Production of Furan Compounds from Rice Straw with Ionic Liquid Treatment

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Furan compounds such as 5-hydroxymethylfurfural and furfural are valuable platform chemicals produced from lignocellulosics that can be used to produce polymers or liquid biofuels. In recent years, formation of furan compounds from glucose or xylose in ionic liquids has been studied. In this study, production of furan compounds from rice straw in various ionic liquids was conducted. 1-Methylimidazolium hydrogensulfate ([MIM]HSO₄) was found to be the most effective ionic liquid. Yields of 7.9 wt% of 5-hydroxymethylfurfural and 4.3 wt% of furfural were achieved at 160°C and 1 wt% rice straw loading in [MIM]HSO₄. It is also found that pretreatment with an ionic liquid, 1-ethyl-3-methylimidazolium acetate effectively enhanced the yield of furan compounds from rice straw by [MIM]HSO₄ treatment.

Key Words
Furan compound, Ionic liquid, Rice straw

1. Introduction
At present, the exhaustion of fossil resources such as coal, petroleum and natural gas and climate change caused by their large consumption are major global concerns. To overcome these problems, much attention has been focused on biomass resources as alternatives for production of liquid fuels and fine chemicals. Amongst various potential biomass sources, lignocellulosics such as wood and rice straw are abundant and do not compete with food resources.

5-Hydroxymethylfurfural (5-HMF) and furfural (FF), which can be derived from hexose and pentose in lignocellulosics, are considered to be important platform chemicals as raw materials for producing fine chemicals, biopolymers and biofuels. Recently, various treatments using water, organic solvents and organic-water mixtures have been studied for producing 5-HMF and FF from lignocellulosics. More recently, ionic liquids have been applied in the production of furan compounds such as 5-HMF and FF. Ionic liquids are organic salts with low, near-ambient melting points. They are regarded as "green solvents" because of their negligible vapor pressure, non-flammability and recyclability. Lansalot-Matras and Moreau reported that 5-HMF can be obtained from fructose by dehydration in 1-butyl-3-methylimidazolium fluoroborate, and various imidazolium-based ionic liquids have been studied to produce 5-HMF from fructose. Zang et al. demonstrated that glucose can be converted to 5-HMF at 70 mol% yield using CrCl₃ as a catalyst in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl). Su and co-workers investigated the conversion of cellulose to 5-HMF in [EMIM]Cl using CuCl₂/
CrCl₃ as a catalyst, showing that nearly 55.4 mol% yield can be achieved through treatment at 120 °C for 8 h. It was reported by Zhang et al. that the dehydronation of xylan and xylose with AlCl₃ as catalyst in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) gave 84.8% and 82.2% FF yields, respectively. Zhang also examined the conversion of lignocellulosics in [BMIM]Cl, retaining a 5-HMF yield of 24.2% and a FF yield of 33.6% from pine wood. In a study on the conversion of grass in [BMIM]Cl in the presence of H₃PW₁₂O₄₀, the yields of 5-HMF and FF were 20.1% and 26.8%, respectively. Other conversions of lignocellulosics to furan compounds have also been studied. However, in many of the cases mentioned above, catalysts were used. In this study, we studied the ability of ionic liquids to produce furan compounds from rice straw without catalysts. Ionic liquid treatment under various reaction conditions was investigated to optimize furan production.

2. Materials and methods

2.1 Samples and chemicals

Rice straw (Oryza sativa) flour between 90 and 180 mesh was used as a lignocellulosics sample. The ionic liquids used in this study are listed in Table 1. 5-Hydroxymethylfurfural (5-HMF), furfural, benzene, sodium chloride, acetic acid, acetonitrile, acetone and sodium hydrate were purchased from Wako Pure Chemical Industries (Osaka, Japan). [N-O-bis(trimethylsilyl)] trifluoroacetamide (BSTFA) was purchased from Sigma-Aldrich (St Louis, MO, USA). Rice straw flour was oven dried at 105 °C for 24 h before use.

2.2 Component analysis of rice straw

2.2.1 Ash

One gram of rice straw flour was heated at 600 °C for 4 h in an electric furnace to obtain the ash. The ash content was determined from the weight of ash measured as the proportion of the weight of sample charged.

2.2.2 Ethanol-benzene extractives

Two grams of rice straw flour were extracted with ethanol-benzene (1/2, v/v) for 24 h in a Soxhlet apparatus. The extracted sample was then dried in an oven at 105 °C for 24 h. The ethanol-benzene extractives content was determined as the proportion of the weight of extracted sample measured after drying to the weight of sample charged.

