

Article

## Sulfonate Ionic Liquid as a Stable and Active Catalyst for Levoglucosenone Production from Saccharides via Catalytic Pyrolysis

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**Abstract:** In this study, various types of ionic liquids (ILs) were examined for catalytic activity in the pyrolysis of cellulose for the production of levoglucosenone, which is a valuable and versatile compound for the synthesis of a variety of novel compounds. Cellulose was simply mixed with the ILs and subjected for the pyrolysis, typically at 300 °C, to produce volatile products, including levoglucosenone, separated from the ILs phase. The type of IL anion significantly affected the catalysis, and the use of ILs bearing sulfonate anion resulted in distinguished yields of levoglucosenone and IL recoveries for the reutilization. Detailed thermogravimetric analysis and discussion on properties of ILs revealed the active and thermally stable nature of the sulfonate ILs. Catalytic pyrolysis with those ILs was applied to the conversion of other saccharides composed of glucose molecules, resulting in a preferential formation of levoglucosenone but at low yields as compared to that from cellulose.

**Keywords:** ionic liquid; cellulose; pyrolysis; catalysis; levoglucosenone

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## 1. Introduction

Ionic liquids (ILs), which show various and diverse physico-chemical properties depending on the type/combination of cation-anion, have attracted interest in many applications such as sensors, fuel cells, batteries, capacitors, thermal fluids, plasticizers, lubricants, ionogels, extractants and solvents in analysis, synthesis, catalysis and separation [1]. Processing of lignocellulosic and cellulosic biomass is one of the most widely studied of the applications. A property of ILs leading to the researchers' interest is a solvent power against cellulose, which is insoluble in conventional organic solvents [2,3]. The dissolution enables homogeneous phase reactions to efficiently convert cellulose to depolymerized and/or dehydrated products such as 5-hydroxymethylfurfural (HMF) especially in the presence of an additional catalytic agent [4–6]. On the other hand, because cellulose regenerated from ILs by addition of a non-solvent such as water is more amorphous, the dissolution and regeneration can be used as a pre-treatment to make enzymatic hydrolysis faster [7]. Research is also directed toward the dissolution of lignin [8–10]. Selective and powerful dissolution of these components, cellulose and lignin, by ILs is leading to a proposal of potential new method for fractionation of lignocellulosic biomass [1].

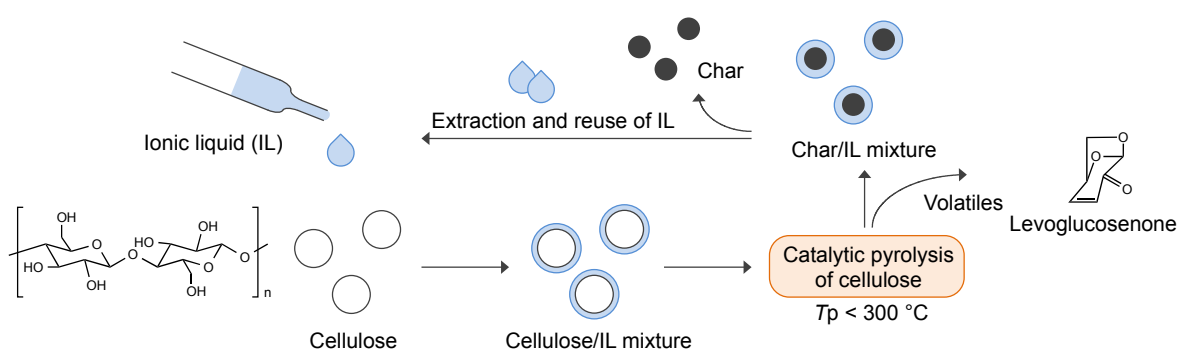
Many studies, thus, have focused on the ability of ILs as a solvent. Meanwhile, relatively little attention has been paid in this field to the intrinsic activity of ILs as a catalyst. ILs are often regarded as a chemically inert solvent, but they do have catalytic activity depending on the type of IL, reacting substances and/or reaction conditions. Jiang *et al.* [11] examined hydrolysis of cellulose dissolved in 1-butyl-3-methylimidazolium chloride using a variety of ILs as catalysts and found that the Brønsted acidity was crucial to the conversion of cellulose to reducing sugars. In a similar approach, Bao *et al.* [12] demonstrated that Lewis acidic IL works as a catalyst better than the Brønsted one for the dehydration of fructose to HMF. Although in these studies ILs used were functionalized to have acidity, less- or non-acidic ILs can also be used as catalysts. For example, Choi *et al.* [13] showed that the hydrogen-bond basicity of ILs correlated well with their activities for the decarboxylation of glycerol carbonate to glycidol, where an IL with  $\text{NO}_3^-$  (as the anion) was active enough to complete the reaction irrespective of the type of cation that is generally responsible for ILs' acidity. Other than the applications in biomass processing, there have been examples of the use of ILs as catalysts even in a near-industrial level [1]; nevertheless, a majority of researches uses ILs as solvents aiming mainly at the activation and stabilization of active species that are added as main catalysts. On the other hand, the addition of catalysts in IL medium renders the product-IL phase separation more complex and, therefore, can negatively affect the recyclability of ILs that still remain expensive.

Recently, we have proposed a process for the production of levoglucosenone, which is an attractive chiral synthon for the synthesis of a wide variety of natural and unnatural compounds due to the highly functionalized structure [14,15], from cellulose by the catalytic pyrolysis using a type of IL as the catalyst (Figure 1) [16]. The IL catalytically changed a mechanism of cellulose pyrolysis in the course of heating up, leading to a yield of levoglucosenone more than 20 wt%. This was more than double the yield from conventionally-used catalytic pyrolysis of cellulose using mineral acids, e.g., phosphoric acid, as an unrecyclable catalyst. Among four typical ILs tested, 1-butyl-2,3-dimethylimidazolium triflate showed the best catalytic activity and thermal stability. Key features of the reaction system are that cellulose undergoes the catalysis with little or no dissolution in the IL phase and that volatiles evolved from cellulose, including levoglucosenone, were thermally separated from IL phase and

obtained in downstream recovery equipment. These enable highly efficient recovery of products and reuse of IL that is simply separated from residue of pyrolysis. It was possible, in fact, that more than 99% of IL with high purity could be recovered and reused for the process with the reproduction of product yields.

The present work supplementally provides information on the catalytic pyrolysis of cellulose by ILs, focusing especially on the influence of types of ILs. Pyrolysis tests with 13 different ILs revealed essential requirements for the catalysts to show sufficient activity. Furthermore, with a view to exploitation of a potential feedstock of levoglucosenone, saccharides other than cellulose were also tested for the reaction.

**Figure 1.** Process flow of cellulose pyrolysis using ionic liquid (IL) as a recyclable catalyst.



## 2. Results and Discussion

### 2.1. Catalytic Pyrolysis of Cellulose/IL Mixtures

#### 2.1.1. Thermogravimetric Analysis

To evaluate the thermal stabilities of ILs used in this study, thermogravimetric analysis (TGA) was performed in the absence of cellulose. The results are shown in Figure 2. The thermal stability was associated significantly with the anionic part of ILs and less with the counterpart cation. The ILs with sulfonate anions and non- or weakly-coordinating anions ( $\text{BF}_4^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  and  $\text{PF}_6^-$ ) showed higher thermal stabilities than the others. This trend agrees with the data reported in the work by Fredlake *et al.* [17], in which they concluded that the thermal stability of IL increases with the increase in anion size. The ILs with [BMMIM] were more stable than the ones with [BMIM] because methyl substitution of C(2)-H of [BMIM], which is responsible for the acidity, can stabilize the cation against decomposition [18].

In general, a significant weight loss of cellulose, in other words, formation of volatiles, in the course of heating up for pyrolysis starts from around 300 °C. From that viewpoint, TGA results can be a reason enough to exclude ILs with  $\text{Cl}^-$ ,  $\text{CF}_3\text{CO}_2^-$  and  $\text{HSO}_4^-$  anions from the candidate as a catalyst for cellulose pyrolysis because they started to lose the weight under 300 °C by the decomposition. The boiling point of levoglucosenone, 254 °C under ambient pressures, also limits the types of ILs usable for the reaction. They must be stable at least as high as the boiling point to separate levoglucosenone from IL phase by the vaporization.

