Inulin conversion to hydroxymethylfurfural by Brønsted acid in ionic liquid and its physicochemical characterization

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Abstract−A simple conversion process of inulin polymer into hydroxymethylfurfural (HMF) was developed using Brønsted acid catalyst (HCl) in the presence of an ionic liquid, 1-octyl-3-methylimidazolium chloride ([OMIM]Cl). In addition, the physicochemical properties of inulin particle and its depolymerixation products were scrutinized. FESEM and XRD diffraction frequency showed that inulin particles are clustered in a granulated formation and their molecular structure is highly amorphous. FT-IR analysis identified five characteristic frequency regions: Region 1; 700-900, Region 2; 900-1,200, Region 3; 1,200-1,350; Region 4; 1,350-1,500, and Region 5; 1,530-1,800 cm^{-1}. HPLC analysis confirmed that the major composition of inulin consists of fructose and glucose. The synthesis of HMF was significantly affected by the Brønsted catalyst and its concentration. Its highest yield (63.1±5.1 dwt%) was achieved at 0.3 M HCl in the presence of [OMIM]Cl. No presence of the Brønsted catalyst exhibited negligible HMF yield (2.3±1.1 dwt%). Our results demonstrate that the Brønsted catalyst plays a pivotal role in the catalytic process of HMF synthesis from inulin polymer.

Key words: Brønsted Acid, Hydroxymethylfurfural, Inulin Polymer, Ionic Liquid

INTRODUCTION

Inulin, a class of carbohydrate polymer, is a natural storage polysaccharide present mainly in plant storage organs such as roots and tubers. This polymer consists of linear chains of fructosyl units with a single glucose moiety at its reducing end, which are linked by *β*-2,1-glycosidic linkages (Fig. 1). Inulin has been used as a renewable resource primarily in the food and pharmaceutical industries. The physicochemical properties of the polymer make its application versatile. For example, the hydroxyl groups in its fructosyl rings and the molecular structure of the polymer contribute to diverse transformation reactions in the production of various chemical products such as drug stabilizer and glycerol [1]. Some recent studies [2-5] have demonstrated that carbohydrate polymers including inulin can be a good renewable feedstock for their conversion to hydroxymethylfurfural (HMF), a key intermediate for the syntheses of valuable compounds including biofuel [6].

To produce HMF from carbohydrate polymers, their depolymerization to such simple sugars as fructose and glucose is essential because they are the substrate feeds for the synthesis of HMF [7-9]. To effectively synthesize HMF from carbohydrate polymers and their depolymerization products, many workers have centered on the development of acid and/or metal catalysts [10-14] because their catalytic activities significantly affect the yield of HMF [10,13]. Moreover, it is known that the structural and physicochemical states of the polymers also have critical influence on their depolymerization process and HMF synthesis [15-18]. In this regard, information on the molecular structure and the physicochemical properties of inulin polymer can be an important factor for the effective syn-
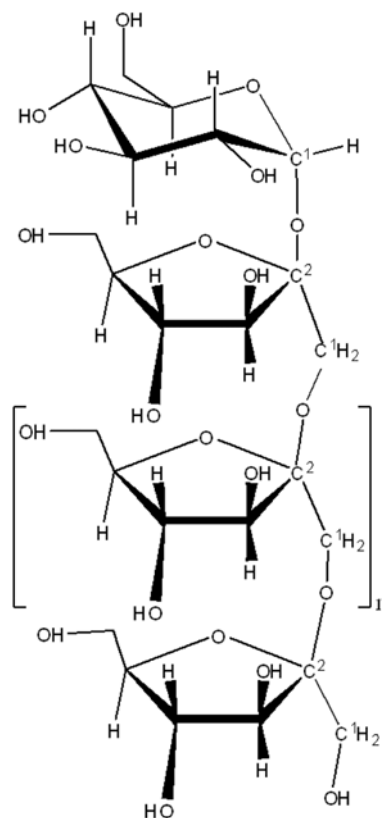

Fig. 1. The chemical structure of inulin polymer.

thesis of HMF from the polymer.

