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Conversion of Glucose to 5-Hydroxymethylfurfural, Levulinic Acid, and Formic Acid in 1,3-Dibutyl-2-(2-butoxyphenyl) -4,5-diphenylimidazolium Iodide-Based Ionic Liquid

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Abstract: The separation process between 5-hydroxymethylfurfural (HMF) and trace glucose in glucose conversion is important in the biphasic system (aqueous–organic phase), due to the partial solubility property of HMF in water. In addition, the yield of HMF via the dehydration reaction of glucose in water is low (under 50%) with the use of Brønsted acid as a catalyst. Therefore, this study was conducted to optimize the production and separation of products by using a new hydrophobic ionic liquid (IL), which is more selective than water. The new IL (1,3-dibutyl-2-(2-butoxyphenyl)-4,5-diphenyl imidazolium iodide) [DBDIm]I was used as a solvent and was optimized for the dehydration reaction of glucose to make a more selective separation of HMF, levulinic acid (LA), and formic acid (FA). [DBDIm]I showed high performance as a solvent for glucose conversion at 100 °C for 120 min, with a yield of 82.2% HMF, 14.9% LA, and 2.9% FA in the presence of sulfuric acid as the Brønsted acid catalyst.

Keywords: imidazolium-based IL; glucose conversion; hydroxymethylfurfural (HMF); levulinic acid (LA); formic acid (FA)

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1. Introduction

The production of fuels, fine chemicals, and polymer precursors from biomass can decrease the current dependence on non-renewable energy sources [1–3]. Furan derivative compounds are frequently used as raw materials for new products to replace the oil-based chemicals and create a new set of biomass-based economies for the production of high-value chemical compounds [1,4,5]. 5-Hydroxymethylfurfural (HMF) is a furan derivative compound and it is one of the products from biomass, glucose, and fructose conversion reactions. In recent years, HMF has been considered as the potential renewable chemical platform to produce liquid fuels, intermediates of polymers, pharmaceutical products, fine chemicals, and other organic derivatives [1,4,6].

Despite many multifunctional applications of HMF, HMF is still not yet produced on an industrial scale due to its high production cost [6–8]. HMF production can be achieved by the dehydration reaction of carbohydrate derivatives such as fructose, glucose, sucrose, or cellulose in water, by adding an acidic catalyst [9]. In general, HMF is typically produced from glucose with low yields, attributed to the stable pyranoside ring structure of glucose [6,10]. Glucose is the most abundant monosaccharide, considered as the preferred raw material to produce HMF [10,11]. However, glucose conversion to HMF, levulinic acid (LA), and formic acid (FA) is more complicated than fructose as substrates [6,12].

Current technologies use an additional isomerization step of glucose to fructose because dehydration of fructose to HMF occurs with better selectivity and higher rates [11,13]. The use of solid catalysts (hydrotalcite, zeolites, and different metal oxides), enzymes, or an aqueous base is renowned in the isomerization step of monosaccharide dehydration [2,6,8,13,14]. However, the high processing cost and the relatively low HMF yields (approximately 20.0–70.0%) are some of the disadvantages in those processes [2,6,8,13,14].

The reviewed literature results showed that HMF production from biomass, glucose, and fructose in an organic solvent as media and metal catalysts still needs more development. The previous studies showed that the glucose conversion to HMF in *N*,*N*-dimethylacetamide with a chromium salt catalyst yielded approximately 50.0% HMF at 100 °C for 5 h [15–17]. Corn and pine sawdust conversion to HMF in *N*,*N*-dimethylacetamide in the presence of a LiCl catalyst at 140 °C for 2 h produced approximately 15.0–40.0% HMF [18]. In 2015, a study reported that the glucose transformation into HMF in DMF, DMA, DMSO, or *n*-butyl alcohol as solvents and $CrCl_3$ as a catalyst at 120 °C, with 10–90 min reaction times, was adept at producing HMF, with the yields ranging from 10.0 to 40.0% [19]. However, the use of a metal salt catalyst for glucose conversion has some disadvantages, such as a high cost, potential toxicity, and the environmental concerns of chromium metal for significant commercial application [18,20,21]. There are many disadvantages of using organic solvents as media for glucose conversion. These include high flammability, low vapor pressure, high toxicity, and high cost of operation [19]. Furthermore, the yield of HMF is relatively low when using organic solvents as media and it is also challenging to regenerate and recycle organic solvents [12,19,22]. The difficulties in the separation of HMF from other side products due to low solubility in the aqueous phase also lead to a decrease in HMF yield [6,23,24]. Therefore, several new technologies are required to improve the glucose dehydration and separation processes, for example, the use of ionic liquid (IL)-based processes or combining IL and membrane separation technology [25–29].