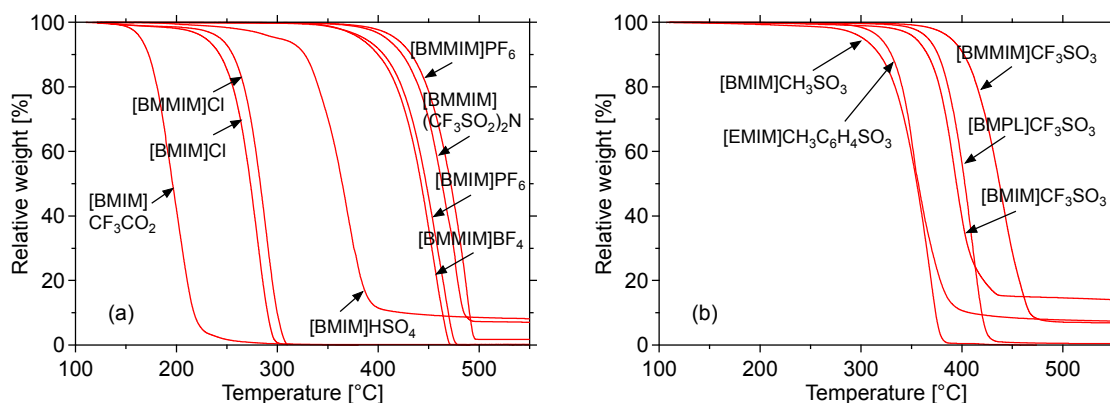
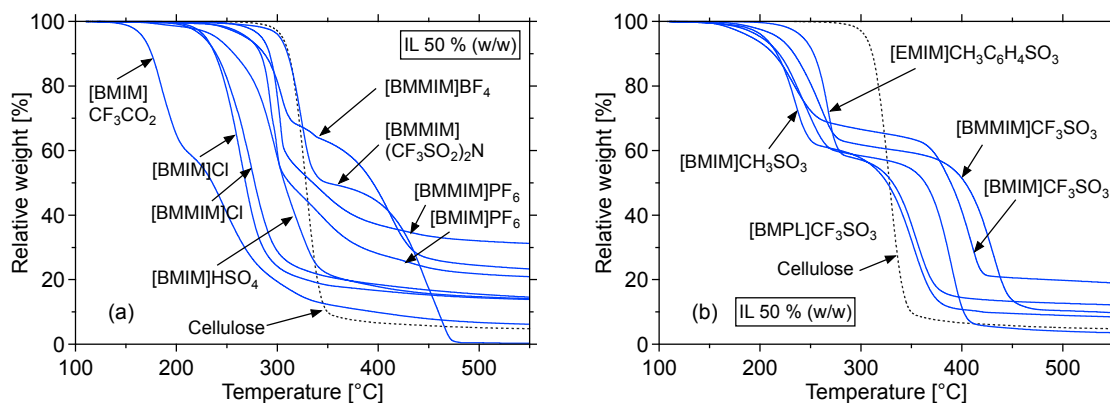
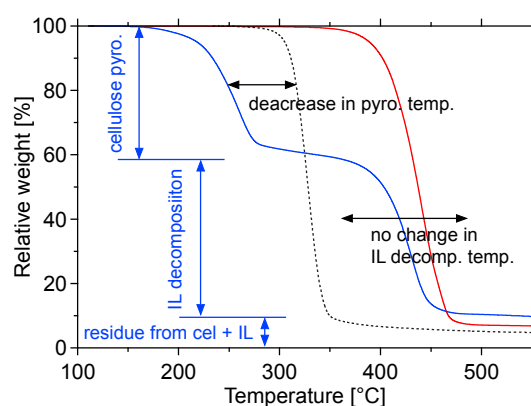
**Figure 2.** Weight loss curves of ILs; TGA under flowing nitrogen with 5 °C/min heating rate.**Figure 3.** Weight loss curves of cellulose and cellulose/IL mixtures; TGA under flowing nitrogen with 5 °C/min heating rate.

Figure 3 shows results of TGA for cellulose/IL mixtures. As with the thermal stability of IL, characteristics of weight loss curves depended on the types of anions with little influence of the cation. The curves could be sorted into two types: (i) clearly separated two-step weight loss and (ii) monotonous or unclear two-step weight loss. The type (i) applied to all the curves of the mixtures with sulfonate ILs (Figure 3b) and [BMMIM]BF<sub>4</sub> and [BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N. The two-step weight loss can be explained by the pyrolysis of cellulose for the first step (on the lower temperature side) and the decomposition of IL for the second step (on the higher temperature side) [16]. The isolation of the temperature ranges for the two steps indicates the possibility of IL recovery from the residue of pyrolysis if the pyrolysis temperature is lower than the onset temperature for the decomposition of IL. The temperature ranges for the second step in the type (i) curves corresponded well to those for the thermal decomposition of respective ILs in Figure 2. This represents that the thermal stabilities of those ILs were not altered by the presence of cellulose. On the other hand, the curves of type (ii) showed that the pyrolysis of cellulose accompanied the decomposition of IL, or *vice versa*. The ILs, which resulted in the type ii) curves, thus cannot be used as a catalyst in the present study. Pyrolysis of cellulose mixed with sulfonate ILs started at lower temperatures than pure cellulose pyrolysis by the catalysis. The presence of [BMMIM]BF<sub>4</sub> also decreased the temperature for cellulose pyrolysis, but [BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N seemed to be inert.

**Figure 4.** Characteristic weight loss curve for cellulose/sulfonate IL mixture (blue line: 50% (w/w) mixture, red line: IL and dashed black line: cellulose).



**Table 1.** Start and onset temperatures for cellulose pyrolysis and IL decomposition.

| IL                                                                  | Cellulose pyrolysis                       |                                           | IL decomposition                         |                                          | $T_{\text{start,IL}} - T_{\text{onset,cel}} [^{\circ}\text{C}]$ |
|---------------------------------------------------------------------|-------------------------------------------|-------------------------------------------|------------------------------------------|------------------------------------------|-----------------------------------------------------------------|
|                                                                     | $T_{\text{start,cel}} [^{\circ}\text{C}]$ | $T_{\text{onset,cel}} [^{\circ}\text{C}]$ | $T_{\text{start,IL}} [^{\circ}\text{C}]$ | $T_{\text{onset,IL}} [^{\circ}\text{C}]$ |                                                                 |
| None                                                                | 292                                       | 310                                       | —                                        | —                                        | —                                                               |
| [BMMIM]BF <sub>4</sub>                                              | 243                                       | 282                                       | 356                                      | 416                                      | 74                                                              |
| [BMMIM](CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N            | 279                                       | 307                                       | 381                                      | 433                                      | 74                                                              |
| [BMIM]CH <sub>3</sub> SO <sub>3</sub>                               | 181                                       | 210                                       | 262                                      | 332                                      | 52                                                              |
| [EMIM]CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> | 223                                       | 251                                       | 299                                      | 333                                      | 48                                                              |
| [BMPL]CF <sub>3</sub> SO <sub>3</sub>                               | 175                                       | 208                                       | 346                                      | 383                                      | 138                                                             |
| [BMIM]CF <sub>3</sub> SO <sub>3</sub>                               | 166                                       | 198                                       | 322                                      | 370                                      | 124                                                             |
| [BMMIM]CF <sub>3</sub> SO <sub>3</sub>                              | 189                                       | 224                                       | 365                                      | 407                                      | 141                                                             |

$T_{\text{start}}$  was defined as the temperature at which the relative weight became 98.5%.  $T_{\text{onset}}$  was determined according to the method reported in ref. [17].