Brønsted acids have been applied as a catalyst for the synthesis of HMF using ionic liquids [9,15,19]. The main role of Brønsted

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acid catalysts is their ability to protonate the oxygen atoms present in sugar ring by H+ released from the catalysts. As a result, the hydrated intermediates rapidly proceed to further dehydration reactions into HMF [19]. We selected HCl as the Brønsted acid catalyst due to its high catalytic efficiency in the depolymerization process of carbohydrate polymers and their conversion into HMF [4,20-22]. Some workers have reported that HCl plays an important role in the synthesis of HMF from some plant sources and sugars such as sucrose and fructose by acting as a strong Brønsted acid catalyst [4,7,19,22].

Carbohydrate polymers are easily dissolved in ionic liquids by increasing the accessibility of their chemical bonds, such as glycosidic linkages, and thus can be converted into other products. The ionic liquids also contribute to the disruption of hydrogen bonds interconnected between the polymer chains by loosening their compact structures and making the polymer chains more susceptible to chemical attacks [15]. Some recent studies illustrated that the combined treatment of Brønsted acid catalyst and ionic liquid significantly enhanced the yield of HMF from raw plant sources [4,11, 22]. Imidazolium-based ionic liquids have a dual cation/anion property conducive to stabilization of the intermediates created during the reaction performance [23]. This dual character facilitates the depolymerization of sugar polymers into smaller sugar molecules [21]. A di-substituted imidazolium-based ionic liquid, 1-octyl-3-methylimidazolium chloride ([OMIM]Cl), was selected for this study due to its high solvent activity in the synthesis of HMF [12].

Our aim is to characterize the physicochemical properties of inulin polymer and its depolymerization products, and to provide some information about the catalytic effect of Brønsted acid catalyst on the synthesis of HMF from inulin polymer.

EXPERIMENTAL

1. Materials and Depolymerization

Inulin and other chemicals used were purchased from commercial suppliers (Alpha Aesar and Sigma-Aldrich). The ionic liquid, 1-octyl-3-methylimidazolium chloride ([OMIM]Cl), was obtained from Iolitec Ionic Liquids Technologies (Germany).

For measurement of depolymerization products of inulin polymer, 0.5 g of the inulin polymer sample (5%) was prepared in 10 mL of 0.3 M HCl. Then, the inulin preparations were depolymerized by heating at 80 °C for 2 h followed by centrifugation at 13,500 ×g for 15 min. After the supernatants were collected, 1 volume of ethanol was added to them to precipitate the soluble sugar products, and then the precipitants were recovered, dried and powdered for the analyses of a field emission scanning electron microscope (FESEM), X-ray diffractometer (XRD), and FT-IR (Fourier transform infrared). In case of HPLC analysis, the inulin hydrolyzate was directly used.

2. Analytical Methods of FESEM, XRD, FT-IR, and HPLC

To analyze the structure of inulin polymer and its depolymerization products, FESEM (JEM-6700F, JEOL) was employed. The samples were prepared by coating them with platinum (20 nm in thickness) using a vacuum ion sputter (108auto, Cressington). The platinum-coated specimen was then scanned with the FESEM microscope at the probe energy level of 5 kV. The image magnifications of each photograph are displayed on the figures.

The diffraction pattern of inulin polymer particles was obtained by using XRD (Rigaku, Japan). The sample powder tightly packed in a cell was exposed to X-rays, which generates the monochromatic CuKa radiation (wavelength; 1.54184 Å at 40 kV and 40 mA) using the diffractometer. The values of the diffraction angle (2θ) were obtained by scanning the range values between 4° and 30° at a rate of 1°/min.

FT-IR measurement was performed by the microscopic FT-IR (Fourier transform infrared)/Raman spectroscope (Vertec 80 V, Bruker). The dried powder samples were treated with KBr pellet, placed on the ATR (attenuated total reflectance) accessory (Vertex 80 V, Bruker), and analyzed. The spectral frequency was recorded between 400 and 4,000 cm^{-1} frequency regions by accumulating 128 scans with a resolution of 4 cm^{-1}.

HMF and sugar products were analyzed using the Waters HPLC system equipped with UV absorbance and IR detectors (Waters), respectively. For the measurement of HMF, a reverse-phase column (Waters Xbridge C$_{18}$, 4.6 mm×150 mm, 5 μm) was used to quantify its yield. A gradient mobile phase was operated at a flow rate of 0.7 mL/min (UV at 320 nm) for the quantification of HMF and the gradient condition was as follows: 100% water phase for 2 min, transition and gradient phase in the ratio of 80% water and 20% methanol for 8 min, and 100% water for 20 min including transition time.

