

Complete Dissolution of Woody Biomass Using an Ionic Liquid

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Birch wood meal was added to the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim][OAc])/dimethyl sulfoxide (DMSO) to investigate the conditions required for the complete dissolution of the lignocellulose. Cellulose was treated with [Emim][OAc], and its molecular weight distribution was analyzed by size exclusion chromatography as a model compound. The solubilities of lignocellulose were compared under different treatment conditions, such as the ball-milling time of the raw material and the temperature of the [Emim][OAc]/DMSO treatment. The insoluble fraction was analyzed by pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) to investigate the lignin structure. Cellulose treated with [Emim][OAc] under a nitrogen atmosphere for 1 to 12 h was remarkably depolymerized. It was demonstrated that lignocellulose is easily dissolved when the temperature of [Emim][OAc]/DMSO and the ball-milling times of lignocellulose are increased; a ball-milled sample was completely dissolved in the ionic liquid. The well-dissolved sample had a low cellulose molecular weight. Ball-milling reduced the primary particle size of the sample and facilitated the dissolution and extraction of guaiacyl lignin units.

Keywords: Dissolution; Lignocellulose; Ionic liquid; Ball-milling; Molecular weight; Cellulose; Lignin

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INTRODUCTION

Lignocelluloses, which include woody biomasses, are an earth-abundant resource and one of the most recycled materials; they can be converted into various chemicals to replace petroleum-based resources. Effective uses of lignocellulose make wood highly valuable. The components of lignocellulose are mainly cellulose, hemicelluloses, and lignin. Cellulose, which is a major component of lignocellulose, has been used in the fiber, membrane, paper, and medical industries. Recently, other components of lignocellulose, such as lignin, have been investigated for their potential uses as chemical raw materials (Funaoka and Abe 1989; Nge *et al.* 2016). However, the efficient utilization of these components is difficult to achieve due to their complex structures.

The dissolution of lignocellulose has been suggested as a way to exploit all of its components (Chen *et al.* 2017a; Miao *et al.* 2017). Wood dissolution could allow the molding of woody materials directly. Also, dissolution could facilitate the separation of the individual constituents. In recent years, ionic liquids have attracted much research attention as a new solvent for lignocellulose; Swatloski *et al.* (2002) reported that these liquids could dissolve cellulose. Ionic liquid is a generic term for a salt with a melting point under 100 °C. It has many applications in a variety of areas involved with chemistry, physics, biology, and engineering (Wang *et al.* 2017).

The use of ionic liquids in the biomass field has been widely investigated. Fort *et al.* (2007) and Kilpeläinen *et al.* (2007) attempted to dissolve lignocelluloses by using ionic liquids, which included 1-*n*-butyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, and 1-allyl-3-methylimidazolium chloride ([Amim][Cl]). However, these ionic liquids only partially dissolve the lignocellulose, and their solutions are hazy, which suggests incomplete lignocellulose dissolution. Ball-milling is a noteworthy treatment that can promote the complete dissolution of a lignocellulose sample. For example, Lu and Ralph (2003) dissolved ball-milled cell wall materials of plants in dimethyl sulfoxide (DMSO) and *N*-methylimidazole at room temperature within 3 h. Qu *et al.* (2013) reported that fir wood, which was milled in a planetary mono ball mill for 8 h under an argon atmosphere, could be completely dissolved in [Amim][Cl] at room temperature with a co-solvent such as *N,N*-dimethylacetamide or pyridine. Zhu *et al.* (2016) succeeded in dissolving lignocellulose without using any organic solvent; the authors completely dissolved Masson pine (that was ball-milled) in aqueous NaOH solution at room temperature. When dissolving lignocellulose without ball-milling, it is necessary to heat the ionic liquid. For example, Sun *et al.* (2009) reported that both southern yellow pine and red oak could be completely dissolved in [Emim][OAc] at 110 °C after 16 h of treatment. Miao *et al.* (2017) achieved the complete dissolution of southern yellow pine wood by using tetrabutylammonium acetate with DMSO. Hence, some structural modification treatments, such as ball-milling of the samples or heating the solvent solutions to high temperatures, are critical for the complete dissolution of lignocellulose.

The complete dissolution of lignocellulose is the key to effectively utilizing this bioresource. In this study, the conditions required for the complete dissolution of lignocellulose in an ionic liquid were investigated. First, pure cellulose samples were treated with the ionic liquid, and their molecular weight distributions were determined compared to appropriate polymer standards of known molecular weights. Next, the solubility of lignocellulose was examined under different treatment conditions, such as the temperature of the ionic liquid and the ball-milling time of the raw material. The factors that altered the solubility of the lignocellulose are discussed.