TGA is thus a powerful approach to easily find a stable and active catalyst for catalytic pyrolysis. The results allowed us to eliminate seven types of ILs (ILs with CF<sub>3</sub>CO<sub>2</sub><sup>−</sup>, Cl<sup>−</sup>, HSO<sub>4</sub><sup>−</sup> and PF<sub>6</sub><sup>−</sup> anions) out of 13 as the candidate of catalysts. Figure 4 summarizes the characteristics of weight loss curves of cellulose/IL mixture when the IL is catalytically active and thermally stable. The start temperature,  $T_{\text{start}}$ , and the onset temperature,  $T_{\text{onset}}$ , obtained by TGA for selected samples are listed in Table 1 for later discussion.

### 2.1.2. Pyrolysis Products

Although TGA classified ILs according to the usability in catalytic pyrolysis of cellulose, pyrolysis experiments were performed also with a part of the unusable ones for reference. Table 2 shows the results.

**Table 2.** Yields of products from pyrolysis of cellulose and cellulose mixed with IL.

| Entry | IL                                                                  | $T_p^a$<br>[°C] | Yields [wt% on a cellulose mass basis] |                                               |                   |                               | IL<br>recovery<br>[%] | Total<br>mass<br>balance<br>[%] |
|-------|---------------------------------------------------------------------|-----------------|----------------------------------------|-----------------------------------------------|-------------------|-------------------------------|-----------------------|---------------------------------|
|       |                                                                     |                 | CO/CO <sub>2</sub>                     | Condensable<br>matter <sup>b</sup><br>(water) | Char <sup>b</sup> | Levoglucosenone<br>(in mol %) |                       |                                 |
| 1     | None <sup>d</sup>                                                   | 350             | 0.8/2.8                                | 57.3 (22.2)                                   | 24.6              | 2.4 (3.1)                     | —                     | 85.5                            |
| 2     | [BMIM]Cl                                                            | 300             | 0.91/8.5                               | 51.4 (34.4)                                   | 51.4              | 3.0 (3.9)                     | 7.3                   | 71.1                            |
| 3     | [BMMIM]BF <sub>4</sub> <sup>d</sup>                                 | 300             | 0.9/4.8                                | 69.9 (20.8)                                   | 63.3              | n.d. (—)                      | 78.6                  | 98.4                            |
| 4     | [BMIM]HSO <sub>4</sub>                                              | 300             | 2.7/17.4                               | 67.9 (39.0)                                   | 67.6              | 1.9 (2.4)                     | 15.5                  | 85.6                            |
| 5     | [BMMIM](CF <sub>3</sub> SO <sub>2</sub> ) <sub>2</sub> N            | 350             | 1.2/3.8                                | 64.4 (31.1)                                   | 23.3              | 1.9 (2.5)                     | 101.1                 | 96.6                            |
| 6     | [BMIM]CH <sub>3</sub> SO <sub>3</sub>                               | 300             | 0.7/3.8                                | 81.3 (40.2)                                   | 27.6              | 20.7 (26.7)                   | 85.3                  | 99.4                            |
| 7     | [EMIM]CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>3</sub> | 300             | 0.8/3.8                                | 77.8 (37.7)                                   | 31.1              | 29.7 (38.2)                   | 81.6                  | 97.6                            |
| 8     | [BMPL]CF <sub>3</sub> SO <sub>3</sub>                               | 300             | 0.2/2.2                                | 52.6 (30.0)                                   | 32.1              | 25.0 (32.1)                   | 96.9                  | 91.9                            |
| 9     | [BMIM]CF <sub>3</sub> SO <sub>3</sub>                               | 300             | 1.1/3.0                                | 59.0 (37.8)                                   | 44.8              | 18.1 (23.3)                   | 94.7                  | 101.3                           |
| 10    | [BMMIM]CF <sub>3</sub> SO <sub>3</sub> <sup>d</sup>                 | 300             | 0.8/2.2                                | 62.0 (32.0)                                   | 32.7              | 21.4 (27.6)                   | 99.4                  | 98.6                            |

<sup>a</sup> Final temperature for pyrolysis. <sup>b</sup> Condensable matter and char can include a portion of decomposed IL. <sup>c</sup> Molar yield of levoglucosenone per molar number of D-glycopyranose units calculated from weight of cellulose. <sup>d</sup> Data reported in ref. [16].

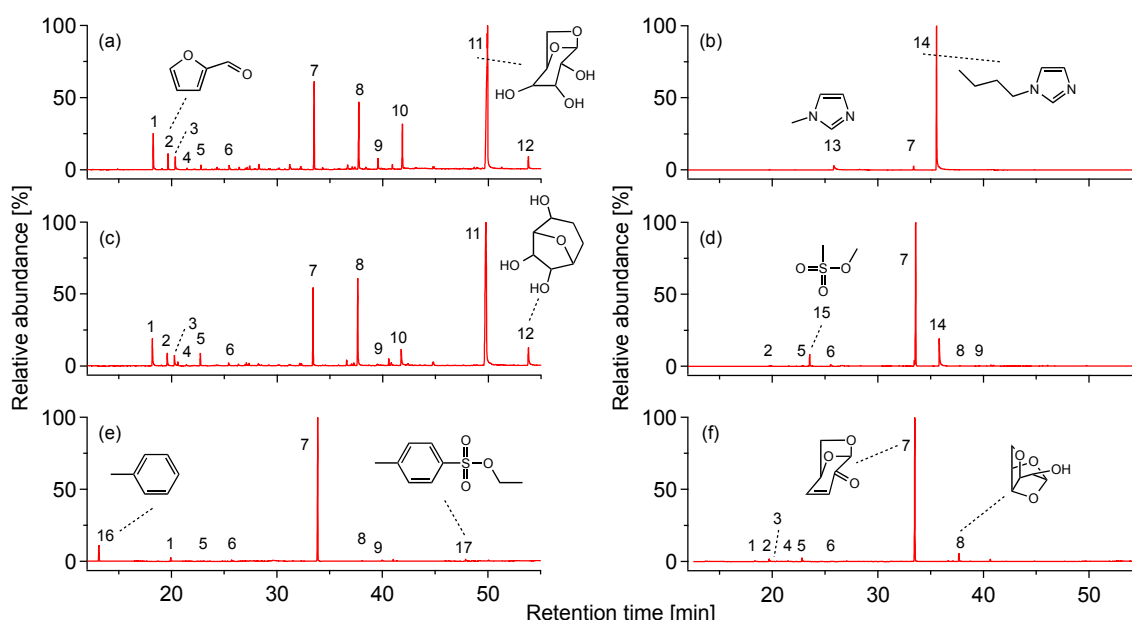
The use of sulfonate ILs resulted in distinguished yields of levoglucosenone as compared to the yields less than 3 wt% by other ILs. The highest yield, 29.7 wt%, was achieved by [EMIM]CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, but the recovery of IL was not high.  $T_{\text{start,IL}}$  and  $T_{\text{onset,IL}}$  (Table 1) of the IL explain the low IL recovery. Analysis of the condensable matter by GC-MS (Figure 5e) identified compounds derived from the IL such as toluene from the anion. The derivatives of IL decomposition were confirmed only when ILs, which have  $T_{\text{start,IL}}$  lower than 300 °C, were used. Detection of methyl- and butyl-imidazoles (Figure 5b) agrees with the thermal degradation pathway of [BMIM]Cl reported by Hao *et al* [19]. Chemical interactions between ILs and cellulose (or char) can also cause the decrease in the IL recovery by a partial incorporation of IL into the char matrix. An example would be the incomplete recovery of [BMIM]CF<sub>3</sub>SO<sub>3</sub>. Because [BMIM] includes an acidic proton, as mentioned above, it has chemically more interactive nature than [BMMIM]. By either or both of these pathways, the ILs are thought to be lost from the bulk liquid phase in the course of pyrolysis.

Main compounds detected in GC-MS analysis of condensable matter from pyrolysis of pure cellulose were furfural, levoglucosenone, DGP, levoglucosan and AGF. The presence of [BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N in the mixture had little influence on the product composition and yield, indicating the inert and stable nature even at the temperature as high as 350 °C. In contrast, the catalysis of sulfonate ILs remarkably changed the composition of products derived from cellulose, leading to the selective production of levoglucosenone. The second highest peak was always DGP for these ILs but far lower than the peak from levoglucosenone.