Sugars were analyzed by using the YMC-Pack Polyamine II column (4.6 mm×250 mm, S-5 μm, 12 nm) and the waters IR detector. The mobile phase (75 : 25, acetonitrile : water) was performed at a flow rate of 1 mL/min.

3. General Reaction Procedures

To determine the effect of reaction time on the synthesis of HMF, six different reaction times (30, 60, 90, 120, 150, and 180 min) were applied and reacted at 130 °C for the given reaction time using the reaction mixture containing the solvent admix (4 g [OMIM]Cl+1 mL ethyl acetate), 0.5 g inulin (5%, w/v), and 5 mL of 0.3 M HCl solution. The reaction mixture then was transferred to a 50 mL volumetric flask and reacted at 130 °C by using a heating mantle.

To examine the effect of Brønsted acid on the synthesis of HMF, HCl was used as the Brønsted acid catalyst. Five different concentrations of HCl (0, 0.1 M, 0.3 M, 0.5 M, and 1 M) were prepared and reacted as above.

For HMF productivity experiment, four different concentrations of inulin feed substrate (5, 10, 15, and 20%, w/v) were prepared in the reaction mixture containing the solvent admix, the given inulin feed concentration, and 5 mL of 0.3 M HCl solution. The reactions were carried out under the same reaction conditions as above.

All measurements are presented with the mean values obtained by calculating four replications and HMF yields are expressed with the value of percent dry weight (dwt%). The productivity was estimated by HMF yield produced per g inulin feed and the relative productivity was evaluated by calculating HMF yield (in dwt%) obtained from 5% of the inulin feed concentration as a control (a value=1).

RESULTS AND DISCUSSION

1. Characterization of Inulin Polymer and Its Depolymerization Products

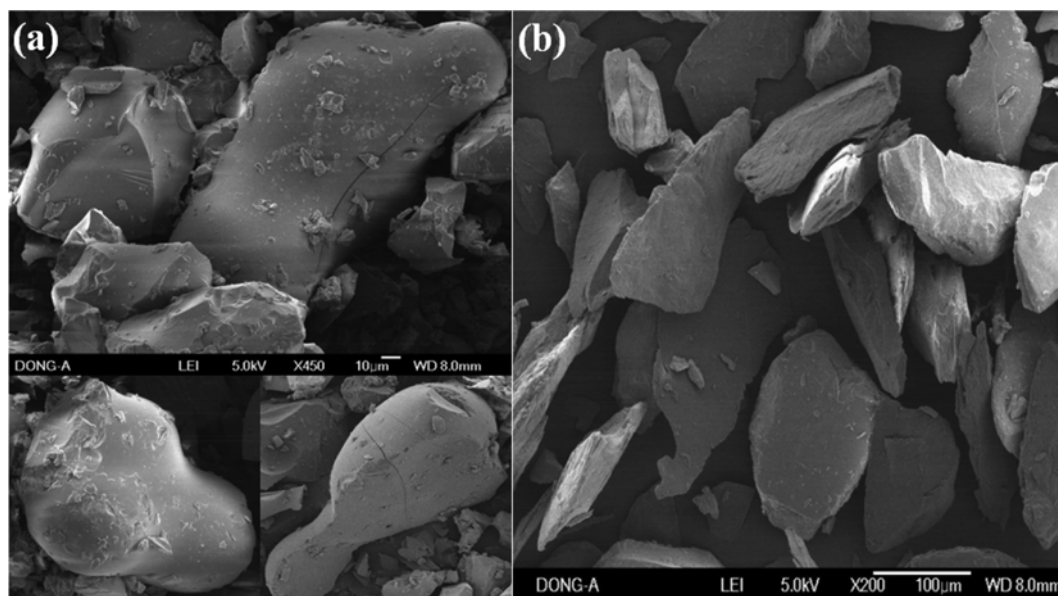We obtained the characteristic morphology of inulin polymer parti-

Fig. 2. The molecular structure of the inulin polymer granules and their depolymerization products. (a); Images of inulin particle granules observed with FESEM and (b) FESEM images of inulin depolymerization products disrupted by the Brønsted acid.

cles from FESEM analysis, which has not been reported in previous study (Fig. 2(a)). As shown in Fig. 2, the inulin particles seem to be clustered in a granulated formation. The surface of the granular formation (designated as inulin granule) looks smooth (Fig. 2(a)) and the size of the inulin granules is assumed to be approximately 300×150 μm. Its overall form is roughly seen like the irregular peanut

shell with small buds on its surface (Fig. 2(a)). However, its structure was changed by acid depolymerization with HCl (Fig. 2(b)). As a result, the morphology of the depolymerization products was modified to the clustered brickbat-like form (Fig. 2(b)), suggesting that the molecular frame of the inulin granules would be disrupted by the Brønsted proton released from HCl. This disruption may facilitate depolymerization of the inulin polymer into sugar products convertible to HMF [20,22].