EXPERIMENTAL

Materials

For this study, α -cellulose and lignocellulose were needed. α -Cellulose was purchased from Nacalai Tesque Inc. (Kyoto, Japan). The lignocellulose sample used was a birch (*Betula platyphylla*) wood powder (< 80-mesh). The wood powder was extracted with alcohol/benzene and was air-dried prior to use. It contained 22.7 % of acid-insoluble lignin and 2.2 % of acid-soluble lignin. The extracted wood powder (2.0 g) was milled in a Retsch PM100 planetary ball mill (Retsch GmbH, Düsseldorf, Germany). A stainless bowl (50 mL) with 15 stainless balls (1-cm diameter) was used for the milling. The milling rotation was set to 400 rpm. The wood powders were repeatedly milled for 5 min at 5 min intervals over the total milling time. The milled wood powders were divided into four different samples depending on the total milling time; samples milled for 2, 6, 12, and 24 h were denoted as “Ball-mill_2 h”, “Ball-mill_6 h”, “Ball-mill_12 h”, and “Ball-mill_24 h”, respectively.

Methods

Changes in molecular weight distribution of α -cellulose

1-Ethyl-3-methylimidazolium acetate (0.30 g) ([Emim][OAc] ionic liquid) and α -cellulose (0.01 g) were added to a test tube. The test tube was heated to 120 °C and was gently stirred under a nitrogen atmosphere. Afterwards, 10 mM LiBr (in DMSO) was added to the test tube. The solutions, which were treated for different reaction times (1, 2, 12, 24, and 48 h), were filtered for analysis with size exclusion chromatography with refractive index detection (SEC/RI) to observe how the reactions differed with respect to treatment time. The SEC/RI system (LC-10 system; Shimadzu Corp., Kyoto, Japan) consisted of a guard column and SEC column (Shodex SB-806M HQ; Showa Denko, Tokyo, Japan); the system used 10 mM LiBr (in DMSO) as the eluent. A calibration curve for the molecular weight (M_w) determination of cellulose was obtained from the retention times of pullulan polymer standards (M_w of 788000, 404000, 212000, 112000, 47300, 22800, 11800, and 5900), as well as maltoheptaose (M_w of 1153), maltotriose (M_w of 504.44), maltose-hydrate (M_w of 360.32), and D-(+)-glucose (M_w of 180.16).

Solubility of lignocellulose (ball-milled wood)

1-Ethyl-3-methylimidazolium acetate (1.0 g), DMSO (2.5 g), and lignocellulose samples (0.01 g) that were milled for different times, as well as a non-milled sample (raw sample), were added to test tubes. The test tubes were heated to 30, 80, or 120 °C and were gently stirred under a nitrogen atmosphere. After 24 h reaction time, the solutions were filtered through a glass filter (1G3), and the retained residuals were washed with DMSO and distilled water. The retained residues were oven-dried at 105 °C. The solubility of the lignocellulose in [Emim][OAc]/DMSO was calculated according to Eq. 1,

$$\text{Solubility (\%)} = 100 \times (Dry - I)/Dry \quad (1)$$

where *Dry* is the mass of the oven-dried sample (g), and *I* is the mass of the insoluble fraction (g).

Particle size distribution measurement of ball-milled wood

The particle size distribution of the ball-milled lignocellulose was measured to determine the correlation between the particle sizes and the sample's solubility. The particle sizes were measured using a Microtrac MT-3300 EX II laser diffraction particle size analyzer (Microtrac Inc., Montgomeryville, PA, USA).

Pyrolysis gas chromatography-mass spectroscopy (Py-GC/MS) analysis of insoluble material

The insoluble material was pyrolyzed; the pyrolyzed gas was sent to a gas chromatograph/mass spectrometer (GC-2010/GCMS-QP2010; Shimadzu Corp., Kyoto, Japan) under a helium atmosphere. Approximately 0.16 to 0.17 mg of the insoluble sample was pyrolyzed at 550 °C for 12 s and loaded into the GC/MS at an injector temperature of 280 °C. The chromatographic isolation was performed with an Agilent J&W GC column DB-5 (30 m \times 0.250 mm \times 1.00 μ m; Agilent Technologies Inc., Santa Clara, CA, USA) using the following temperature program: 100 °C to 270 °C at a 4 °C/min rate and a 1.7 mL He/min carrier gas flow rate. The mass spectrum was recorded in the electron ionization (EI) mode at 0.8 kV.

RESULTS AND DISCUSSION

Changes to the Molecular Weight Distribution of α -Cellulose with Heating Time

To understand the effects of lignocellulose dissolution, the molecular weight of purified cellulose that was dissolved in the solution was measured.