Irrespective of the cations and the type of sulfonate, it is plausible for all the sulfonate ILs that optimization of the temperature for pyrolysis provides a complete IL recovery simultaneously with a sufficient levoglucosenone yield. However, the weight loss curves in TGA imply the difficulty to find the optimum temperature for some sulfonate ILs.  $T_{\text{start,IL}} - T_{\text{onset,cel}}$  in Table 1 represents the value of temperature after onset of cellulose pyrolysis and before start of IL decomposition. The smaller the

value is, the more difficult the two reactions are separated. Therefore, for a process with high IL recovery and levoglucosenone yield, it is not recommended to use [BMIM]CH<sub>3</sub>SO<sub>3</sub> and [EMIM]CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, which showed  $T_{\text{start,IL}} - T_{\text{onset,cel}}$  of 52 and 48 °C, respectively, even if the pyrolysis temperature is modified. The best IL, thus found, was [BMMIM]CF<sub>3</sub>SO<sub>3</sub>, followed by [BMPL]CF<sub>3</sub>SO<sub>3</sub> among the ILs used in this study.

**Figure 5.** GC-MS chromatograms of condensable matter from pyrolysis of (a) cellulose; (b) cellulose/[BMIM]Cl; (c) cellulose/[BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N; (d) cellulose/[BMIM]CH<sub>3</sub>SO<sub>3</sub>; (e) cellulose/[EMIM]CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub> and (f) cellulose/[BMMIM]CF<sub>3</sub>SO<sub>3</sub>. The main peaks are assigned as follows: 1: not confirmed, 2: furfural, 3: 2-propylfuran, 4:  $\alpha$ -angelica lactone, 5: 2-acetylfuran, 6: 5-methylfurfural, 7: levoglucosenone, 8: DGP, 9: HMF, 10: not confirmed, 11: levoglucosan, 12: AGF, 13: methylimidazole, 14: butylimidazole, 15: methyl methanesulfonate, 16: toluene, 17: ethyl 4-methylbenzenesulfonate.



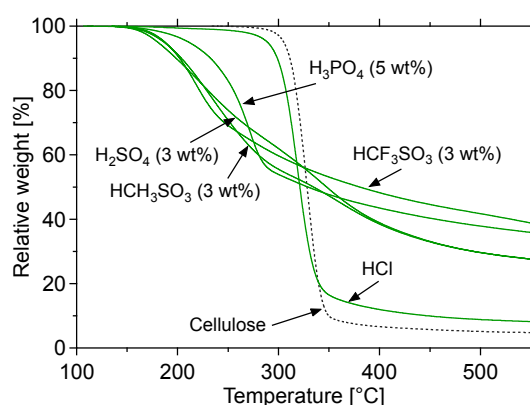
### 2.1.3. Discussion on Catalysis of Sulfonate ILs

To summarize the influence of IL types on the production of levoglucosenone from cellulose, the anion had a key role in the catalysis. Although a few types of anions among the common ones [20] were not examined in this study (e.g., chloroaluminates, dicyanamide and metal complexes), it is fair to say that sulfonate anion is indispensable for levoglucosenone production.

Meanwhile, the presence of cation in ILs should not be ignored in the discussion of the catalysis. To investigate the effect of IL cations, pyrolysis tests were carried out using cellulose impregnated with inorganic or organic acids including sulfonic acid (HCF<sub>3</sub>SO<sub>3</sub>). Figure 6 and Table 3 show the results of TGA and pyrolysis tests, respectively. The weight loss curve for cellulose-HCl indicated that HCl had little influence on the pyrolysis of cellulose. On the other hand, impregnations of the other acids significantly changed the curves, and a part of them, H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>, showed catalysis leading to an increase in the yield of levoglucosenone. In fact, it has been known that the impregnation of H<sub>3</sub>PO<sub>4</sub> is effective for the levoglucosenone production [21,22], and the activity of H<sub>2</sub>SO<sub>4</sub> (or SO<sub>4</sub><sup>2-</sup>) has recently

been reported by Sui *et al* [23]. The anions incorporated by the acid impregnation into cellulose induce the formation of high yields of char in return for the levoglucosenone formation. The impregnations of sulfonic acids also induced the char formation, but the levoglucosenone yields were comparable with that from pure cellulose in spite of high activities of the anions in the form of ILs (e.g., [BMIM]CH<sub>3</sub>SO<sub>3</sub> and [BMIM]CF<sub>3</sub>SO<sub>3</sub>). These results suggest that, for sulfonate anions, the presence of cations, which can form ILs, is indispensable to be stable and active for the levoglucosenone formation.

**Figure 6.** Weight loss curves of cellulose and cellulose impregnated with inorganic or organic acids; TGA under flowing nitrogen with 5 °C/min heating rate.



**Table 3.** Yields of products from pyrolysis of cellulose impregnated with organic or inorganic acids.

| Entry | Acid                                                | $T_p$ [°C] | Yields [wt% on a cellulose mass basis] |                            |      |                          | Total mass balance [%] |
|-------|-----------------------------------------------------|------------|----------------------------------------|----------------------------|------|--------------------------|------------------------|
|       |                                                     |            | CO/CO <sub>2</sub>                     | Condensable matter (water) | Char | Levoglucosenone (in mol) |                        |
| 11    | H <sub>3</sub> PO <sub>4</sub> (3 wt%) <sup>a</sup> | 300        | 1.1/2.7                                | 42.8 (32.9)                | 57.3 | 8.9 (11.5)               | 97.4                   |
| 12    | HCl (3 wt%)                                         | 300        | 0.2/1.0                                | 21.9 (13.0)                | 71.6 | 1.6 (2.0)                | 94.9                   |
| 13    | H <sub>2</sub> SO <sub>4</sub> (3 wt%)              | 300        | 1.4/3.2                                | 39.4 (25.0)                | 56.6 | 8.4 (10.8)               | 100.7                  |
| 14    | CH <sub>3</sub> SO <sub>3</sub> H (3 wt%)           | 300        | 1.3/3.5                                | 41.7 (34.5)                | 53.2 | 1.9 (2.5)                | 99.7                   |
| 15    | CF <sub>3</sub> SO <sub>3</sub> H (3 wt%)           | 300        | 2.3/4.7                                | 34.9 (24.1)                | 57.5 | 3.3 (4.2)                | 99.4                   |

<sup>a</sup> Data reported in ref. [16].

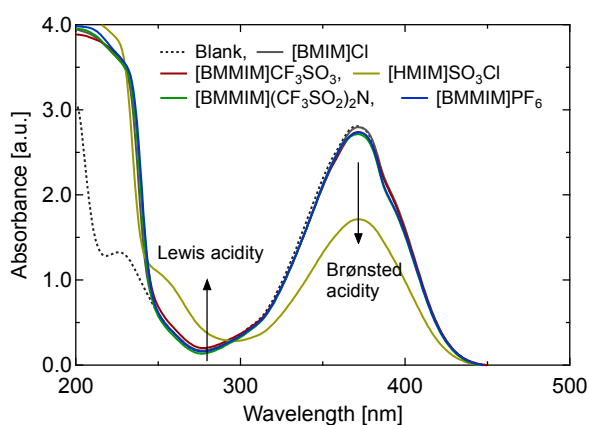
The reason for the high levoglucosenone yields with sulfonate ILs has yet to be definitively determined, but it is possible to correlate or uncorrelate the catalytic activities with their properties. The catalytic activity of ILs can be related to  $T_{\text{onset, cel}}$ : lower  $T_{\text{onset, cel}}$  indicates higher catalytic activity (sulfonate ILs > [BMMIM]BF<sub>4</sub> > [BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N).