The XRD powder analysis from the inulin polymer sample showed no sharp diffraction peak (Fig. 3) that is typically observed from amorphous materials, implying that the inulin particles would have
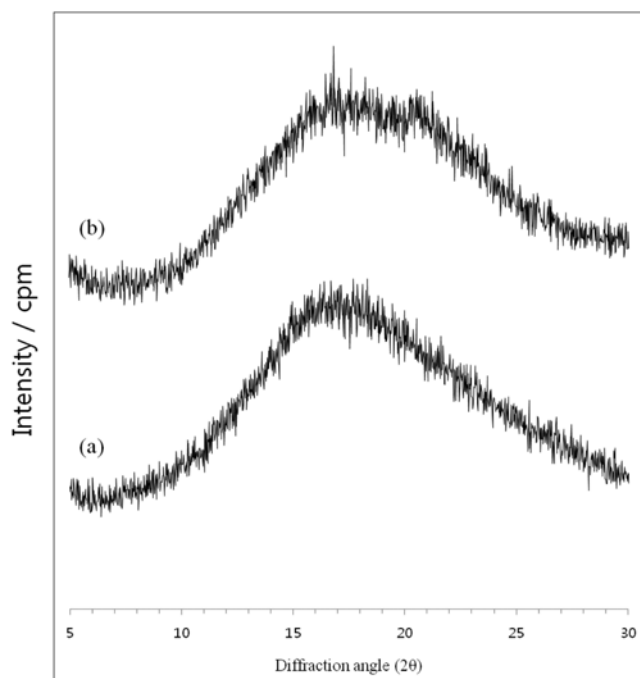

Fig. 3. XRD diffraction patterns of inulin powder particles and their depolymerization products. (a); XRD diffraction pattern of inulin powder particles and (b) XRD diffraction pattern of inulin depolymerization products disrupted by the Brønsted acid.
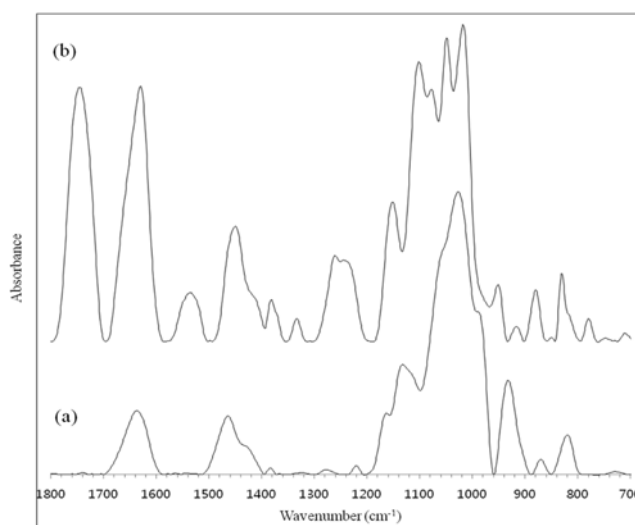

Fig. 4. FT-IR spectral profiles of inulin powder particles and their depolymerization products. (a); FT-IR spectral profiles of inulin powder particles and (b) FT-IR spectral profiles of inulin depolymerization products disrupted by the Brønsted acid.

amorphous structure [24,25]. At the 2θ value of 16.7°, one peak was observed from the inulin particles (Fig. 3(a)), which may be characteristic for inulin polymer. However, after acid depolymerization, two peaks were identified at the 2θ values of 15.8° and 21.2° (Fig. 3(b)). It is thought that the main reason for the above result would be due to the crystallinity change of the inulin polymer, which could be caused probably by the action of the Brønsted proton released from HCl. The crystallinity change may result from decrease of the amorphous inulin particles due to their depolymerization [16,18,25].