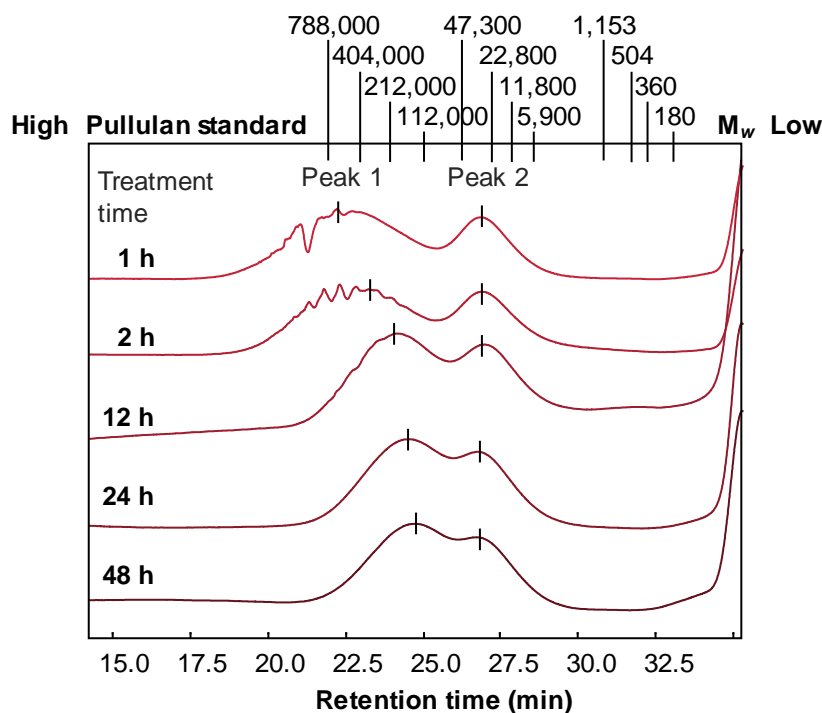


Fig. 1. SEC elutions of heat-treated α -cellulose solutions when dissolved in [Emim][OAc] at different treatment times (120 °C)

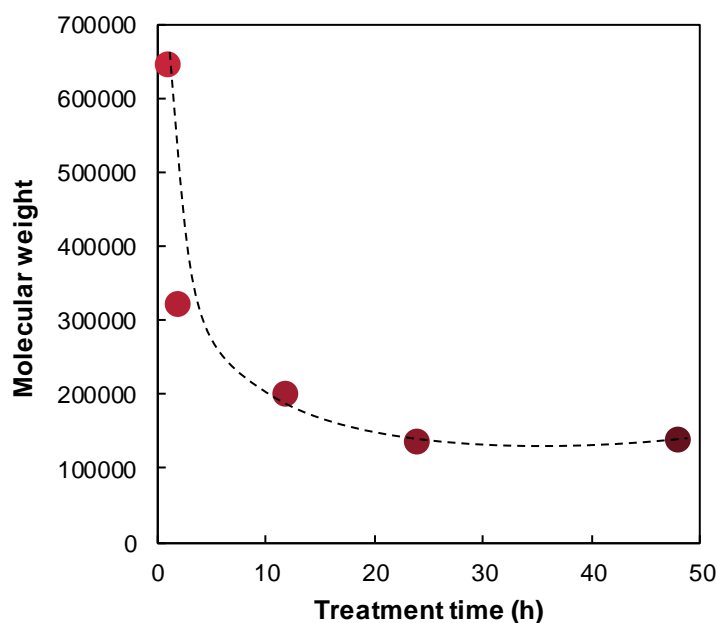


Fig. 2. Correlation of treatment time in ionic liquid at 120 °C versus α -cellulose molecular weight

Figure 1 shows the correlation of the treatment time *versus* the cellulose molecular weight in [Emim][OAc] at 120 °C. It was observed that α -cellulose dissolved in [Emim][OAc] within a 1 h period. Treated α -cellulose under a nitrogen atmosphere was remarkably depolymerized within the 1 to 12 h period, whereas the rate of depolymerization slowed after 24 h. In an earlier study, it was found that the molecular weight distributions of α -cellulose treated in [Emim][OAc] at 80 °C were almost the same for 10 min and 24 h treatment times. The molecular weight distributions of α -cellulose in the earlier study (80 °C) were similar to the values observed in this study at 120 °C for 1 h. The current study observed an even lower cellulose molecular weight after 1 h, which indicated that α -cellulose was more depolymerized when the time increased at the high treatment temperatures (Fig. 2).

Solubility of Lignocellulose: Heating Temperature and Ball-milling Time

The solubility of lignocellulose was also examined. The lignocellulose samples were treated differently in terms of treatment temperature (30, 80, or 120 °C) and ball-milling time (2 h-milled, 6 h-milled, 12 h-milled, 24 h-milled, or non-milled (*i.e.*, raw material)). The lignocellulose was treated in the [Emim][OAc]/DMSO for 24 h because the α -cellulose reaction stabilized after 24 h when at 120 °C (Fig. 2).