The conjugate acid of triflate (CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>) is known as a superacid, and those of other sulfonate anions are strong acids. Therefore, the acidity of the conjugate acid of IL anion seems like a factor influencing the catalytic activity. However, the inertness of [BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N against cellulose pyrolysis rejects the idea because H(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N is more acidic than triflic acid, HCF<sub>3</sub>SO<sub>3</sub>. Miran *et al.* reported that  $pK_a$  values of conjugate acids of (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>−</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>, CH<sub>3</sub>SO<sub>3</sub><sup>−</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>−</sup> anions are

−10.0, −7.0, −2.0 and 0.5, respectively. Likewise, the acidity of IL cannot explain the catalytic activity. Although the definition of acidity of IL still remains controversial, there are a number of reports using Hammett acidity function. Hallet *et al.* [24] summarized Hammett acidities of various types of ILs in their review paper, but none of them were in the superacid range. While neat sulfuric acid has the value of −12, those of sulfonate ILs are even higher than 0, indicating their low acidities. To confirm this, acidic properties of ILs used in this study were investigated as shown in Figure 7. As a reference, 1-methylimidazolium chlorosulfate ([HMIM]SO<sub>3</sub>Cl) was synthesized according to the reported method [25] and used for the measurement. The shift of peak intensities at 270–280 and 370–390 nm reveals Lewis and Brønsted acidities, respectively. [HMIM]SO<sub>3</sub>Cl exhibited features of both Lewis and Brønsted acidities, and the calculated Hammett acidity (for Brønsted acidity) was higher than 0. In contrast, for ILs of this study, there was no detectable change in UV-visible spectra, suggesting little acidities of them.

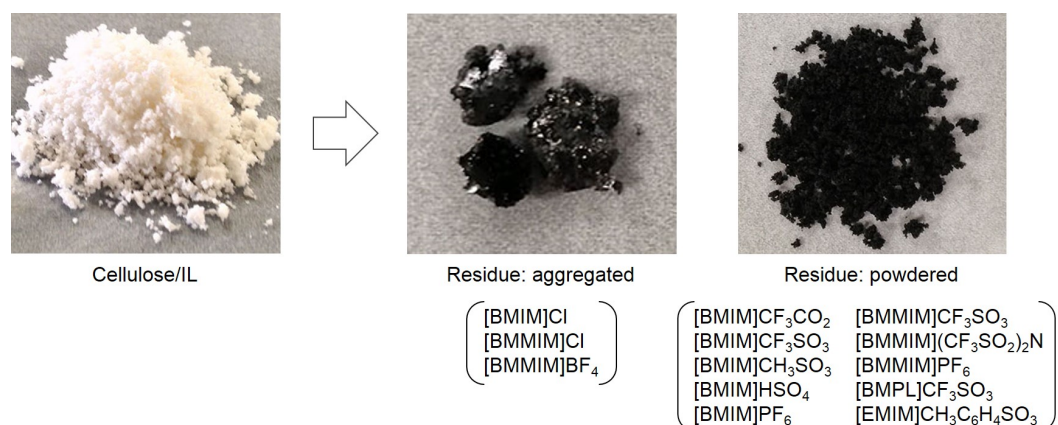
The acidities of ILs and conjugate acids of the anions, thus, could not contribute to the explanation of their catalytic activities. However, it must be noted that they are not the values or properties at the reaction conditions such as temperature, where the pyrolysis of cellulose is taking place.

**Figure 7.** UV-visible spectra of *p*-nitroaniline in methanol containing IL at 80 mM ([BMIM]Cl, [BMMIM]CF<sub>3</sub>SO<sub>3</sub> and [HMIM]SO<sub>3</sub>Cl) or at 20 mM ([BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N and [BMMIM]PF<sub>6</sub>).



One might suspect that the dissolution of cellulose is related to the levoglucosenone formation. In fact, some ILs, such as [BMIM]Cl, can readily dissolve cellulose even at temperatures lower than 100 °C. The occurrence of the dissolution was visually apparent from the residue of pyrolysis in this study. As shown in Figure 8, the residue was aggregated with a smooth surface when ILs had a solvent power, while in most cases the residue was still dispersed as with the starting material. The former one was observed only when [BMIM]Cl, [BMMIM]Cl and [BMMIM]BF<sub>4</sub> were used. Therefore, the dissolution could not be directly related to the levoglucosenone formation.

**Figure 8.** Examples of cellulose/IL mixture and two types of residue (char/IL): aggregated and powdered ones.



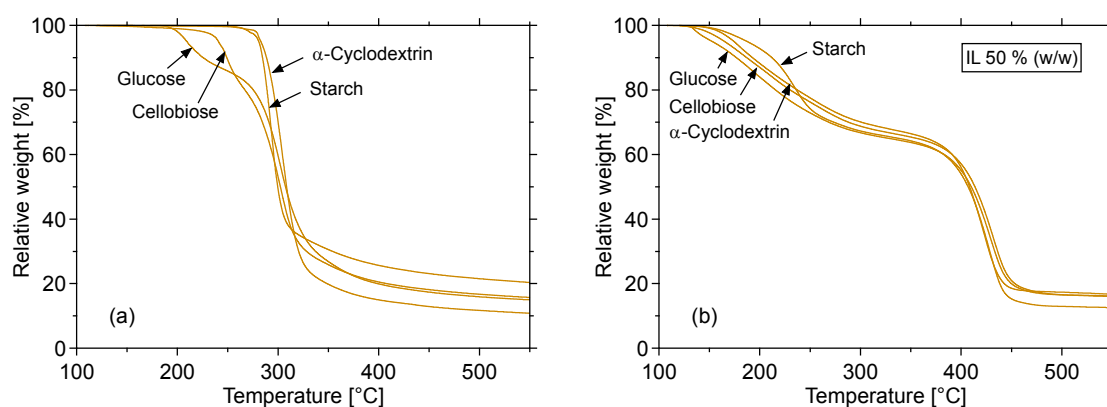
However, a property of IL relevant to the cellulose dissolution may be correlated with the catalytic activity. The dissolution mechanism of cellulose in ILs involves the oxygen and hydrogen atoms of cellulose-OH in the formation of electron donor-electron acceptor (EDA) complexes, which interact with the IL [3]. Although the ability of IL for EDA complex formation depends on both cation and anion mainly as hydrogen bond donor and hydrogen bond acceptor, respectively, it has been thought that the anion is the major contributor in the dissolution [1]. The activity of the anion as hydrogen bond acceptor is described by hydrogen bond basicity ( $\beta$  value) in Kamlet-Taft parameters [24]. Now, here are assessed the correlation between the  $\beta$  values and the catalytic activities of ILs. The  $\beta$  value for [BMMIM] ILs reported by Crowhurst *et al.* [26] decreased in the following order with the type of anion:  $\text{CF}_3\text{SO}_3^-$  (0.464) >  $\text{BF}_4^-$  (0.376) >  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  (0.243). The same trend was reported in other literatures [13,24]. This order agrees with their catalytic activities for levoglucosenone production of this study. Because the formation of levoglucosenone from cellulose progresses along with dehydration reactions that require protonation of hydroxyl group, the effect of  $\beta$  value, which is associated with the interaction between IL anion and hydrogen atom, seems to be convincing explanation of the catalysis. On the other hand, [BMIM]Cl has much higher  $\beta$  value, 0.83–0.87, in spite of the low catalytic activity for the levoglucosenone formation. It seems that such strong hydrogen bond basicity does not cause the catalysis, but only results in the dissolution of cellulose. In other words, the  $\beta$  value may have an optimum value at around that of  $\text{CF}_3\text{SO}_3^-$  (0.464) to give the catalytic activity. Accordingly, it is plausible that, during cellulose pyrolysis, ILs with excess  $\beta$  value are incorporated into cellulose/char matrix by the interaction between them, and the ones with too low  $\beta$  value behave as inert. Although the  $\beta$  values for other sulfonate ILs such as [BMIM] $\text{CH}_3\text{SO}_3$  and [EMIM] $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3$  could not be found in literatures, the values should be lower than that of [BMIM]Cl because their anions are larger than  $\text{Cl}^-$ . A similar tendency was seen in the work by Pulati *et al.* on treatment of coal samples using [BMIM]Cl, [BMIM] $\text{CF}_3\text{SO}_3$  and [BMIM] $\text{BF}_4$  [27]. The first one was effective to disperse the coal by the strong interaction at 100 °C, and the last one did not result in any appreciable dispersion. The use of [BMIM] $\text{CF}_3\text{SO}_3$  at elevated temperatures significantly modified the nature of the coal to be soluble in pyridine (more than 90% of the coal).

Thus, the  $\beta$  value was well correlated with the activity of IL toward formation of levoglucosenone. Our future work will deal with how the sulfonate ILs work to change the pyrolysis mechanism.