In this experiment, the chemical properties of inulin polymer and its depolymerization products generated by the Brønsted acid were examined by FT-IR analysis. Fig. 4 displays their spectral profiles measured from inulin polymer (Fig. 4(a)) and its depolymerization products (Fig. 4(b)). Based on the functional groups and their vibration modes, the absorption bands were grouped into five characteristic frequency regions: region 1 (700-900 cm^{-1}, region 2 (900-1,200 cm^{-1}), region 3 (1,200-1,350 cm^{-1}), region 4 (1,350-1,500 cm^{-1}), and region 5 (1,530-1,800 cm^{-1}) (Table 1). In region 1, two absorbance peaks of 820 and 870 cm^{-1} were observed (Fig. 4(a)) in inulin polymer, whereas in its depolymerization products, three peaks (780, 830, and 879 cm^{-1}) appeared. This change in their frequency may indicate the presence of fructose after acid depolymerization of the inulin polymer because the peaks of fructose are frequently observed around 830 and 780 cm^{-1} [17]. In regions 2, 4 and 7 absorbance peaks were determined for inulin polymer and its depolymerization products, respectively (Table 1). This absorbance region is represented with the broad overlapped peaks that are generally known as the fingerprint region for carbohydrates because of the presence of complex stretching modes of C-C,C-O, and C-O-H/C-O-C deformation modes [17,26]. This region contains the major absorption bands for the exo-/endocyclic bond modes in the oligo/polysaccharides [11]. Region 3 also represents C-H, C-O, and C-OH stretching modes in both the pyranose and furanose ring. In particular, the absorption band at 1,334 cm^{-1} may be a signal specific for furanose ring because this band is frequently observed in fructose sugar [27]. In region 4, two main vibration modes (C-O-H stretching in pyranose ring and C-H deformation in ester bonds) were found and these modes may contribute to ketose sugars such as fructose. In region 5, the frequency signals conducive to the absorption bands of COO-/C=O stretching and C-O in exocyclic bonds were identified [26,

28]. In this frequency region, one interesting absorbance band (at 1,745 cm^{-1}) was found in the acid depolymerization products (Fig. 4(b)), being indicative of the presence of ketose sugar in the product mixture because this spectral signal is specific for ketose functional group [28]. The above spectral data support the elucidation that the chemical properties of inulin polymer are changed by Brønsted acid, and thus, their change may facilitate its depolymerization into smaller product sugars such as fructose and glucose. HPLC analysis also supports that the main depolymerization products are fructose and
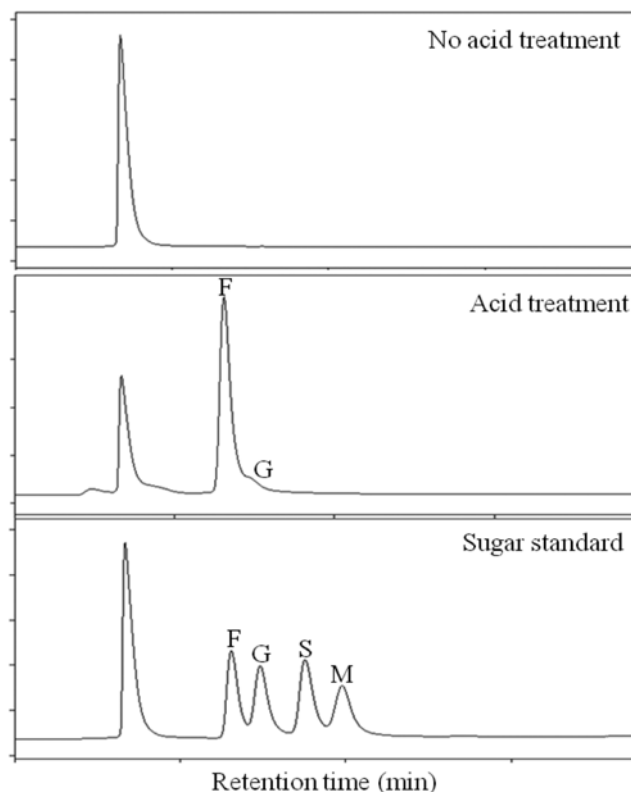
Fig. 5. HPLC analysis of inulin polymer and its depolymerization products. Top; HPLC measurement analyzed before HCl treatment, middle; HPLC measurement analyzed after HCl treatment, and bottom; HPLC measurement of sugar standards. F; fructose, G; glucose, S; sucrose, and M; maltose.