The solubilities of these samples are shown in Fig. 3. The solubility of the raw sample increased remarkably between 80 and 120 °C; *i.e.*, its solubility increased as the temperature of the solution increased, which was consistent with the observed outcome with α -cellulose. However, it was observed that the raw sample was not completely dissolved even when the temperature reached 120 °C. These observations suggested that the complete dissolution of lignocellulose did not solely depend upon the temperature of the ionic liquid.

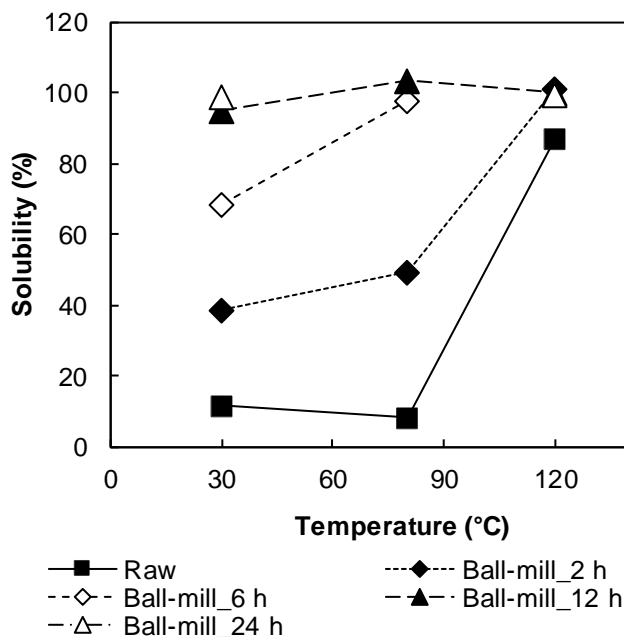


Fig. 3. Solubility of ball-milled lignocellulosic samples in [Emim][OAc]/DMSO

The ball-milled samples tended to dissolve well as the ball-milling times increased. A major observation was that when the sample was ball-milled for 24 h, it dissolved almost entirely in [Emim][OAc]/DMSO at 30 °C. In addition, samples ball-milled for the shortest time (2 h) dissolved completely at 120 °C. These results indicated that the lignocellulose tended to dissolve well when the temperature of the ionic liquid was raised in combination with increased ball-milling times. Figure 4 shows the SEC analysis of the solution obtained by dissolving the ball-milled sample in [Emim][OAc]/DMSO. This analysis confirmed that the molecular weight of the cellulose decreased to a slightly lower value *versus* Peak 1 of the non ball-milled α -cellulose. Therefore, it is proposed that the improvement in the solubility of lignocellulose was due to the molecular weight reduction of the cellulose that was caused by ball-milling.

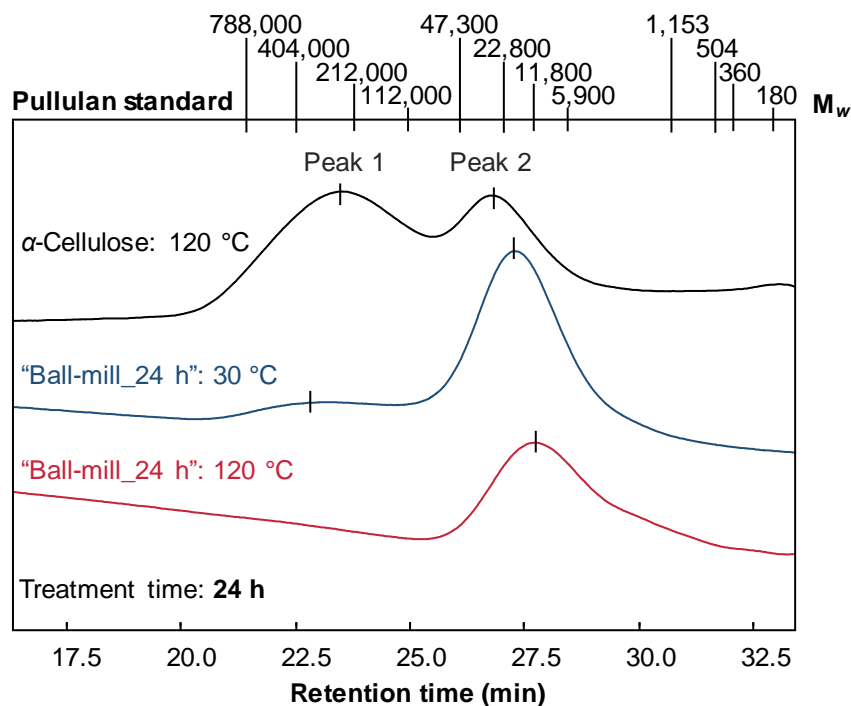


Fig. 4. SEC elutions of [Emim][OAc]/DMSO solutions of α -cellulose (black) and ball-milled samples (blue and red)

