TBPH solution. The solution was placed quietly in a room at 25 °C.

**Sugar analysis of poplar, extract and residue**

**Table S1** Components of treated poplar woods. Sugar analysis was undertaken for poplar woods before and after treatment with TBPH containing 40 wt% water for 1 hour and also for the extract from poplar. The value of the glucan ratio essentially indicates the amount of cellulose.

| | Xylan | Mannan | Galactan | Glucan | Klason lignin | Acid soluble lignin |
|---|---|---|---|---|---|---|
| Before treatment | 19.8 | 2.17 | 2.08 | 53.8 | 19.7 | 2.51 |
| Treated extract | 30.9 | 3.50 | 2.99 | 53.1 | 8.18 | 1.25 |
| Treated residue | 10.9 | 3.00 | 5.48 | 45.8 | 31.9 | 2.94 |

**Xylan dissolution test**

Xylan from beechwood was purchased from Tokyo Chemical Industry Co., Ltd., and it was sieved and collected as the uniform powder (75-100 μm). The xylan powder was put in TBPH solutions, which contains several amount of water, to become 3 wt% at final concentration. The mixture was stirred for 30 minutes at 25 °C and the turbidity change was measured with visual observation (Table S2).

**Table S2** Correlation between water content of TBPH and xylan dissolution.

| Water content of TBPH (wt%) | Xylan state |
|---|---|
| 90-50 | Dissolved |
| 40 | Partially dissolved[a] |
| 30 | Almost insoluble[b] |

[a] The turbidity of the mixture was slightly decreased after 24 h.

[b] The turbidity changing of the mixture was not observed.

**Sugar analysis of extracts from poplar in several conditions**

**Table S3** Component ratio of extracts. The materials were extracted from poplar that had been treated with TBPH containing 40 wt% or 70 wt% water with 1 hour stirring, and the precipitated materials which was extracted by adding water to the solution of TBPH containing 40 wt% water that dissolved poplar.

| water content of TBPH solution | Poor solvent | Xylan | Mannan | Galactan | Glucan | Klason lignin | Acid soluble lignin |
|---|---|---|---|---|---|---|---|
| 40 | methanol | 30.9 | 3.50 | 2.99 | 53.1 | 8.18 | 1.25 |
| 70 | methanol | 46.2 | 5.47 | 3.72 | 31.6 | 11.7 | 1.31 |
| 40 | water | 11.9 | 3.54 | 3.11 | 68.3 | 12.1 | 1.10 |

**Xylan-rich material extraction from wood**

Poplar was treated with TBPH containing 70 wt% water for 1 h at 25 °C as similar to TBPH containing 40 wt% water. After the poplar dissolving treatment by using TBPH containing 70 wt% water, the residue was separated with centrifugation. After that, the poplar dissolving TBPH was diluted with about 10 times its mass methanol to precipitate the dissolved material. The precipitated material was collected with filtration and washed several times with methanol. The chemical structure of the extracted material was investigated with FT-IR measurements. Infrared spectra were obtained with fourier transform infrared spectroscopy (FT/IR-4200, JASCO) using KBr pellets. The absorption at 1046 $cm^{-1}$ is attributed to the C-C, C-O stretching or C-OH bending in hemicelluloses.[1,2] Xylan also show the similar absorption at 1045 $cm^{-1}$. By contrast, cellulose absorbed at 1066 and 1025 $cm^{-1}$, instead of 1045 $cm^{-1}$. This result suggests that the main component of the extract from poplar is hemicellulose such as xylan. $^{13}$C-NMR measurements were conducted at 140 °C on a α-400 (JEOL). The extract was dissolved in an ionic liquid 1-ethyl-3-methylimidazolium methylphosphonate (2 wt% at final concentration) and DMSO-d6 containing TMS in a capillary was used as external reference (double-chamber NMR tube). A total of 15,000 scans were collected in all cases. In the case of cellulose, the signals at 102.7, 79.5, 74.5 and 60.6 ppm corresponding to C-1, C-4, C-2 and C-6 carbons were observed.[3] The signals around 76.5 ppm were unclear and difficult to separate, but it is known that the signals of C-5 and C-3 appeared close to each other. On the other hand, the signals at 102.1, 76.2, 74.7, 73.9, and 63.5 ppm corresponding to C-1, C-4, C-3, C-2, and C-5 carbons were observed in the case of xylan.[1] Although the signals in the case of the extract were unclear, the existence of the signal at 63.0 ppm and the absence of the signal at 79.5 ppm mean that the extract was xylan-rich material.