Table 1. Characteristic absorbance peaks for identification of inulin polymer and its depolymerization products generated by Brønsted acid (in wavenumber value; cm^{-1})

Spectral region	Acid treatment		Remark
	Before	After	
Region 1	820, 870	780, 830, 879	The spectral bands for aromatic ring vibration modes
Region 2	932, 1027, 1132, 1162	917, 952, 1017, 1049, 1078, 1101, 1151	The spectral bands for carbohydrates; C-O stretching in exo- and endocyclic bonds and C-O-C/C-O-H deformation modes of various oligo-polysaccharides
Region 3	1220, 1278	1244, 1261, 1334	The spectral bands for C-H, C-O, and C-OH stretching in pyranose and furanose ring
Region 4	1383, 1464	1383, 1449	The spectral bands for C-O-H stretching in pyranose ring and C-H deformation in esters
Region 5	1635	1535, 1635, 1745	The spectral bands for COO$^-$ and C=OH stretching and C-O in exocyclic bonds
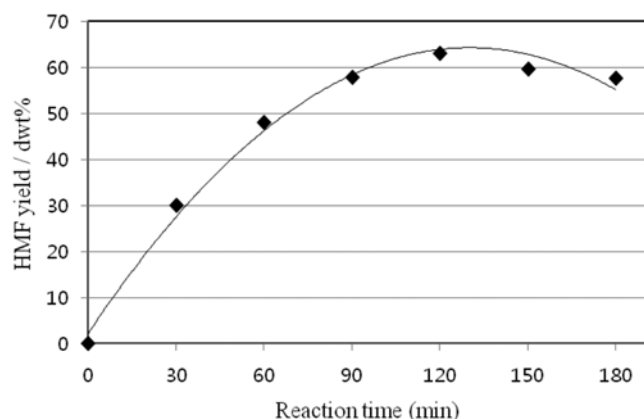
Fig. 6. Effect of reaction time on the synthesis of HMF from inulin polymer. The reaction mixture containing the solvent admix (4 g [OMIM]Cl+1 mL ethyl acetate), 0.5 g inulin (5%, w/v), and 5 mL of 0.3 M HCl solution was reacted at 130 °C for 6 different reaction times of 30, 60, 90 120, 150, and 180 min.

Fig. 7. Catalytic effect of the Brønsted acid catalyst on HMF synthesis from inulin polymer. Five different concentrations of HCl (0, 0.1 M, 0.3 M, 0.5 M, and 1 M) were prepared in the reaction mixture containing the solvent admix (4 g [OMIM] Cl+1 mL ethyl acetate), 0.5 g inulin (5%, w/v), and 5 mL of the given concentration of HCl solution and reacted at 130 °C for 2 h.

glucose that are easily convertible to HMF (Fig. 5).

2. Effects of Brønsted Acid on the Synthesis of HMF

Brønsted acids have been used as a useful catalyst for a wide range of synthetic processes of various compounds [29]. In this experiment, HCl was used as the Brønsted acid catalyst because it functions as a strong proton donor to protonate the receptor molecule. In the synthetic process of HMF from inulin polymer, the proton released from HCl may contribute not only to its depolymerization into smaller sugar products by protonating the sugar molecules, but also their further dehydration reaction into HMF [4,22]. In this experimental section, the role of HCl as the Brønsted acid catalyst was examined by synthesizing HMF from inulin polymer.

In the first round of this experimental section, the reaction time was examined to choose an optimal reaction time for the effective synthesis of HMF from inulin polymer. For this, HCl was added to the reaction mixture because the absence of the acid catalyst in the reaction mixture resulted in no production of HMF. Fig. 6 shows the effect of reaction time on the yield of HMF from inulin polymer. The best reaction time for inulin conversion into HMF was identified at 2 h because the highest HMF yield (63.1±5.1 dry weight%; dwt%) was achieved at this reaction time (Fig. 6). This figure also illustrates that between 0 and 120 min reaction time, the HMF yield increased as the reaction time elapsed. However, after 120 min reaction time, its yield showed a slow decline with slight fluctuations. This reaction behavior implies that the reaction time may have a hyperbolic relationship with respect to HMF yield. A relatively sharp increase in the HMF yield was found during the initial 30 min reaction time compared to those of other reaction times (Fig. 6). One possible reason for this result may be due to relatively lower rehydration rates of the produced HMF to other byproducts such as levulinic acid and formic acid compared with those occurring during the extended reaction times [12,19], and thus the sharp increase (higher reaction rates; 1 mg/mL/min) appeared. However, after 120 min reaction time, the HMF yields were slowly decreased (Fig 6), suggesting that more rapid HMF conversion into other sugar degradation byproducts including solid humins occurred [19,30].

