Chromium halides mediated production of hydroxymethylfurfural from starch-rich acorn biomass in an acidic ionic liquid

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Abstract

Chromium halides were introduced for the sustainable production of hydroxymethylfurfural (HMF) from raw acorn biomass using an acidic ionic liquid. The free sugars (glucose and maltose) released by the acidic hydrolysis of the biomass were confirmed by the FT-IR absorption bands around 995–1014 cm\(^{-1}\) and HPLC. FESEM analysis showed that the acorn biomass contains various sizes of starch granules and their structures were severely changed by the acidic hydrolysis. An optimal concentration of HCl for the HMF yields was 0.3 M. The highest HMF yield (58.7 ± 1.3 dwt %) was achieved in the reaction mixture of 40% [OMIM]Cl + 10% ethyl acetate + 50% 0.3 M HCl extract containing a mix of CrBr\(_3\)/CrF\(_3\). The combined addition of two halide catalysts was more effective in the synthesis of HMF (1.2-fold higher on average) than their single addition. The best productivity of HMF was found at 15% concentration of the biomass and at 50%, its relative productivity declined down to ca. 0.4-fold.

1. Introduction

In current, the sustainability issue in the chemical industry has been considerably spread because of its importance on the protection of environment and the utilization of energy against the depletion of fossil fuel. Now, the most attractive resources for chemical sustainability can be derived from plant kingdom because plants are the reservoir of carbon sources that can be used as platform intermediates for the production of diverse carbon-depletion of fossil fuel. Now, the most attractive resources for chemical sustainability can be derived from plant kingdom because plants are the reservoir of carbon sources that can be used as platform intermediates for the production of diverse carbon-derived compounds.\(^1\)–\(^4\) For example, hydroxymethylfurfural (HMF), which is the platform chemical for the syntheses of various carbohydrate compounds including liquid biofuels, such as dimethylfuran (DMF), liquid alkanes, thermo-resistant polymers and complex macrocycles, and some pharmaceutical precursors, can be synthesized from biomass-derived carbohydrates.\(^5\)–\(^7\) Recent studies showed that HMF can be produced from various carbohydrate sources, such as fructose, glucose, sucrose, starch, inulin, cellulose, lignocellulose, and other simple sugars.\(^8\)–\(^13\) Among these, cellulose and lignocellulosic biomass resources are more abundant than other ones. However, more improved biorefinery technologies are required for the synthesis of HMF from them because not only its yields are low but also its synthetic process is not easy when raw cellulose/lignocellulosic biomass materials are directly used. In contrast, starch, which is the most abundant carbohydrate conserved in many plants, can be more easily depolymerized into simple sugars (mainly glucose) and transformed into HMF by simple processes.\(^12\)–\(^14\)

In particular, the direct use of raw biomaterials containing high amounts of starch eliminates its purification step and thus can be contributive to reduction of energy and CO\(_2\) emission in synthesizing HMF. In this context, raw acorn is a good biomaterial for the sustainable production of HMF because it is obtainable from a wild perennial tree which can grow in the barren soils, meaning that there is no need for its systematic farming, and contains high amounts of starch (ca. 70–72% by dry weight).

HMF is synthesized from carbohydrates via thermal dehydration reaction in the presence of acid and metal catalysts.\(^7\) A recent work demonstrated that HMF could be produced from the purified acorn starch in the acidic ionic liquid (1-octyl-3-methylimidazolium chloride, [OMIM]Cl).\(^{13}\) Because [OMIM]Cl, a disubstituted imidazolium-based ionic liquid, has high miscibility with water, less viscosity, high thermal stability, low vapor pressure, low melting points, and other physico-chemical properties favorable to chemical reactions, it can be used as both solvent and catalyst for the synthesis of HMF.\(^{12,13,15}\)