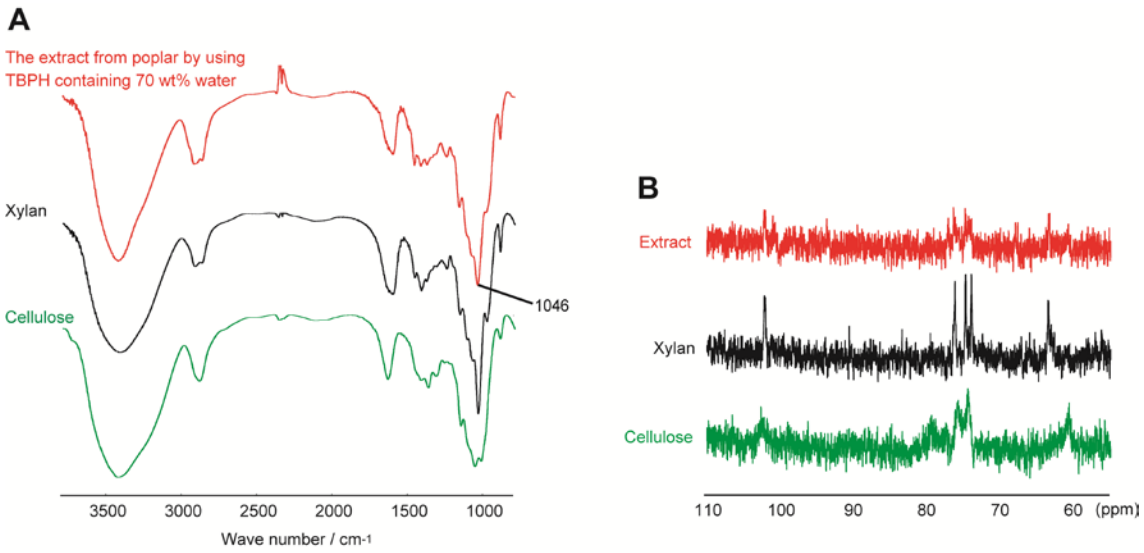



**Fig. S3** Characterization of the extracted material from poplar by using TBPH containing 70 wt% water. The spectra of xylan and cellulose are shown as a reference. (A) FT-IR spectra of the extracted material from poplar and polysaccharides. (B) $^{13}$C-NMR spectra of the extract from poplar.

**Polysaccharides precipitation test**

Cellulose and xylan powder were put in TBPH containing 40 wt% water to become 3 wt% at final concentration. The mixture was stirred for 30 min at 25 °C. After that, poor solvents, methanol or water was added to the polysaccharide solutions. We determined the minimum quantity of poor solvent to precipitate the dissolved polysaccharides by investigation of the turbidity change measured with visual observation.