In the second round experiment, the effect of the Brønsted acid
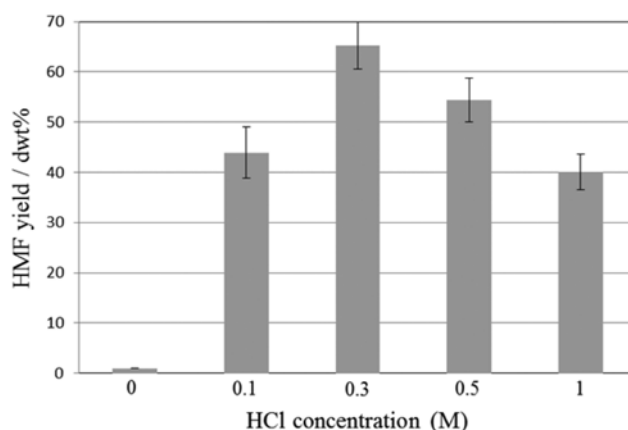
catalyst on the yield of HMF from inulin polymer was investigated to compare its catalytic capability. For this, five concentrations of HCl (0, 0.1, 0.3, 0.5, and 1 M) were prepared. In this experiment, the interesting finding was that the yield of HMF from inulin polymer was significantly affected by the difference between the concentrations of HCl (Fig. 7). The presence of HCl in the reaction mixture highly promoted HMF yields. In contrast, negligible yield of HMF was observed in the reaction mixture with no HCl (Fig. 7). When HCl was added to the reaction mixture, the highest HMF yield (65.2±6.3 dwt%) was detected at 0.3 M HCl concentration, whereas the lowest one (40.1±3.6 dwt%) was at 1 M HCl (Fig. 7). The lower HMF yields at over 0.3 M HCl (0.5 M and 1 M HCl) indicate that the optimal concentration of HCl for the efficient production of HMF from inulin polymer would be around 0.3 M. The above results clearly provide evidence that HCl as the Brønsted acid catalyst plays a pivotal role in the synthetic process of HMF from inulin polymer. In addition, another notable point was that little catalytic effect of the ionic liquid, [OMIM]Cl, was identified in the synthetic process of HMF from inulin polymer. This is based on the fact that negligible yields (2.3±1.1 dwt%) were observed in the reaction mixture ([OMIM] Cl+ethyl acetate) with no HCl, but much higher HMF yields were synthesized in the reaction mixture containing HCl (Fig. 7). Accordingly, we could assume that the combined reactivity of HCl and the ionic liquid may be responsible for the catalytic promotion of HMF yield. In the presence of HCl, the ionic liquid may facilitate its synthetic process of HMF by stabilizing the intermediates and transition state occurring during the Brønsted acid-catalyzed conversion reaction of the sugar products (by depolymerization of inulin polymer) into HMF [9,13,23]. Therefore, we could conclude that the high HMF yields are attributed to the incorporative activity of the Brønsted acid catalyst and the ionic liquid solvent. In addition, the gradual decrease in the HMF yields at over 0.3 M HCl may be due to excess proton activity probably caused by the surplus presence of H^+ released from higher HCl concentration [22,31].