Chromium halides have been primarily used as a cocatalyst to promote the chemical oxidation reaction of various alkylic compounds.\(^{16}\) Some recent reports demonstrated that chromium-based catalysts and other metal halides play a key role in the synthetic reactions of some organic compounds including HMF.\(^{5,12,13,17–19}\) They provided evidence that the yields of HMF was highly improved by the addition of lithium halides and chromium chloride to its synthetic processes using sugar polymers, such as cellulose, lignocellulose, and starch.\(^{5,12,13,17–19}\) In our work, we examined the catalytic activity of 4 different chromium halides on the yield of HMF.
in an acidic ionic liquid using raw acorn biomass and the structural changes of its chemical components were characterized by FT-IR spectroscopy in order to provide basic information about the sustainable production of HMF.

2. Experimental

2.1. Reaction procedure

The acorn samples were dehulled, sliced into small pieces, and dried. The dried pieces were then pulverized into powder (Fig. 1) using a sample mill (Cyclotech 1093). Four chromium halides, CrCl2 (97%, anhydrous), CrCl3 (99.5%, 6H2O), CrBr3 (crystalline, 4H2O), and CrF3 (98%, hydrate), were purchased from a commercial supplier (Alfa Aesar, Mass., USA). [OMIM]Cl was obtained from Merck (Germany) and other chemicals were also purchased from commercial suppliers.

In the first step, the extracts of the acorn powder were prepared using 10% (w/v) powder suspended in four different HCl concentrations (0, 0.3, 0.5, and 1 M) by heating at 80 °C for 2 h with stirrings. After the suspensions were centrifuged at 13,500 g for 60 min, the supernatants (extracts) were collected and stored for further uses (Fig. 1).

The effects of HCl and the reaction time on the yields of HMF were investigated in a reaction mixture containing the reaction solvent (4 g [OMIM]Cl + 1 mL ethyl acetate) mixed with 5 mL of the extract prepared in different concentrations of HCl as described above. The relative productivity of HMF was determined for 30, 60, 90, or 120 min using a heating mantle. For the reaction with halide catalysts, the reactant containing [OMIM]Cl and the catalyst was pre-heated at 120 °C for 15 min before the biomass extract and ethyl acetate were added. For the effect of single addition of the catalysts, 0.2 g of each catalyst was added to the reaction mixture. For the combined addition of two catalysts, 0.1 g each of two catalysts (total 0.2 g) was mixed with the reaction mixture. The reactions were conducted for 60 min or 90 min.

For the test of HMF productivity, nine different concentrations (10, 15, 20, 25, 30, 35, 40, 45, and 50%) of the acorn biomass were prepared in 0.3 M HCl and hydrolyzed at 80 °C for 2 h. The reaction for the production of HMF was performed at 120 °C for 90 min in the same reaction mixture with a mix of two catalysts (each 0.1 g; CrCl3/CrF3 because of much cheaper than other ones) as described above. The relative productivity of HMF was determined using the HMF yield obtained from 10% of the acorn biomass as a control (a value = 1).

All measurements were estimated with the mean values of at least four independent reactions and expressed with standard deviations.

2.2. FT-IR analysis

Fourier transform infrared (FT-IR) method was used to measure the sugar samples prepared by precipitating the extracts with ethanol. The FT-IR analysis was performed with microscopic FT-IR/Raman spectroscopy equipped with a diamond crystal ATR (attenuated total reflectance) accessory (Vertex 80 V, Bruker). About 2 mg of the sample was placed onto the ATR crystal. The FT-IR spectra were recorded on Bruker spectrometer (Germany) in the spectral range of 4000–550 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). Between determinations, the crystal was carefully cleaned with ethyl alcohol and memory effects were avoided by consecutively recording the replica spectra.

2.3. FESEM analysis

For field emission scanning electron microscopy (FESEM), the samples were vacuum-dried and then they were coated with platinum (Pt) (20 nm thick) using a vacuum ion sputter (108auto, Cressington, UK). Each Pt-coated specimen was then observed with a field emission scanning electron microscope (JEM-6700F, JEOL, Japan) at the probe energy level of 5.0 kV and its image was photographed at magnifications of 1000× or 3000×.