2.2.3 Hot water extractives

One gram of rice straw flour after extraction with ethanol-benzene and drying as described above was extracted with distilled water for 24 h in a Soxhlet apparatus. The extracted sample was then dried in the oven at 105 °C for 24 h. The content of hot water extractive was determined as a proportion of the extracted sample weight measured after drying to the weight of the sample charged.

2.2.4 Holocellulose

One gram of rice straw flour extracted with ethanol-benzene was loaded into a conical flask. Then, 75 mL of distilled water, 0.5 g of sodium chlorite and 0.1 mL of acetic acid were added to the flask and heated to 70-80 °C. Subsequently, 0.5 g of sodium chlorite and 0.1 mL of acetic acid was added into the flask every hour. After 6 h, the reaction media was filtered through a glass filter. The residue was washed with distilled water and then washed with acetone several times, oven-dried at 105 °C for 24 h and weighed to calculate the content of holocellulose in the sample.

2.2.5 α-Cellulose

Two grams of holocellulose and 5 mL of 17.5% sodium hydroxide were placed into a beaker. After 4 min, holocellulose was compressed and stirred for 5 min with a glass bar. After 20 min, 5 mL of distilled water was poured into the beaker and left for 5 min. This media was then filtered through a glass filter. The residue obtained was washed with an excess of distilled water and then washed with 40 mL of 10% acetic acid, oven-dried at 105 °C for 24 h and weighed to calculate the content of α-cellulose in the sample.

2.2.6 Acid-insoluble lignin and acid-soluble lignin

One gram of rice straw flour extracted with ethanol-benzene and 5 mL of 72% sulfuric acid were mixed and left for 4 h with compressing and stirring every hour. 560 mL of distilled water was added to this media, and the mixture obtained was boiled for 4 h. The mixture was then filtered through a glass filter. The residues obtained were then oven-dried at 105 °C for 24 h and weighted to calculate the content of acid-insoluble lignin in the sample. The filtrate was analyzed by UV spectrophotometer to determine the content of acid-soluble lignin. The content of acid-soluble lignin was calculated using following equation:

\[
\text{Content of acid-soluble lignin (\%)} = \frac{DV (As - Ab) \times 100}{a \times W}
\]

where \(D\) = dilution rate, \(V\) = volume of filtrate, \(As\) = absorbance of filtrate at 210 nm, \(Ab\) = absorbance of 3% sulfuric acid at 210 nm, \(a\) = absorbance index of lignin and \(W\) = weight of sample used.
| Ionic liquid                                               | Structural formula                                      | Supplier                        |
|----------------------------------------------------------|--------------------------------------------------------|---------------------------------|
| 1-Methyl-1-propylpyrrolidinium                           | ![Structural formula](image)                           | Kanto Chemical                  |
| hexafluorophosphate                                       | ![Structural formula](image)                           |                                 |
| 1-Butylpyridinium                                         | ![Structural formula](image)                           | Kanto Chemical                  |
| bis[(fluorosulfonyl)imidide]                              | ![Structural formula](image)                           |                                 |
| 1-Hexyl-1,4 diaza [2.2.2] bicycle octanium                | ![Structural formula](image)                           | Kanto Chemical                  |
| bis[(strifluoromethylsulfonyl)imidide]                    | ![Structural formula](image)                           |                                 |
| 1-Butylpyridinium                                         | ![Structural formula](image)                           |                                 |
| hexafluorophosphate                                       | ![Structural formula](image)                           | Wako pure chemical industry     |
| 1-Methylimidazolium                                       | ![Structural formula](image)                           | Kanto Chemical                  |
| trifluoro methanesulfate                                  | ![Structural formula](image)                           |                                 |
| 1-Methylimidazolium                                       | ![Structural formula](image)                           |                                 |
| bis[(strifluoromethylsulfonyl)imidide]                    | ![Structural formula](image)                           |                                 |
| Trihexyltetradecylphosphonium                             | ![Structural formula](image)                           | Kanto Chemical                  |
| bis[(strifluoromethylsulfonyl)amide]                      | ![Structural formula](image)                           |                                 |
| 1-Methyl-1-propylpyrrolidinium                           | ![Structural formula](image)                           |                                 |
| hexafluorophosphate                                       | ![Structural formula](image)                           | Kanto Chemical                  |
| Trihexyltetradecylphosphonium                             | ![Structural formula](image)                           |                                 |
| hexafluorophosphate                                       | ![Structural formula](image)                           | Kanto Chemical                  |
| Bis[1-Ethyl-3-methylimidazolium]                          | ![Structural formula](image)                           | Kanto Chemical                  |
| tetraethio cyanatecobaltate                               | ![Structural formula](image)                           |                                 |
| 1-Butyl-3-methylimidazolium                              | ![Structural formula](image)                           | Sigma Aldrich                   |
| hexafluoroantimonate                                      | ![Structural formula](image)                           |                                 |
| 1-Ethyl-3-methylimidazolium chloride                     | ![Structural formula](image)                           | Tokyo Chemical Industry         |
| ![Structural formula](image)                             | ![Structural formula](image)                           |                                 |
| 1-Ethyl-3-methylimidazolium methanesulfate               | ![Structural formula](image)                           | Kanto Chemical                  |
| ![Structural formula](image)                             | ![Structural formula](image)                           |                                 |
| 1-Ethyl-3-methylimidazolium p-toluenesulfonate           | ![Structural formula](image)                           | Tokyo Chemical Industry         |
| ![Structural formula](image)                             | ![Structural formula](image)                           |                                 |
| Tetrabutylammonium salicylate                            | ![Structural formula](image)                           | Tokyo Chemical Industry         |
| ![Structural formula](image)                             | ![Structural formula](image)                           |                                 |
| 1-Ethyl-3-methylimidazolium hydrogensulfate              | ![Structural formula](image)                           | Tokyo Chemical Industry         |
| ![Structural formula](image)                             | ![Structural formula](image)                           |                                 |
| 1-Methylimidazolium                                       | ![Structural formula](image)                           | Sigma Aldrich                   |
| hydrogensulfate                                           | ![Structural formula](image)                           |                                 |
| ![Structural formula](image)                             | ![Structural formula](image)                           |                                 |
2.3 Treatment with ionic liquids