Relationship Between Solubility and Particle Size

As a factor of the increase of solubility by ball-milling, it was predicted that the accessibility of the ionic liquid to lignocellulose (*i.e.*, the solubility of lignocellulose) would increase by decreasing the particle size of samples. Therefore, the particle sizes of the various lignocellulose samples milled for different times were investigated. As shown in Table 1, the particle sizes of the lignocellulose samples increased as the ball-milling time increased from 2 to 24 h. The authors attribute this to the surfaces of primary particles, which were activated and aggregated (Ono *et al.* 1995), while the primary particle size decreased as the milling time was extended (Hatakeyama and Takahashi 2018). Therefore, the increase in particle size by the extension of ball-milling time was due to the aggregation of primary particles, and it is suggested that the solubility improvement caused by ball-milling depended on the reduction of the primary particle size.

Table 1. Particle Size of Ball-milled Samples

	Particle Size (μm)
Raw	106.7
Ball-mill_2 h	49.7
Ball-mill_6 h	54.6
Ball-mill_12 h	59.4
Ball-mill_24 h	78.4

In addition, the ball-milling treatment may have destroyed the crystalline structure of cellulose (Wang *et al.* 2009) and assisted with the extraction of lignin into the solution (Lee *et al.* 1981). Overall, various factors are considered to be involved in the improved dissolution of lignocellulose in the ionic liquid with ball-milling treatment time.

Py-GC/MS Analysis of Insoluble Residue

Kanbayashi and Miyafuji (2015) reported that the secondary wall lignin was removed from wood chips, whereas a large amount of compound middle lamella lignin was not removed when the chips were treated with 1-ethylpyridinium bromide ([EtPy][Br]) for 72 h. Wang *et al.* (2019) dissolved unbleached birch wood fibers, which were produced from acid hydrothermal fractionation (AHF) (Bian *et al.* 2017; Chen *et al.* 2017b), using *p*-toluenesulfonic acid in 1,5-diazabicyclo[4.3.0]non-5-enium acetate ([DBNH][OAc]). The authors investigated effects of the amount of lignin and its chemical structure on the ionic liquid dissolution of the lignocellulosic fibers. As a result, wood fibers were not completely dissolved in the ionic liquid even with the mild AHF treatment; the lignin contained in the insoluble residue had a high proportion of guaiacyl-type lignin (*i.e.*, G unit).

In contrast, Lee *et al.* (1981) reported that when milled-wood lignin (MWL) was extracted from birch wood flour (ball-milled for 24 to 216 h), the lignin that was extracted during the early stage contained a large number of condensed G units. Syringyl-type lignin (S unit) is abundant in the secondary wall, and G unit lignin is abundant in the compound middle lamella (Terashima *et al.* 1986). Therefore, the solubility of lignocellulose in [Emim][OAc] may be improved after ball-milling because the compound middle lamella lignin, which is considered to inhibit the dissolution, tends to elute easier. In the current study, the relationship between the dissolution of lignocellulose and the lignin structure was investigated by observing the changes to the S/G ratio of the lignin contained in insoluble fraction after the [Emim][OAc]/DMSO treatment.

Figure 5 shows the Py-GC/MS chromatograms of the raw sample and of the insoluble residue after [Emim][OAc]/DMSO treatment. Table 2 and Fig. 6 list the structural features of the lignin that were identified after its pyrolysis. The peaks indicating lignin structures from G units (red arrow) increased with the raw sample treated at 120 °C, while the peak indicating lignin structures from S units (brown-yellow arrow) increased with the “Ball-mill_6 h” sample treated at 30 °C. Figure 7 shows the calculated S/G ratio obtained by dividing the total area of the peaks of S units by the total area of the peaks of G units. No residue was obtained from the ball-milled sample treated at 120 °C for 24 h. The residue obtained by the raw sample treated with [Emim][OAc]/DMSO at 120 °C had a low S/G ratio and a large amount of G unit structures. In contrast, the S/G ratio was high for the residue obtained by the ball-milled sample with [Emim][OAc]/DMSO at 30 °C; this ratio increased as the ball-milling treatment time increased. In other words, a longer ball-milling time resulted in more G unit lignin structures that were dissolved and extracted. Therefore, it is suggested that the solubility of lignocellulose was improved by ball-milling

because it was easy to extract G unit lignin structures that were contained in the compound middle lamella.