2.4. HMF and sugar analysis by HPLC

HMF and sugars were analyzed with a high performance liquid chromatography (HPLC, Waters). An absorbance detector (Waters) and a refractometer (Waters) were used for their determination. HMF was quantified with a Waters XBridge C18 reversed-phase column (4.6 mm × 150 mm, 5 μm) using a gradient mobile phase at a flow rate of 0.7 mL/min (UV at 320 nm). The gradient condition was as follows: 100% (v/v) water phase for 2 min, transition and gradient phase in the ratio of 80% (v/v) water and 20% (v/v) MeOH for 8 min, and 100% (v/v) water for 20 min including transition time. For quantification of sugars, a YMC-Pack Polyamine II column (4.6 mm × 250 mm, 5-5 μm, 12 nm) was used with a mobile phase (75:25, acetonitrile/water) at a flow rate of 1 mL/min.

3. Results and discussion

3.1. Characterizations of raw acorn biomass and its chemical components by FT-IR and FESEM analyses

Acorn, which contains high amount of starch (70–72% by dry weight), can be an excellent raw biomaterial for high yield of HMF because starch is a good feed material in the synthesis of HMF.\(^{13}\) Starch hydrolysis to simple sugars is an important step for high yield of HMF (Fig. 1). Thus, the first goal of this study was to establish the reaction condition allowing efficient hydrolysis of raw acorn to carbohydrates which can be converted into HMF. Its efficiency was monitored by FT-IR\(^{20,21}\) and FESEM analyses.\(^{22}\) Figure 2 shows FT-IR spectra of the acorn biomass and its component carbohydrates. In the raw acorn biomass, some major absorbance peaks, which typically appear for C–OH and C–O–C stretching modes of carbohydrates\(^{23,24}\) were identified between 900 and 1200 cm\(^{-1}\) region (BP in Fig. 2A). These infrared spectra
were compared with those from the native acorn starch preparations (SP in Fig. 2A). Their band pattern was very similar with each other, confirming that the main component of acorn biomass would be starch because the infrared absorption peaks around 997 and 1149 cm\(^{-1}\) were detected in both samples (Fig. 2A), which would be attributed to the \(\alpha-1,4/1,6\)-glycosidic linkages (\(\alpha-C_1-O-C_4/\alpha-C_1-O-C_6\) vibration modes) present in starch molecules and the C–C stretching appearing in pyranose sugars.\(^{20,24-27}\) However, when an acid (HCl) was applied, a small change in the FT-IR spectra was observed around the peak region of 995–1014 cm\(^{-1}\) in the acid hydrolysates (Fig. 2B), which was not found in the raw acorn biomass (Fig. 2A). This shift of the absorption band after acid hydrolysis may indicate that some changes in the chemical structure of the acorn starch occurred, implying its depolymerization into glucose units or other small pyranose sugars such as maltose. The reason for this explanation is based on the fact that the peak region (1149 cm\(^{-1}\)) contributing to pyranose sugars\(^{20}\) was present and the strong peak around 995 cm\(^{-1}\) was found (Fig. 2B), which appears for glucose\(^{28}\) as shown in the absorption band of glucose standard (Fig. 2B–G). HPLC analysis supported the above spectral characterization from FT-IR determination by providing evidence that the free glucose and maltose in the hydrolysates from the raw acorn biomass were present after acid hydrolysis (Fig. 3).