Three grams of ionic liquids were heated at 120, 140, 160 or 180 °C in a glass flask. Samples were added into the flask at 1, 3 or 10 wt% loading by weight, and the ionic liquids and the reaction media were gently stirred.

2.4 Pretreatment with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), followed by ionic liquid treatment

Three grams of [EMIM]OAc were heated at 120 °C. 0.09 g of samples were added into [EMIM]OAc and reacted for 1 h with magnetic stirring. Then, 100 mL of distilled water was poured into the reaction media and stirred overnight. This mixture was filtered and the obtained residue was not dried. 0.03 g of residues were treated with 3 g of [MIM]HSO4 at 160 °C.

2.5 Evaluation methods

The products from samples in ionic liquids were analyzed by high performance liquid chromatography (HPLC) or gas chromatography (GC).

The samples for HPLC analysis were prepared as follows: 40 μL of the reaction medium was mixed with 360 μL of distilled water and then filtered through a 0.45-μm filter. The filtrates were analyzed under following conditions: column, Shodex Sugar KS-801; flow rate, 1 mL/min; eluent, ultrapure water; column temperature, 80 °C; detector, refractive index detector (RID) and ultraviolet-visible (UV) detector set 280 nm.

The samples for GC analysis were prepared as follows: 20 μL of the reaction medium was homogeneously added into 200 μL of acetonitrile. After dehydration with sodium sulfate, the obtained mixture was filtered using a 0.45-μm filter. Then, 150 μL of the filtrate was silylated at room temperature using 100 μL of BSTFA. The silylated liquids were analyzed by GC under following conditions: column, InertCap 17 (GL Sciences); column temperature, 60 °C (0 → 1 min), 60 → 250 °C (1 → 10.5 min) and 250 °C (10.5 → 40 min); carrier gas, helium; flow rate, 1 mL/min; detector, flame ionization detector (FID); injector and FID temperature, 250 °C and 230 °C, respectively.

The yield (wt %) of products was calculated using the following equation:

\[ \text{Yield (wt %)} = \frac{\text{weight of products}}{\text{weight of sample loaded}} \times 100 \]  

3. Results and discussion

3.1 Analysis of components on rice straw

Prior to studying the ability of various ionic liquids to produce 5-HMF and FF from rice straw, an analysis of the components of the rice straw used in this study was conducted. The content of rice straw is shown in Table 2. The contents of cellulose, hemicellulose and lignin, which are main components of lignocelluloses, were 26.3%, 16.5% and 16.6%, respectively. Compared with the values reported previously by He et al. (33.4% cellulose, 28.2% hemicellulose and 7.4% lignin), cellulose and hemicellulose were 7.1% and 11.7% lower, and lignin was 9.2% higher. In addition to these three components, the ash and hot-water extractives contents were also high, at 15.6% and 18.4%, respectively. The ash content of our rice straw was higher than that in other lignocelluloses such as wheat straw or willow wood, and 75% of the ash was found to be Si.