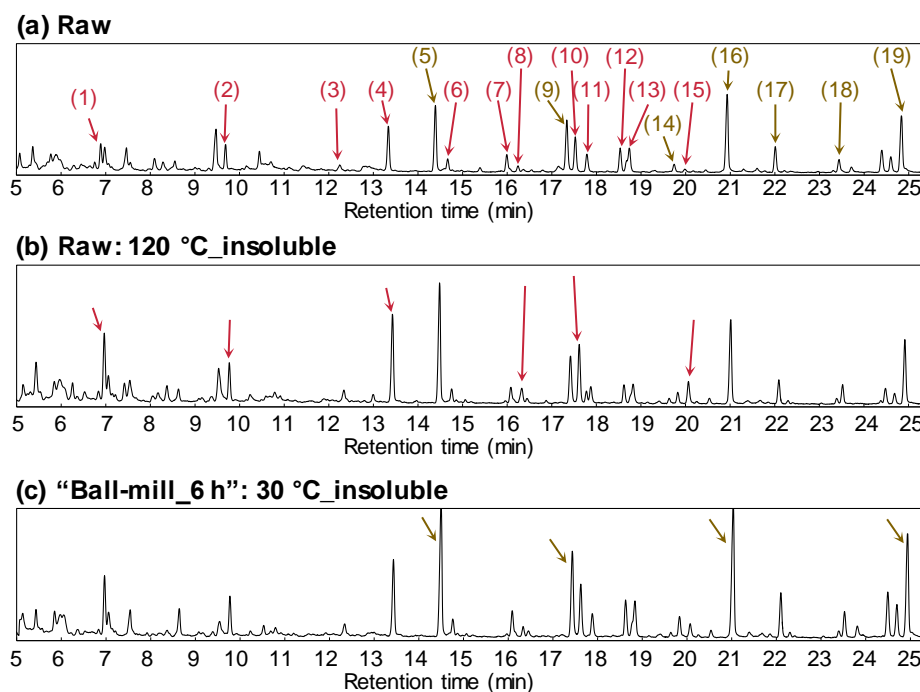


Fig. 5. Py-GC/MS chromatograms from insoluble residue in [Emim][OAc]/DMSO: (a) raw, (b) insoluble residue after treating the wood meal at 120 °C in ionic liquid mixture, and (c) insoluble residue after treating the 6 h ball-milled wood meal at 30 °C in ionic liquid mixture (note: numbers in parentheses correspond to the compounds listed in Table 2 and Fig. 6)

Table 2. Chemical Compounds Detected in Py-GC/MS Chromatograms (Fig. 5)

No.	Retention Time (min)	Derived from G Units of Lignin	Derived from S Units of Lignin	Similarity (%)
1	6.9	Guaiacol		93
2	9.7	<i>p</i> -Methylguaiacol		94
3	12.2	<i>p</i> -Ethylguaiacol		89
4	13.3	<i>p</i> -Vinylguaiacol		88
5	14.4		2,6-Dimethoxyphenol	94
6	14.7	<i>p</i> -Allylguaiacol		93
7	16.0	Vanillin		95
8	16.2	<i>p</i> -Propenylguaiacol		89
9	17.3		2,6-Dimethoxy- <i>p</i> -methylphenol	*
10	17.5	<i>p</i> -Propenylguaiacol		97
11	17.8	Guaiacylpropane		77
12	18.5	Guaiacylpropadiene		*
13	18.7	Guaiacylpropadiene		*
14	19.7		<i>p</i> -Ethyl-2,6-dimethoxyphenol	*
15	20.0	Guaiacylacetone		90
16	20.9		2,6-Dimethoxy- <i>p</i> -vinylphenol	*
17	22.0		<i>p</i> -Allyl-2,6-dimethoxyphenol	92
18	23.4		<i>p</i> -Allyl-2,6-dimethoxyphenol	90
19	24.8		<i>p</i> -Allyl-2,6-dimethoxyphenol	90
* Lin and Dence (1992)				