## 2.2. Catalytic Pyrolysis of Saccharides Other than Cellulose by ILs

Because cellulose is a highly polymerized glucose, it is easy to assume that other saccharides comprised of glucose, such as glucose, cellobiose,  $\alpha$ -cyclodextrin and starch, can also be used as the feedstock of levoglucosenone. As compared to plentiful studies on the pyrolysis of cellulose, those saccharides are rarely considered as the feedstock of pyrolysis due to their lower availabilities. Instead, they are often used as a model compound to investigate the mechanisms of reactions relevant to cellulose pyrolysis [28]. However, when the target of a process is a highly value-added product such as levoglucosenone, they can also be the feedstock depending on the availability and usability.

**Figure 9.** Weight loss curves of (a) glucose, cellobiose,  $\alpha$ -cyclodextrin and starch and (b) their mixtures with [BMMIM]CF<sub>3</sub>SO<sub>3</sub>; TGA under flowing nitrogen with 5 °C/min heating rate.



**Table 4.** Yields of products from pyrolysis of glucose, cellobiose,  $\alpha$ -cyclodextrin and starch in the absence/presence of [BMMIM]CF<sub>3</sub>SO<sub>3</sub>.

| Entry | Sample <sup>a</sup> | T <sub>p</sub> [°C] | Yields [wt% on a cellulose mass basis] |                |      |                 | IL recovery<br>[%] | Total mass<br>balance<br>[%] |
|-------|---------------------|---------------------|----------------------------------------|----------------|------|-----------------|--------------------|------------------------------|
|       |                     |                     | Condensable                            |                |      |                 |                    |                              |
|       |                     |                     | CO/CO <sub>2</sub>                     | matter (water) | Char | Levoglucosenone |                    |                              |
| 16    | Glucose             | 350                 | 2.27                                   | 54.7 (36.0)    | 33.1 | 0.4             | –                  | 97.2                         |
| 17    | Cellobiose          | 350                 | 1.92                                   | 51.0 (29.4)    | 34.3 | 0.8             | –                  | 94.0                         |
| 18    | α-Cyclodextrin      | 350                 | 2.52                                   | 51.3 (31.2)    | 32.5 | 0.9             | –                  | 93.2                         |
| 19    | Starch              | 350                 | 1.83                                   | 54.6 (36.9)    | 31.3 | 1.7             | –                  | 93.9                         |
| 20    | Glucose/IL          | 300                 | 1.08                                   | 55.4 (38.0)    | 44.1 | 4.1             | 95.8               | 100.7                        |
| 21    | Cellobiose/IL       | 300                 | 1.08                                   | 55.5 (33.0)    | 42.8 | 4.2             | 96.5               | 100.1                        |
| 22    | α-Cyclodextrin/IL   | 300                 | 1.12                                   | 54.6 (35.8)    | 44.8 | 3.9             | 94.4               | 99.6                         |
| 23    | Starch/IL           | 300                 | 1.13                                   | 56.6 (34.1)    | 41.0 | 7.6             | 95.9               | 99.5                         |

<sup>a</sup> IL: [BMMIM]CF<sub>3</sub>SO<sub>3</sub>.

Experiments were conducted in a similar manner to those for cellulose using [BMMIM]CF<sub>3</sub>SO<sub>3</sub>. The results of TGA, shown in Figure 9, confirm that the IL is stable and active. Table 4 compares the yields of products from the pyrolysis in the absence/presence of IL. Increases in the yields of water and char by the presence of IL reveal that the saccharides were catalytically dehydrated. More than 94% of IL could be recovered after pyrolysis, but none of them reached near-100%. One of the possible reasons for the recovery is the dissolution of the saccharides. Compared to a robust hydrogen bonding

network of cellulose, inter- or intra-molecular hydrogen bondings of these saccharides are easily broken by IL, and then they form EDA complexes throughout the substances, resulting in the dissolution with increase in the temperature. In fact, all of the residues after pyrolysis were aggregated as with that of cellulose/[BMIM]Cl (shown in Figure 8). The IL thus surrounding the saccharides was possibly involved in the char formation reaction and incorporated in the resulting char. For a related reason, the nature of these saccharides more prone to form char than cellulose also influences the recovery.

**Figure 10.** Yields of major compounds detected in GC-MS analysis from pyrolysis of glucose, cellobiose,  $\alpha$ -cyclodextrin and starch in the (a) absence and (b) presence of [BMMIM]CF<sub>3</sub>SO<sub>3</sub>.

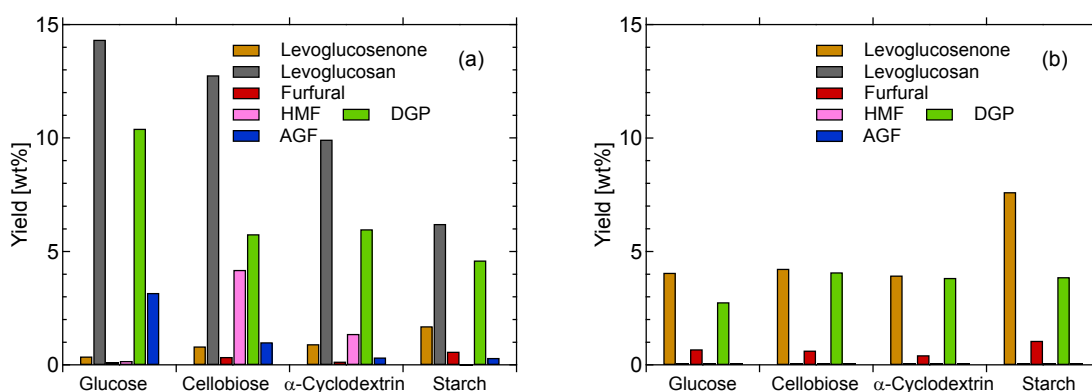


Figure 10 presents the change in major compounds detected in GC-MS analysis by the effect of IL. Clear differences appeared in the yields of levoglucosan, which was not detected in the catalytic pyrolysis. The yields of levoglucosenone obviously increased with the use of IL, but were not comparable to that from cellulose. It is known that glucose produces less levoglucosan and more furans (HMF in particular) than cellulose via pyrolysis [28]. This means that the formation of dehydrated sugars, such as levoglucosan and levoglucosenone, is less significant for these saccharides because the highest yield of levoglucosan + levoglucosenone in non-catalytic pyrolysis was achieved by glucose. The low yields of levoglucosenone from the saccharides other than cellulose are, therefore, reasonable.

In our previous work [16], it was confirmed that levoglucosenone formed from levoglucosan by the dehydration in the presence of IL. However, in this study, the yields of levoglucosenone in catalytic pyrolysis were clearly lower than those of levoglucosan in non-catalytic pyrolysis except for the case with starch. The difference in their yields indicates the loss of levoglucosan before the conversion into levoglucosenone by some reactions such as decomposition, polymerization and/or the existence of another pathway to form levoglucosenone directly from the saccharides.

Levoglucosan, HMF and AGF were undetected in the product of catalytic pyrolysis. This would be related to the catalysis of IL against hydroxyl group in the molecules. On the other hand, DGP, which also has hydroxyl group, survived the catalysis. In the catalytic pyrolysis of cellulose as well, DGP was the main by-product with the yield at 1.0 wt%. Non-hydroxy furanic compounds, furfural in particular, were identified as the second main by-product. It is necessary for the production of levoglucosenone with high purity to avoid or suppress the formation of these by-products, DGP and furans, which depends mainly on the nature of feedstock.

Saccharides other than cellulose, thus, could be used as the feedstock of levoglucosenone, although the yields/selectivities and the IL recoveries were relatively low. As a general trend, including cellulose, higher degree of polymerization seems to contribute to the formation of levoglucosenone.