3.2 Production of furan compounds with ionic liquid treatment

To study the ability of ionic liquids to produce furan compounds, rice straw was treated in the various ionic liquids listed in Table 1. Fig. 1 shows HPLC chromatograms of samples treated in [MIM]HSO4 and [EMIM]MES at 140 °C for 2 h. Although 5-HMF and FF were detected in [MIM]HSO4, peaks for furan compounds cannot be observed in [EMIM]MES. This suggested that [MIM]HSO4 can produce furan compounds, while [EMIM]MES has no ability to produce furan compounds. The maximum yields of 5-HMF and FF from rice straw were calculated from HPLC analyses of the ionic liquids after treatment at 140 °C for 6 h, and are shown in Table 3. Amongst the various ionic liquids, [EMIM]HSO4 and [MIM]HSO4 were effective in producing 5-HMF with yields of 3.9 and 3.7 wt%, respectively. FF were produced at yields of 1.5 wt% in [MIM]HSO4 and 0.5 wt% in [EMIM]HSO4. Lower yields of these furan compounds was achieved in [EMIM]Tos, while [THP]PF6, [EMIM]CoTSCN and [EMIM]Cl could produce only

Table 2 Chemical composition of rice straw used in this study

| Components                   | Content (%) |
|------------------------------|-------------|
| α-Cellulose                  | 26.3        |
| Hemicellulose                | 16.5        |
| Klason lignin                | 14.7        |
| Acid soluble lignin          | 1.9         |
| Ethanol/Benzene extractives  | 2.9         |
| Hot-water extractives        | 18.4        |
| Ash                          | 15.6        |
have the same cation as [MIM]HSO₄, could not produce furan compounds at all. Therefore, it is thought that cations of ionic liquids used in this study have no influence on the production of furan compounds. However, further researches are necessary to elucidate the effects of cations.

From these results, ionic liquids containing the HSOf⁻ anion are concluded to be suitable for the conversion of rice straw to furan compounds, with the most effective ionic liquid amongst those tested being [MIM]HSO₄.

For [MIM]HSO₄, various reaction conditions were studied to attain higher yields of furan compounds. Figs. 2 and 3 show the yields of 5-HMF and FF, respectively, produced at various temperatures. As shown in Fig. 2, the yield of 5-HMF at 120 °C increased gradually as reaction time increased, while those at 140, 160 and 180 °C reached a maximum at between 15 min and 1 h. A higher reaction

5-HMF. Various ionic liquids other than those mentioned above have no ability to produce furan compounds. Furan compounds were produced from polysaccharides via two steps, depolymerisation of them by hydrolysis followed by subsequent dehydration of monosugar produced. It is reported that the hydrolysis and dehydration are promoted by acid. Since [MIM]HSO₄ and [EMIM]HSO₄ contain HSOf⁻ that is strong acid anion, high yields of furan compounds were achieved with the treatment of these ionic liquids. As for cation, [MIM]TFSI and [MIM]CF₃SO₃, which

Table 3 Maximum yields of 5-HMF* and FF** obtained from rice straw using various ionic liquids

| Ionic liquid     | Maximum yield (%) | 5-HMF | FF  |
|------------------|-------------------|-------|-----|
| [MPPR]PF₆        | 0.0               | 0.0   |     |
| [BPYR]FSI        | 0.0               | 0.0   |     |
| [HDaOTFSI]       | 0.0               | 0.0   |     |
| [BPYR]PF₆        | 0.0               | 0.0   |     |
| [MIM]CF₃SO₃      | 0.0               | 0.0   |     |
| [MIM]TFSI        | 0.0               | 0.0   |     |
| [THP]TFSI        | 0.0               | 0.0   |     |
| [MPPR]PF₆        | 1.0               | 0.0   |     |
| [THPP]PF₆        | 1.0               | 0.0   |     |
| [EMIM]2CoTSCN    | 0.4               | 0.0   |     |
| [EMIM]SbF₆       | 0.0               | 0.0   |     |
| [EMIM]Cl         | 0.0               | 0.0   |     |
| [EMIM]MES        | 0.0               | 0.0   |     |
| [EMIM]Tos        | 1.1               | 0.7   |     |
| [N14H4S]Sal      | 0.0               | 0.0   |     |
| [EMIM]HSO₄       | 3.9               | 0.5   |     |
| [MIM]HSO₄        | 3.7               | 1.5   |     |

* 5-HMF is an abbreviation of 5-hydroxymethylfurfural.
** FF is an abbreviation of furfural.