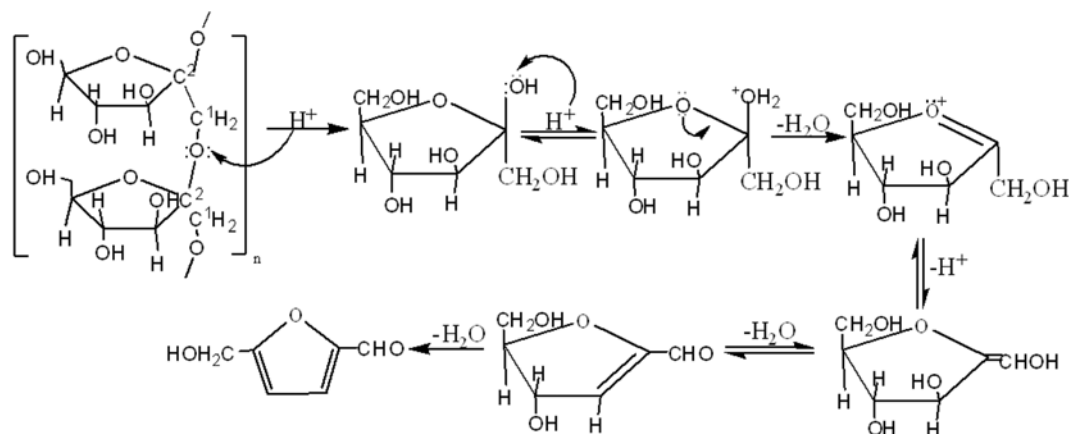The catalytic mechanism of the Brønsted acid catalysts such as

Fig. 8. The putative mechanistic pathway of inulin conversion into HMF by Brønsted acid catalyst.

HCl in the synthetic process of HMF from inulin polymer is not fully understood. However, Antal et al. [32] proposed a mechanistic pathway for the Brønsted acid-catalyzed synthesis of HMF from fructose and sucrose. Based on their pathway, it is thought that the inulin conversion into HMF by the Brønsted acid catalyst (HCl) proceeds via four major processing steps as outlined in Fig. 8: Breaking down of inulin glycosidic bonds into depolymerization products (mainly fructose) by the Brønsted acid hydrolysis; protonating of oxygen atom at the anomeric carbon (C-2 carbon) of the fructose sugar by the Brønsted proton (released from HCl); forming of the keto-enol intermediate by tautomeric change; and then the successive dehydrating into HMF.

3. Effect of Inulin Feed Concentration on the Productivity of HMF

The productivity of HMF was evaluated to estimate its economic production capacity. From Fig. 9, the relative HMF productivity of all concentrations of inulin substrate feed is in the range of 0.94 and 1.01, indicating that there is no significant difference between them. This result implies that at over 5% feed concentration, the concentration of inulin feed may have little influence over HMF yield. Nonetheless, it is likely that the promising inulin feed concentration for the efficient production of HMF would be between 5-10% (w/v) because slightly higher HMF productivity was achieved at both feed

concentrations (Fig. 9). The above data could be useful information for the economical design of the industrial production of HMF from inulin polymer.

CONCLUSIONS

Inulin is an industrially and pharmaceutically useful carbohydrate polymer with unique physicochemical properties. In this work, we provide some information about characteristic chemical and structural properties of inulin polymer and its depolymerization product using FESEM, FT-IR, and XRD. Our study also demonstrates that it can be an excellent renewable feedstock for sustainable production of HMF that can be used as an important platform chemical including biofuel. We provide for the first time a characteristic morphology of inulin particle, which has not been observed before. XRD and FT-IR analyses confirmed that inulin particles are highly amorphous and its chemical composition consists of fructose and glucose units. HMF yield from inulin was significantly affected by the Brønsted acid catalyst (HCl in this study) and its concentration. 0.3 M HCl was most effective for the synthesis of HMF from inulin polymer in the presence of the ionic liquid, [OMIM]Cl. Our study reveals that the Brønsted acid catalyst plays an important role in the synthetic process of HMF from inulin polymer.
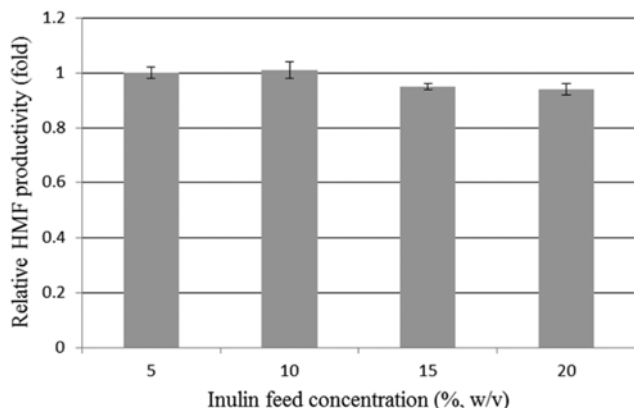
Fig. 9. Effect of inulin feed concentration on the relative productivity of HMF. The relative productivity of HMF was evaluated by calculating HMF yield (in dwt%) obtained from 5% of the inulin feed concentration as a control (a value=1).

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