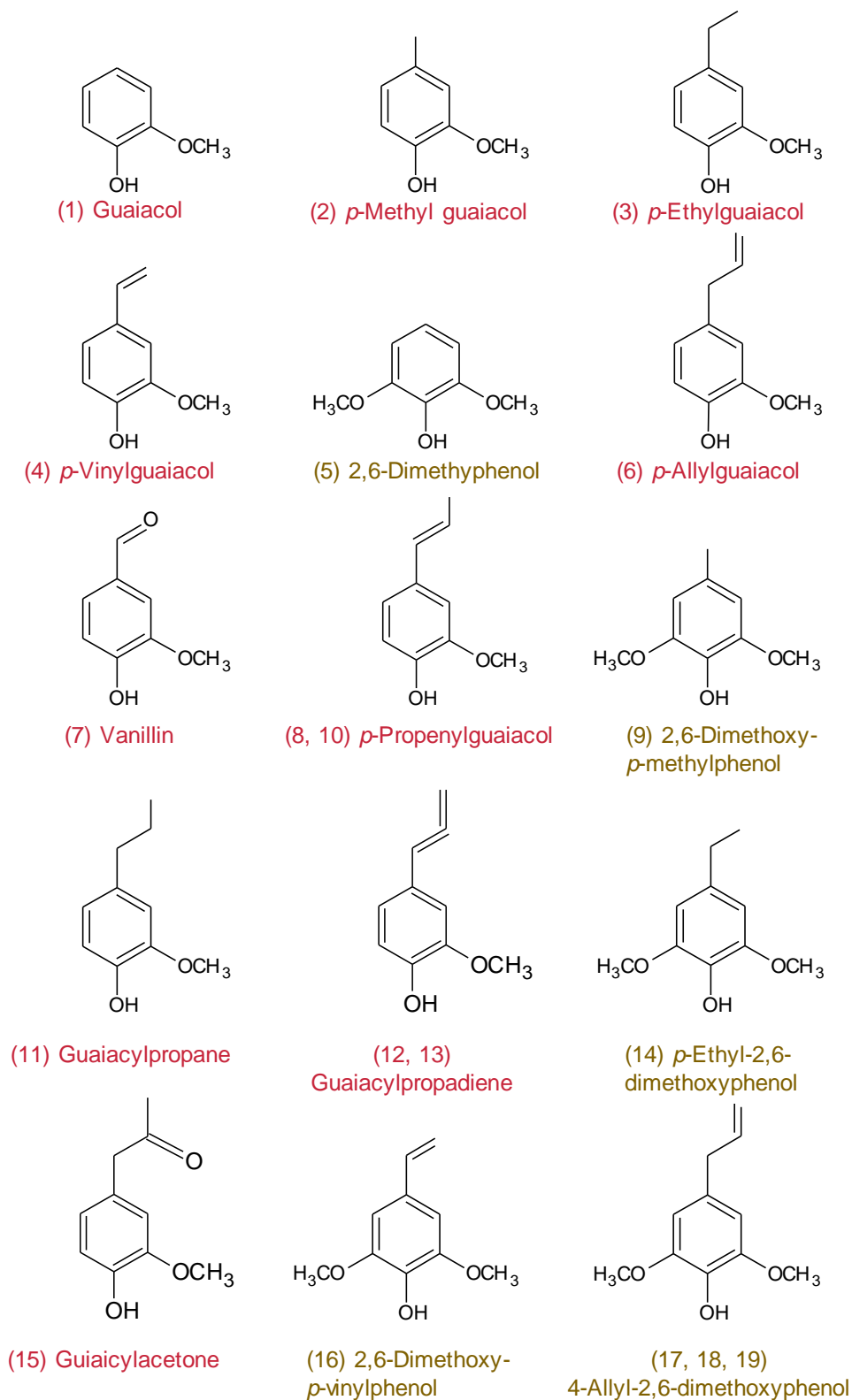


Fig. 6. Identified structures from Py-GC/MS analysis of the insoluble fraction from [Emim][OAc]/DMSO treatment

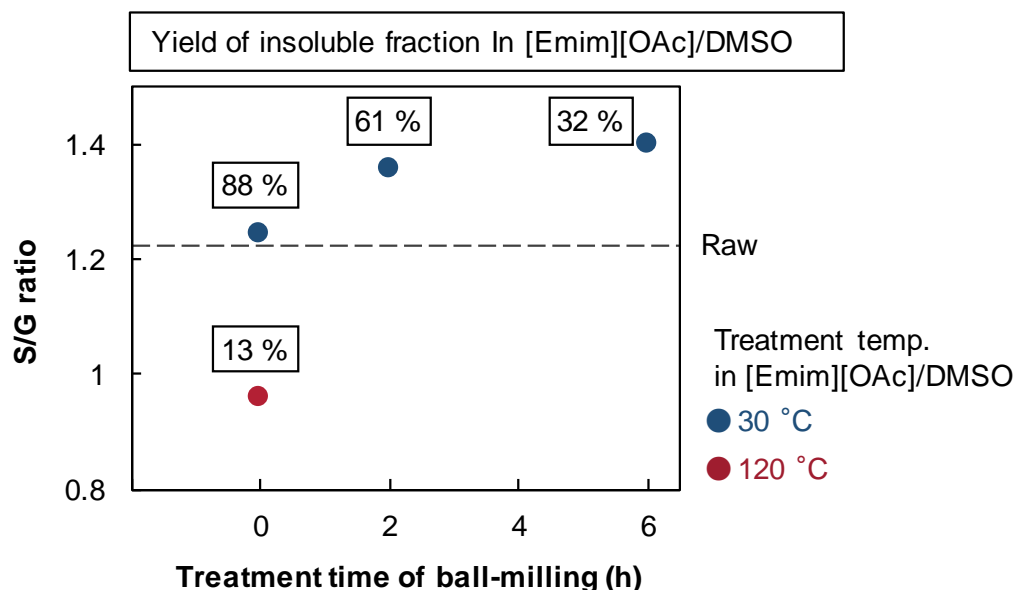


Fig. 7. Relationship between the ball-milling time and the S/G ratio of the insoluble material from [Emim][OAc]/DMSO mixed solution treatment