Figure 4 reveals the structural changes of the raw acorn biomass by acid hydrolysis. The FESEM observation before acid hydrolysis displays the native image of raw acorn biomass sample, showing a variety of different shapes (some are spherical or ellipsoidal) and sizes that ranged from approximately 3 \(\mu\)m to 8 \(\mu\)m. This image also shows the presence of some debris and the substantial amounts of starch granules in the biomass sample (Fig. 4A). In contrast, the FESEM observation after acid hydrolysis (in 0.3 M HCl solution) reveals completely disrupted surfaces of the starch granules, which are typically found by acid hydrolysis (Fig. 4B). This disrupted image may explain that the starch and other carbohydrates contained in the starch granules would have been released into its solution medium.\(^{29,30}\)

### 3.2. Effects of HCl concentration and reaction time on the yields of HMF from raw acorn biomass

It is known that acid catalysts play an important role in the synthesis of HMF.\(^5\) Some recent publications have demonstrated that HCl and \(\text{H}_2\text{SO}_4\) are effective acid catalysts for its synthesis from carbohydrates, such as fructose, glucose, sucrose, and starch in the presence of an ionic liquid.\(^{12,13,31}\) In this experiment, the effects of HCl concentration and reaction time on the yields of HMF were surveyed to select an optimal concentration of HCl and reaction time in synthesizing HMF from raw acorn biomass. As seen in Figure 5, the absence of HCl (at 0 M HCl) showed negligible yields of HMF, whereas the presence of HCl in the reaction mixture positively affected the synthesis of HMF. Its highest yield (28.4 \(\pm\) 1.6 dwt %; % of dry weight) was achieved in the reaction mixture with 0.3 M HCl by undergoing its reaction for 90 min, indicating that 0.3 M HCl would be the most effective for the synthesis of HMF from raw acorn biomass. However, above 0.3 M HCl, its yields began to decline (Fig. 5). The negative effect at higher HCl concentrations (0.5 and 1 M HCl) on the yield of HMF may be due to the overactivity of H\(^+\) caused probably by high H\(^+\) density derived from its high concentrations.\(^{32}\) This explanation was supported by other works that HCl concentrations above a critical level
decreased the yields of HMF.13,33,34 Another finding was that a rapid increase in the yields of HMF occurred after 30 min reaction time in all reactions except no HCl, and after 60 min (at 0.5 M and 1 M HCl) or 90 min (at 0.3 M HCl), its yields began to decrease (Fig. 5). The above results illustrate that the interaction between HCl concentration and the reaction time could be a critical factor for the high yield of HMF from the acorn biomass. In particular, although HCl functions as an important factor in synthesizing HMF, there has been no direct evidence on its reaction mechanism. Nonetheless, one explanation may be possible: As a Brønsted acid catalyst, the proton from HCl would act as a mediator for the hydrolysis of starch present in the acorn biomass into simple sugars that are convertible into HMF by attacking the glycosidic oxygen in the starch, resulting in protonated glycosides. These protonated forms of the glycosides are rapidly liberated into free sugars (mainly glucose units in this case). The interaction between H⁺ activity (from HCl) and the dual properties (cation and anion) of [OMIM]Cl present in the reaction medium would help induce the dehydration reaction of the free sugars into HMF by forming the key intermediates such as 1,2-enediol via their isomerization reaction.5,33,35,36 However, more studies are required for further detailed explanation.

3.3. Effects of chromium halides on the yields of HMF

It is known that chromium halides, such as chromium bromide and chloride promote the reaction rate in organic synthesis by catalyzing its oxidation reactions.16 A recent study first introduced CrCl₂ for high yields of HMF from the purified carbohydrates.18 In our work, four chromium halides (CrCl₂, CrCl₃, CrBr₃, and CrF₃) were employed to scrutinize their effects on the yields of HMF that are produced directly from raw acorn biomass. Figure 6 displays that the addition of halide catalysts contributed to an increase in the HMF yields on the whole. Moreover, the combined addition of two halide catalysts enhanced the HMF yields up to ca. twofold compared to that with no catalyst. The highest yield of HMF (58.7 ± 1.3 dwt %) was observed in the reaction mixture with the combined catalysts of CrBr₃/CrF₃ by undergoing its reaction for 90 min (Fig. 6). Among the reactions with single addition of the halide catalysts, CrCl₂ was most effective for the HMF yield (46.7 dwt % at 30 min and 52.8 dwt % at 90 min reaction time), whereas CrF₃ was lowest in its yield (4.1 dwt % at 30 min and 36.7 dwt % at 90 min reaction time). The positive effect of the halide catalysts on the HMF yield may be involved with the interactive coordination mechanism of the halide catalysts with the free carbohydrates (mainly glucose) released from the acorn biomass by acid hydrolysis in the presence of [OMIM]Cl ionic liquid.18 This mechanism is based on the fact that, in the presence of [OMIM]Cl, the Cr metal with halides plays a critical role by coordinating with...
the hydroxyl proton located at the anomeric carbon of the free glucose. This may lead to isomerization of the glucose to fructofuranose via glucose mutarotation by forming an enolate in the chromium halide–sugar complex, the key intermediate in their pathways. Through their consecutive reactions, the intermediate products are rapidly dehydrated into HMF.18,37