**Table S4** Necessary quantity of poor solvents to precipitate the dissolved polysaccharides.

| Polysaccharides | Poor solvents / TBPH aq. (vol/vol) | |
|---|---|---|
| | Methanol | Water |
| Cellulose | 0.7 | >5 |
| Xylan | 1 | >200 |

**Cellulose-rich material extraction from wood**

Poplar was treated with TBPH containing 40 wt% water for 1 h at 25 °C. After the poplar dissolving treatment, the residue was separated with centrifugation. After that, the poplar dissolving TBPH was diluted with about 10 times its mass water instead of methanol to precipitate the dissolved material. The precipitated material was collected with filtration and washed several times with water. The chemical structure of the extracted material was investigated with FT-IR measurements. FT-IR measurements were conducted by using KBr pellets. The absorption at 1062 and 1024 $cm^{-1}$ are associated to the typical of cellulose.[2] By contrast, xylan absorbed at 1045 $cm^{-1}$ which is attributed to the C-C, C-O stretching or C-OH bending in hemicelluloses.[1,2] This result suggests that the main component of the precipitated material by water addition from poplar dissolving TBPH is cellulose. $^{13}$C-NMR measurements were conducted at 140 °C on a α-400 (JEOL). The extract was dissolved in an ionic liquid 1-ethyl-3-methylimidazolium methylphosphonate (2 wt% at final concentration) and DMSO-d6 containing TMS in a capillary was used as external reference (double-chamber NMR tube). In the spectrum of the precipitated material, signals at 79.0, 76-74.5 and 61.0 ppm corresponding to C-1, C-5, C-3, C-2, and C-6 carbons of cellulose were observed. On the other hand, a signal at 63.0 ppm corresponding to C-5 of xylan also observed, but the signal peak was weak a little. This means that the precipitate was not pure cellulose, but cellulose-rich material.

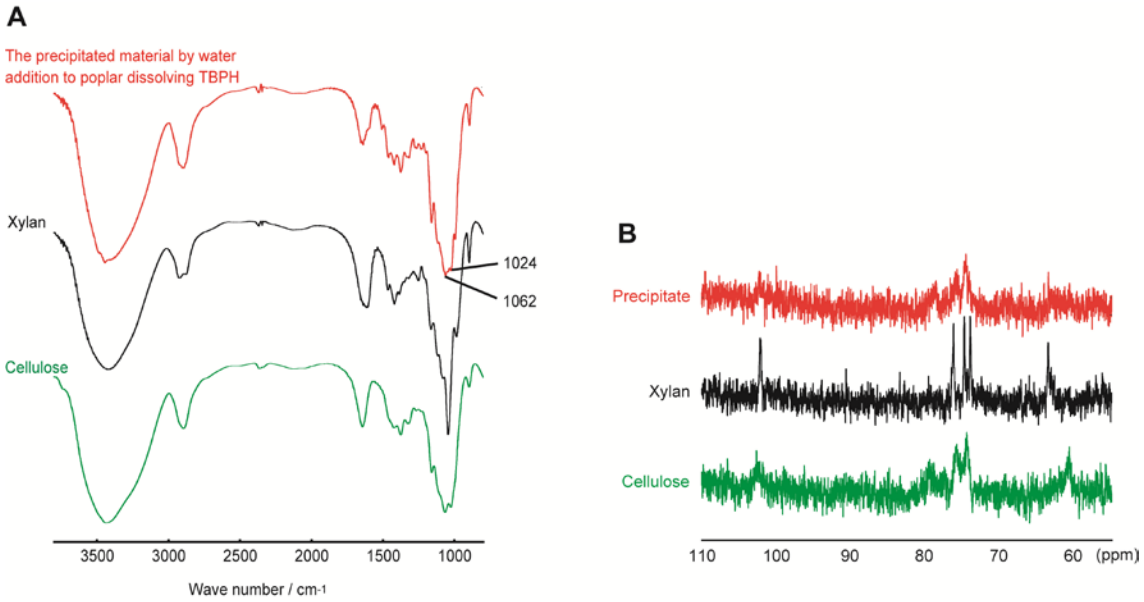



**Fig. S4** Characterization of the precipitated material by water addition to popla dissolving TBPH that contains 40 wt% water. The data of xylan and cellulose are shown as a reference. (A) FT-IR spectra of the extracted material from poplar and polysaccharides. (B) $^{13}$C-NMR spectra of the extract from poplar.

## Reference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