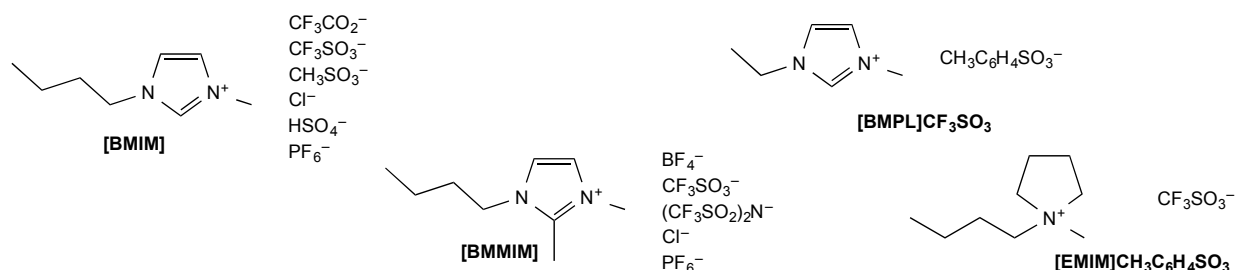
### 3. Experimental Section

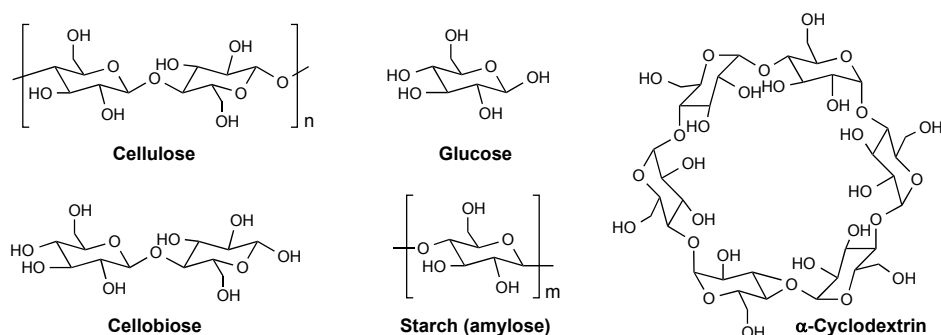
#### 3.1. Materials

The structures of ILs used in this study are displayed in Figure 11. All of the ILs are commercially available ones and used as received without further purifications. 1-Butyl-2,3-dimethylimidazolium chloride ([BMMIM]Cl), 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BMMIM]PF<sub>6</sub>), 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BMMIM]BF<sub>4</sub>, 98%), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, ≥ 98.0%), 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO<sub>4</sub>, ≥ 97.0%) and 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMIM]CF<sub>3</sub>SO<sub>3</sub>) were purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan; 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([BMPL]CF<sub>3</sub>SO<sub>3</sub>, ≥ 95.0%), 1-butyl-3-methylimidazolium methanesulfonate ([BMIM]CH<sub>3</sub>SO<sub>3</sub>, ≥ 95.0%), 1-butyl-3-methylimidazolium trifluoroacetate ([BMIM]CF<sub>3</sub>CO<sub>2</sub>, ≥ 96.5%) and 1-ethyl-3-methylimidazolium tosylate ([EMIM]CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, ≥ 98.0%) from Sigma-Aldrich Co. LLC., St. Louis, USA; 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ([BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N, > 98.0%) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM] PF<sub>6</sub>) from Tokyo Chemical Industry Co., Ltd., Tokyo, Japan; 1-butyl-2,3-dimethylimidazolium triflate ([BMMIM]CF<sub>3</sub>SO<sub>3</sub>, > 99.0%) was purchased from IoLiTec Ionic Liquids Technologies GmbH, Heilbronn, Germany. The ILs bearing CH<sub>3</sub>SO<sub>3</sub><sup>−</sup>, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>−</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> anions correspond to commonly termed sulfonate ILs.

Microcrystalline cellulose (powder, Aldrich) was used as the cellulose sample. As the feedstock for catalytic pyrolysis, the following saccharides (all from Wako Pure Chemical Industries, Ltd., Osaka, Japan) consisting mainly of glucose molecules were also examined: D(+)-glucose (glucose), D(+)-cellobiose (cellobiose), α-cyclodextrin and corn starch (starch), which correspond to mono-, di-, oligo- and poly-saccharides, respectively, as seen in Figure 12. The feedsotcks were used with predrying in *vacuo* at ambient temperatures overnight.

**Figure 11.** The structures and abbreviations of ILs used in this study.



**Figure 12.** The structures of saccharides used in this study.

### 3.2. Pyrolysis and the Product Analysis

Cellulose or other saccharide samples were mixed with IL at a ratio of 1:1 on a weight basis by stirring in a glass bottle for at least 15 min under ambient conditions. When the IL has melting point higher than a room temperature, the bottles were heated to a proper temperature (e.g., 60 °C for [BMMIM]CF<sub>3</sub>SO<sub>3</sub>) on a hotplate to melt the salt.

A complete description of the experimental rigs and methods for catalytic pyrolysis are reported in [16]. Briefly, the mixture of saccharide/IL (1 g) in a glass tube reactor was heated at a rate of 5 °C/min to a prescribed temperature with holding time of 20 min. The volatile products from pyrolysis were purged with nitrogen during the period of the reaction, and the condensable matter was collected in a series of two cold traps (kept at −30 and −70 °C) and an aerosol filter located downstream of the reactor. Non-condensable gases (typically CO and CO<sub>2</sub>) were collected with a gasbag for analysis by gas chromatography-flame ionization detection (GC-FID).

The collected condensable matter was recovered with methanol and subjected to the following analyses. The yield of levoglucosenone was determined by high-performance liquid chromatography (HPLC; Shimadzu LC-20 prominence series) equipped with a photo diode array detector (Shimadzu SPD-M20A) and Phenomenex Synergi Hydro-RP column using UV detection at 210 nm. Other major compounds in the condensable matters such as 1,6-anhydro-β-D-glucofuranose (AGF), 1,4:3,6-dianhydro-α-D-glucopyranose (DGP), furfural, HMF and levoglucosan were identified and quantified by gas chromatography-mass spectrometry (GC-MS; Perkin-Elmer Clarus SQ 8) equipped with a capillary column (GL Sciences TC-1701). Because of the unavailability of analytical standards for AGF and DGP, levoglucosenone (purchased from Carbosynth Ltd., Berkshire, UK) was used to semi-quantitatively determine their yields. Water content in the product was calculated from Karl Fischer titration using a Kyoto Electronics MKC-210.

The solid residue from pyrolysis was suspended in ethanol, stirred overnight, filtered and dried in *vacuo*. The resulting solid residue was defined as char. Ethanol in the filtrate was evaporated using a rotary evaporator operated at 60 °C and 175 mbar for 5 h, and the residue was defined as recovered IL. Above mentioned experimental procedures permit to obtain four types of products, *i.e.*, gas, condensable matter, char and recovered IL. The total mass balance was calculated from the weights of feedstock mixture and these products.

For comparison of catalysis, cellulose impregnated with organic or inorganic acids was prepared and examined for pyrolysis tests. An aqueous solution of acids (3 or 5 wt% based on dry cellulose) was

mixed with cellulose (cellulose/acid solution = 1:5 by weight), and the water was gently evaporated under vacuum at 40 °C for the impregnation. For pyrolysis tests, 0.5 g of the sample was used.

### 3.3. Characterizations

TGA data was acquired using a SII Nano Technology EXSTAR TG/DTA 7200. A sample placed on a platinum crucible was heated under flowing nitrogen with 5 °C/min heating rate up to 600 °C. Weight loss curves were determined by normalization of the sample weight on a dry mass basis. The dry mass was obtained by holding the temperature at 110 °C for 30 min during the measurement.

Acidity of ILs was characterized using a UV-visible spectroscopy (Perkin-Elmer LAMBDA 25) according to the reported method [12,25] that is theoretically capable of quantitative measurement of acidity for ILs. Each of ILs was dissolved in methanol, containing *p*-nitroaniline (0.025 g/L) as an indicator, at 30–80 mM and subjected to analysis.