Proposed Mechanism of Wood Meal Dissolution in [Emim][OAc]/DMSO

To investigate the dissolution of lignocellulose in the ionic liquid mixture, the molecular weight distribution of the cellulose was characterized to note its depolymerization behavior and to relate its solubility changes with regards to treatment conditions (*i.e.*, temperature and ball-milling time). Figure 8 shows the proposed dissolution mechanism based on the results of this study.

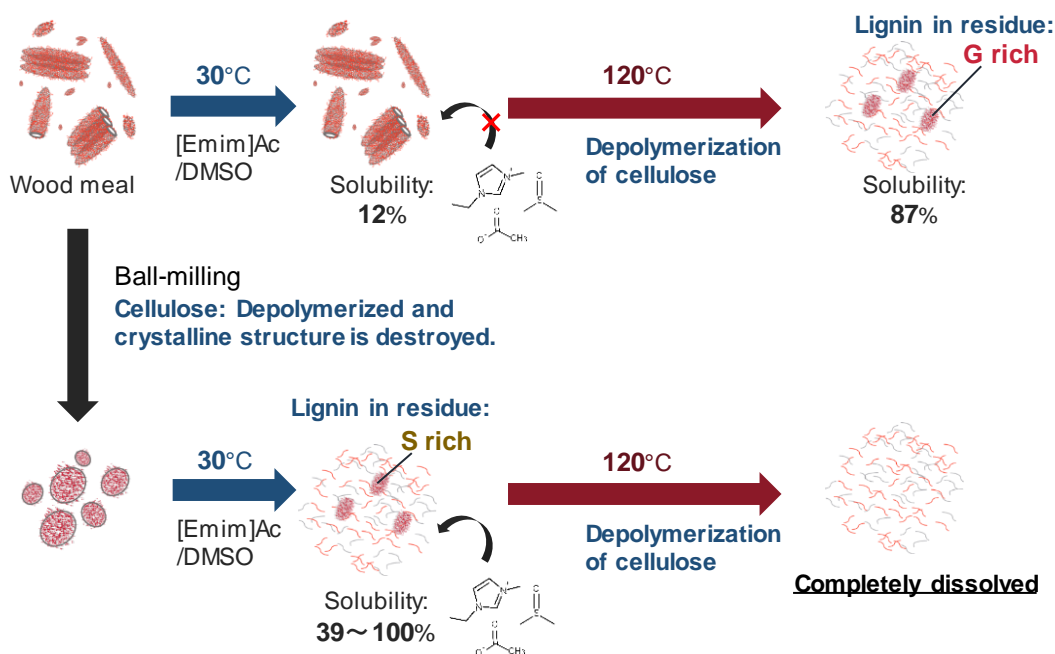


Fig. 8. Proposed mechanism of birch wood meal dissolution in [Emim][OAc]/DMSO

Approximately 87% of the birch wood was dissolved in [Emim][OAc]/DMSO when the temperature was raised to 120 °C; this was due to the low molecular weight of the cellulose. The residue contained more G unit lignin structures, which suggested it came from the compound middle lamella. The ball-milling treatment improved the solubility of the birch wood in [Emim][OAc]/DMSO at temperatures as low as 30 °C; the sample that was ball-milled for 24 h was completely dissolved in the ionic liquid mixture. Larger reduction in the molecular weight of cellulose by ball-milling than that by [Emim][OAc] treatment at 120 °C caused easier elution of the compound middle lamella lignin, resulting in the complete dissolution of lignocellulose. This finding should contribute to the effective utilization of lignocellulose for wood molding and for separating its components, which should then lead to the practical chemical usages of the woody biomass material.

CONCLUSIONS

1. α -Cellulose treated in the ionic liquid [Emim][OAc] under a nitrogen atmosphere for 1 to 12 h was remarkably depolymerized; the depolymerization slowed after 24 h.
2. Lignocellulose dissolved more easily in the ionic liquid mixture when the treatment temperature and the ball-milling time of the lignocellulose were increased.
3. The molecular weight of cellulose was reduced by ball-milling larger than that by [Emim][OAc] treatment at 120 °C, and only the ball-milled sample was completely dissolved in [Emim][OAc]/DMSO.
4. Ball-milling reduced the primary particle size of the sample, and facilitated the dissolution and extraction of guaiacyl-type lignin structures.

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