Fig. 1 HPLC chromatograms for products from rice straw in ionic liquids at 140 °C.

Fig. 2 Yields of 5-HMF from rice straw treated with [MIM]HSO₄ at various temperatures.

Fig. 3 Yields of FF from rice straw treated with [MIM]HSO₄ at various temperatures.
temperature reduced the duration of treatment required to achieve a maximum yield. These maximum values ranged from 3.4 to 6.8 wt%. However, the maximum at 160 °C was around 6 wt%, which was almost the same as that at 180 °C. It has been found that 5-HMF and FF are not stable and degrade under acidic conditions to form humins. [MIM] HSO₄ is an acidic ionic liquid and thus, 5-HMF is thought to decrease after reaching the maximum yield, through degradation in [MIM]HSO₄.

In contrast to the results for 5-HMF production, the yields of FF at all reaction temperatures studied in this paper reached a maximum value, as shown in Fig. 3. The trend in yields gave results similar to those for 5-HMF. That is, a higher yield was attained at higher reaction temperatures, over shorter reaction times. However, above 140 °C, the maximum yield was achieved within 10 min, which is shorter than the treatment time for 5-HMF. There was no significant difference in the maximum yield obtained at 160 °C and 180 °C. However, maximum yields for total of 5-HMF and FF were the highest at 160 °C. Thus, 160 °C was chosen as a suitable reaction temperature for subsequent experiments.

Yields of 5-HMF and FF at various rice straw loadings are shown in Figs. 4 and 5, respectively. As in Fig. 4, the highest yield of 5-HMF at 7.5 wt % was obtained at a loading of 1 wt%. When the loading increased to 3 or 10 wt%, the yield of 5-HMF decreased to around 3.5 wt%. Thus, at lower loadings, a higher yield can be achieved through homogeneous reaction with [MIM]HSO₄. Little difference in the yields of FF can be observed in Fig. 5, although the yield of FF was slightly higher at a loading of 1 wt%. Thus, 1 wt% loading was applied in the experiments below.

Fig. 6 shows the 5-HMF and FF yields with time at a loading of 1 wt% and 160 °C, which are thought to be the most suitable reaction conditions for attaining high yields of 5-HMF and FF. The maximum yields of 5-HMF and FF were 7.9 wt% at 30 min and 4.2 wt% at 3 min, respectively. These yields were the highest achieved in the absence of the pretreatment of rice straw described below.

### 3.3 Effect of pretreatment with 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc)

To enhance the yield of chemicals produced from lignocellulosics, various pretreatments that break their rigid cellular structures have been investigated. A previous study reported that [EMIM]OAc is an effective pretreatment for enzymatic hydrolysis of lignocellulosics because it can weaken various chemical bonds. To investigate the influence of pretreatment with [EMIM] OAc...
on furan production by [MIM]HSO₄ treatment, rice straws were treated with [EMIM]OAc at 120 °C for 1 h before the treatment with [MIM]HSO₄. The maximum yields of 5-HMF and FF obtained are shown in Table 4, as well as the total amounts of 5-HMF and FF produced. The maximum yields of 5-HMF and FF were 16.0 wt% and 14.7 wt%, respectively. The yields of 5-HMF and FF from sample with pretreatment were markedly increased compared with that from untreated rice straw. Moreover, the reaction times required to reach maximum yields of both 5-HMF and FF was shorter than without pretreatment. This may have been because the strong chemical bonds within cellulose and hemicellulose were weakened by treatment with [EMIM]OAc, and consequently the reactivity between [MIM]HSO₄, and the sample was increased. From these results, [EMIM]OAc is concluded to be an effective ionic liquid for pretreatment of lignocellulosics.

4. Conclusion

It was found that a number of ionic liquids are able to convert rice straw into furan compounds. Rice straw was converted to furan compounds in ionic liquids that contain the sulfonyl group and, in particular, [MIM]HSO₄, was effective. 12.1 wt% yields of furan compounds were obtained with [MIM]HSO₄ treatment at 160 °C with a rice straw loading of 1 wt %.

The yields of 5-HMF and FF obtained from samples pretreated with [EMIM]OAc were 16.0 wt% and 14.7 wt%, respectively, which were both higher than those from untreated samples. Pretreatment with [EMIM]OAc may weaken the strong chemical structure of rice straw.

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