



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 CrBr₃/CrF₃. 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.

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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-derived compounds.^{1–4} For example, hydroxymethylfurfural (HMF), which is the platform chemical for the syntheses of various carbon 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.^{5,8–13} Among these, cellulosic 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 cellulosic/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 CO₂ 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.⁵ 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 alkyl 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.^{8,12,13,17–19} 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.^{8,13,19} In our work, we examined the catalytic activity of 4 different chromium halides on the yield of HMF

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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, CrCl_2 (97%, anhydrous), CrCl_3 (99.5%, $6\text{H}_2\text{O}$), CrBr_3 (crystalline, $6\text{H}_2\text{O}$), and CrF_3 (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 $13,500g$ 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 at 120°C for the specified reaction time (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 preheated 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; $\text{CrCl}_3/\text{CrF}_3$ 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 $4000\text{--}550\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} . Between determinations, the crystal was carefully cleaned with ethyl alcohol and memory effects were avoided by inconsecutively 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 $1000\times$ or $3000\times$.

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 C_{18} reversed-phase column ($4.6\text{ mm} \times 150\text{ mm}$, $5\text{ }\mu\text{m}$) 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 ($4.6\text{ mm} \times 250\text{ mm}$, $S\text{-}5\text{ }\mu\text{m}$, 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 analysis.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

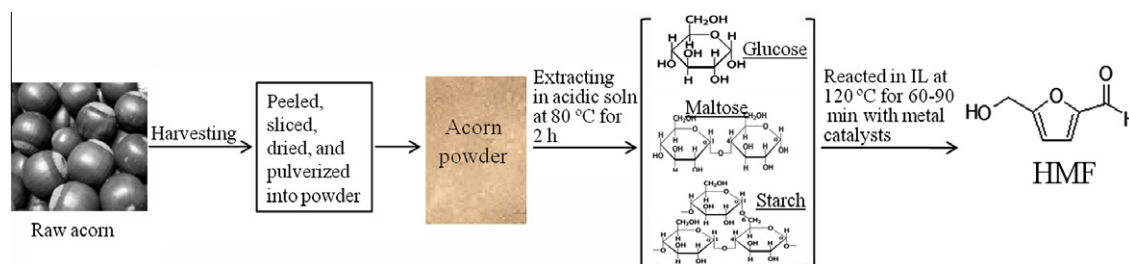


Figure 1. Synthetic process of hydroxymethylfurfural (HMF) from raw acorn biomass. The acorn samples harvested were peeled, sliced, dried, and pulverized into powder using a sample mill. Then, the sample powder was suspended in the given HCl solution and hydrolyzed at 80°C for 2 h. The hydrolyzed suspension was centrifuged at $13,500g$ for 60 min and the supernatant was collected and used as the biomass extract for the synthesis of HMF. Soln; solution and IL; ionic liquid.

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