## 4. Conclusions

Catalytic pyrolysis was conducted using various types of ILs as catalysts and saccharides as feedstocks aiming at the production of levoglucosenone. TGA was identified as a powerful approach to distinguish the activities of ILs, resulting in the selection of [BMMIM]BF<sub>4</sub>, [BMMIM](CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N and sulfonate ILs. Among them, sulfonate ILs showed the highest catalytic activity toward the formation of levoglucosenone from cellulose with the yield between 18.1–29.7 wt%. The IL cation had little influence on the catalytic activity of the IL; however, impregnation of the corresponding acid (sulfonic acids) into cellulose was not effective for the formation of levoglucosenone, indicating the importance of the presence of cation that forms IL with the anion. The values of  $T_{\text{start,IL}} - T_{\text{onset,cel}}$  confirmed the stability and activity of ILs bearing CF<sub>3</sub>SO<sub>3</sub><sup>−</sup> anion and indicated lower stability of the other sulfonate ILs, [BMIM]CH<sub>3</sub>SO<sub>3</sub> and [EMIM]CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>, during the pyrolysis of cellulose. The best IL from the viewpoint of levoglucosenone yield and IL recovery, among ILs examined in this study, was [BMMIM]CF<sub>3</sub>SO<sub>3</sub>. Discussion on the catalysis of sulfonate ILs revealed that the catalytic activities of ILs were supposedly related to their hydrogen bond basicity. Glucose, cellobiose, α-cyclodextrin and starch also could produce levoglucosenone via the catalytic pyrolysis using [BMMIM]CF<sub>3</sub>SO<sub>3</sub>, but at low yields, selectivities and recoveries of IL.

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## Conflicts of Interest

The authors declare no conflict of interest.

## References

1. Olivier-Bourbigou, H.; Magna, L.; Morvan, D. Ionic liquids and catalysis: Recent progress from knowledge to applications. *Appl. Catal. A* **2010**, *373*, 1–56.
2. Swatloski, R.P.; Spear, S.K.; Holbrey, J.D.; Rogers, R.D. Dissolution of Cellulose with Ionic Liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
3. Feng, L.; Chen, Z.-L. Research progress on dissolution and functional modification of cellulose in ionic liquids. *J. Mol. Liq.* **2008**, *142*, 1–5.
4. Lansalot-Matras, C.; Moreau, C. Dehydration of fructose into 5-hydroxymethylfurfural in the presence of ionic liquids. *Catal. Commun.* **2003**, *4*, 517–520.
5. Binder, J.B.; Raines, R.T. Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals. *J. Am. Chem. Soc.* **2009**, *131*, 1979–1985.
6. Tao, F.; Song, H.; Chou, L. Catalytic conversion of cellulose to chemicals in ionic liquid. *Carbohydr. Res.* **2011**, *346*, 58–63.
7. Dadi, A.; Schall, C.; Varanasi, S. Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment. *Appl. Biochem. Biotechnol.* **2007**, *137–140*, 407–421.
8. Pu, Y.; Jiang, N.; Ragauskas, A.J. Ionic Liquid as a Green Solvent for Lignin. *J. Wood Chem. Technol.* **2007**, *27*, 23–33.
9. Lee, S.H.; Doherty, T.V.; Linhardt, R.J.; Dordick, J.S. Ionic liquid-mediated selective extraction of lignin from wood leading to enhanced enzymatic cellulose hydrolysis. *Biotechnol. Bioeng.* **2009**, *102*, 1368–1376.
10. Cox, B.J.; Ekerdt, J.G. Depolymerization of oak wood lignin under mild conditions using the acidic ionic liquid 1-*H*-3-methylimidazolium chloride as both solvent and catalyst. *Bioresour. Technol.* **2012**, *118*, 584–588.
11. Jiang, F.; Zhu, Q.; Ma, D.; Liu, X.; Han, X. Direct conversion and NMR observation of cellulose to glucose and 5-hydroxymethylfurfural (HMF) catalyzed by the acidic ionic liquids. *J. Mol. Catal. A* **2011**, *334*, 8–12.
12. Bao, Q.; Qiao, K.; Tomida, D.; Yokoyama, C. Preparation of 5-hydroxymethylfurfural by dehydration of fructose in the presence of acidic ionic liquid. *Catal. Commun.* **2008**, *9*, 1383–1388.
13. Choi, J.S.; Simanjuntaka, F.S.H.; Oh, J.Y.; Lee, K.I.; Lee, S.D.; Cheong, M.; Kim, H.S.; Lee, H. Ionic-liquid-catalyzed decarboxylation of glycerol carbonate to glycidol. *J. Catal.* **2013**, *297*, 248–255.
14. Awad, L.; Demange, R.; Zhu, Y.H.; Vogel, P. The use of levoglucosenone and isolevoglucosenone as templates for the construction of C-linked disaccharides. *Carbohydr. Res.* **2006**, *341*, 1235–1252.
15. Samet, A.V.; Lutov, D.N.; Firgang, S.I.; Lyssenko, K.A.; Semenov, V.V. A concise approach to chiral chromenes based on levoglucosenone. *Tetrahedron Lett.* **2011**, *52*, 3026–3028.
16. Kudo, S.; Zhou, Z.; Norinaga, K.; Hayashi, J.-i. Efficient levoglucosenone production by catalytic pyrolysis of cellulose mixed with ionic liquid. *Green Chem.* **2011**, *13*, 3306–3311.
17. Fredlake, C.P.; Crosthwaite, J.M.; Hert, D.G.; Aki, S.N.V.K.; Brennecke, J.F. Thermophysical Properties of Imidazolium-Based Ionic Liquids. *J. Chem. Eng. Data* **2004**, *49*, 954–964.

18. Hunt, P.A. Why Does a Reduction in Hydrogen Bonding Lead to an Increase in Viscosity for the 1-Butyl-2,3-dimethyl-imidazolium-Based Ionic Liquids?. *J. Phys. Chem. B* **2007**, *111*, 4844–4853.
19. Hao, Y.; Peng, J.; Hu, S.; Li, J.; Zhai, M. Thermal decomposition of allyl-imidazolium-based ionic liquid studied by TGA–MS analysis and DFT calculations. *Thermochim. Acta* **2010**, *501*, 78–83.
20. Freemantle, M. Chapter 1 Introduction. In *An Introduction to Ionic Liquids*; RSC Publishing: Cambridge, UK, 2010; pp. 3–4.
21. Dobelev, G.; Rossinskaja, G.; Telysheva, G.; Meier, D.; Faix, O. Cellulose dehydration and depolymerization reactions during pyrolysis in the presence of phosphoric acid. *J. Anal. Appl. Pyrolysis* **1999**, *49*, 307–317.
22. Dobelev, G.; Dizhbite, T.; Rossinskaja, G.; Telysheva, G.; Meier, D.; Radtke, S.; Faix, O. Pre-treatment of biomass with phosphoric acid prior to fast pyrolysis. *J. Anal. Appl. Pyrolysis* **2003**, *68–69*, 197–211.
23. Sui, X.W.; Wang, Z.; Liao, B.; Zhang, Y.; Guo, Q.X. Preparation of levoglucosenone through sulfuric acid promoted pyrolysis of bagasse at low temperature. *Bioresour. Technol.* **2012**, *103*, 466–469.
24. Hallett, J.P.; Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. *Chem. Rev.* **2011**, *111*, 3508–3576.
25. Bao, Q.; Qiao, K.; Tomida, D.; Yokoyama, C. 1-Methylimidazolium Chlorosulfate ([HmIm]SO<sub>3</sub>Cl): A Novel Ionic Liquid with Dual Brønsted–Lewis Acidity. *Chem. Lett.* **2010**, *39*, 728–729.
26. Crowhurst, L.; Mawdsley, P.R.; Perez-Arlandis, J.M.; Salter, P.A.; Welton, T. Solvent–solute interactions in ionic liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790–2794.
27. Pulati, N.; Sobkowiak, M.; Mathews, J.P.; Painter, P. Low-Temperature Treatment of Illinois No. 6 Coal in Ionic Liquids. *Energy Fuels* **2012**, *26*, 3548–3552.
28. Sanders, E.B.; Goldsmith, A.I.; Seeman, J.I. A model that distinguishes the pyrolysis of D-glucose, D-fructose, and sucrose from that of cellulose. Application to the understanding of cigarette smoke formation. *J. Anal. Appl. Pyrolysis* **2003**, *66*, 29–50.