Another interesting finding was that the effect of the halide catalysts on the HMF yield was different with each other (Fig. 6), suggesting that their catalytic activity varied with the type of halide. The order of the promotion effect on their catalytic activity was CrCl$_2$ > CrCl$_3$ > CrBr$_3$ > CrF$_3$. Moreover, the promotion effect was higher in chloro-halide groups (CrCl$_2$ and CrCl$_3$) than in other halide ones (CrBr$_3$ and CrF$_3$) (Fig. 6). This difference may result from their different coordination ability of halo-groups with chromium center.17 That is, the reason for higher catalytic activity of chloro-groups would be due to their stronger coordination ability with chromium center than that of other two halo-groups (bromo- and fluoro-group).

Figure 6 also provides data that the combined addition of two halide catalysts to one reaction was more effective in the synthesis of HMF from the raw acorn biomass compared with that of their single addition because its yields in the former were higher (ca. 1.2-fold on average) than in the latter. However, contrary to our expectations, the highest promotion effect on the HMF yield was achieved in the combined addition of CrBr$_3$/CrF$_3$ and the lowest was found in CrCl$_3$/CrBr$_3$ (Fig. 6). These data suggest that their promotion efficiency may be dependent on the synergistic coordination ability of the two catalysts (as a ligand) used with chromium metal under the given reaction condition.8,17,19 In addition, the reaction time should be considered for high HMF yield from the raw acorn biomass because after 90 min reaction time, insoluble solid products began to occur (data not shown). Our data indicated that the optimal reaction time would be between 60 and 90 min (Fig. 6) and lengthening the reaction time resulted in the formation of some insoluble solid products (data not shown).

3.4. Effects of biomass concentration on the productivity of HMF

The productivity of HMF is an element of economical importance for its industrial uses because it could be a factor in determining the production cost of HMF. Its productivity was
examined with nine concentrations of acorn biomass from 10% to 50% (w/v) at intervals of 5% to compare their relative productivity. As shown in Figure 7, the highest productivity was identified with a value of ca. 1.2-fold greater at 15% concentration of the biomass than the control one (10%). However, over 20% concentration its productivity began to decrease and reached down to a value of ca. 0.4-fold at 50% (Fig. 7). In particular, much lower HMF productivity began to decrease and reached down to a value of 1.2-fold greater at 15% concentration of the biomass compared to 10% (Fig. 7). However, over 20% concentration its productivity began to decrease and reached down to a value of ca. 0.4-fold at 50% (Fig. 7).

4. Conclusions

We provide a new route to the sustainable production of HMF using raw acorn biomass obtainable from the oak perennial that can grow in the wild soils and is a non-food plant. FT-IR spectroscopy, FESEM, and HPLC analysis confirmed that the major hydrolysis products of the biomass were glucose and maltose. The combined addition of two halide catalysts was more effective for the synthesis of HMF than their single addition. The highest yield of HMF occurred in the reaction mixture containing a mix of CrBr₃/CrF₃. The best productivity was achieved at 15% concentration of the biomass, indicating that it would be suitable for the practical production of HMF from the biomass.

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References