IL is an organic or inorganic salt with a low melting point (under 100 °C), high thermal stability, chemical stability, low vapor pressure, and environmentally friendly as a solvent and catalyst [30–33]. Several notable applications of ILs include the use as a solvent or media in biomass conversion, as a catalyst for reaction, as corrosion inhibitors, and as a supporting material in membrane separation [3,14,25–27,30]. IL can act as a green solvent, with a wide range of solubility, and as a catalyst to increase the HMF yield [3,25–27,34]. [BMIm]Cl-based IL and hydroxyl apatite-supported chromium chloride were used for glucose conversion and produced HMF with a yield of 40.0% [15,35]. In 2007, [EMIm]Cl (1-ethyl-3-methylimidazolium chloride) and $CrCl_2$ were applied for glucose dehydration, producing a nearly 70.0% HMF yield [16]. In previous studies, Hsu et al. [36] used imidazolium-based IL, namely, [EMIm]Cl and [Epyr]Cl, in glucose dehydration. Both ILs demonstrated better recoverability, recyclability, and ability to perform as double agents (solvent and catalyst) than conventional organic solvents [33,36–38]. Stahlberg et al. [38] investigated IL's usage with lanthanide as catalysts in glucose conversion, obtaining an approximately 24.0% HMF yield [39]. The literature review results showed that IL acted as a more powerful solvent and Lewis acid catalyst in biomass conversion [3,6,14,23,25,27,28,40,41]. However, several ILs still have drawbacks in the hydrolysis process of biomass, glucose, and fructose due to the incompatible chemical structures of the ILs, resulting in a low HMF yield. The chemical structures of ILs play an essential role in glucose conversion [3,18,23,30,39]. An adequate and suitable chemical structure of ILs (more hydrophobic as main priority) is required as a medium and catalyst to assist the dehydration reaction, accelerate the glucose conversion process to HMF, and increase the yield of HMF. Therefore, it is important to find more hydrophobic ILs and study their potential as media or solvents in glucose conversion.

We selected a 1,3-dibutyl-2-(2-butoxyphenyl)-4,5-diphenylimidazolium iodide ([DBDim]I)–based IL as a medium in glucose conversion due to its highly hydrophobic structure, good thermal resistance, and ability to dissolve a wide range of solutes [30]. The main objective of this study was to evaluate the performance of [DBDIm]I as a hydrophobic solvent for glucose conversion to HMF, LA, and FA under various temperatures and reaction times. The results showed that [DBDIm]I is a potential medium for glucose conversion to several biofuel precursors.

2. Materials and Methods

2.1. Materials

Glucose and sulfuric acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). The IL ([DBDIm]I) was synthesized in the laboratory using the MAOS (Microwave-Assisted Organic Synthesis) method, according to the previously reported method developed by the authors [25]. A total of 201 mmol of 1-iodobutane and 67 mmol of 2-(2-hydroxyphenyl)-4,5-diphenylimidazole were reacted in a CEM microwave reactor at a temperature of 190 °C for 2 h. The course of the synthesis reaction of [DBDIm]I was monitored by thin-layer chromatography using ethyl acetate:methanol (3:7 (v/v)) as eluents. The crude product was purified by liquid–liquid extraction method using *n*-hexane. The [DBDIm]I was dried in a vacuum oven for 4 h. The chemical structure of [DBDIm]I was confirmed using FTIR, NMR, HR-ESI-MS spectroscopy, and elemental analysis, as previously reported by the authors [25,30].

2.2. Glucose Conversion

The optimization of glucose conversion was performed at various operating conditions, which include temperatures and reaction times. The glucose conversion was carried out at different reaction times, ranging from 20 to 120 min. The optimum temperature of the glucose conversion was observed at the range of 80–105 °C, as reported previously [15,36,42].

Glucose was reacted in an oven in a 7 mL-ampoule tube. Each of the nine 7 mL ampoules was filled with 0.5 g of glucose and 1 g of [DBDIm]I. Three of the ampoules were filled with 0.5 g of glucose, 1 g of [DBDIm]I, and 0.5 mL demineralized water. The other three ampoules were mixed with 0.5 mL of water and 0.5 mL of 1 M H_2SO_4. In a control system, three ampoules were provided with 0.5 g of glucose in water. To study the Brønsted acid's effect, H_2SO_4 was added to three ampoules with glucose, water, and 1 M H_2SO_4. The total volume of the mixture in each ampoule was approximately 2–3 mL. All ampoules were incubated in an oven at pre-set temperatures. After completion of the reaction, conversion products were analyzed.

2.3. Analytical Methods

The glucose conversion products in the water phase were analyzed using HPLC (High-Performance Liquid Chromatography). The %mole yield of each conversion product was calculated based on the peak area of the HPLC chromatograms. The calculation methods were adopted from previously published reports based on the number of carbon atoms in the products [16,43].

Based on the HPLC chromatograms analysis, the concentration of each conversion product was determined and the exact concentration of each product was calculated by multiplying the obtained concentration with the dilution factor. Percentages of conversion products were further calculated based on the peak area of the HPLC chromatograms obtained by entering the actual concentration data to the Equations (1)–(4) given below [16,42]. The calculation was defined based on the number of the C atoms present in the conversion products; for example, HMF has 6 C atoms, LA has 5 C atoms, and FA has one atom C. Therefore, the calculation was formulated as follows:

$$\text{mole\% yield of product} = \frac{\frac{amount\ of\ C_{atom}}{C_{product}}}{W_{sample}} \times 100\% \tag{1}$$

$$\text{mole\% yield of LA} = \frac{\frac{5}{C_{LA}}}{W_{sample}} \times 100\% \tag{2}$$

$$\text{mole\% yield of HMF} = \frac{\frac{6}{C_{HMF}}}{W_{sample}} \times 100\% \quad (3)$$

$$\text{mole\% yield of FA} = \frac{\frac{1}{C_{FA}}}{W_{sample}} \times 100\% \quad (4)$$

where,

C_{LA} = real concentration of LA produced (mole);
C_{HMF} = real concentration of HMF produced (mole);
C_{FA} = real concentration of FA produced (mole);
W_{sample} = weight of sample (gram).

The details of this method are given in our recently published work [29]. The HPLC retention time data (in minutes) of the standards used were as follows: glucose: 10.26; formic acid (FA): 15.39; acetic acid: 16.67; levulinic acid (LA): 17.49; and hydroxymethylfurfural: 33.38–35.86—as shown in the Supplementary Materials.

2.4. Statistical Analysis

The optimization studies were conducted with five replications, as per the methods described previously [41,42]. All the results of the glucose conversion at optimum conditions showed standard deviations under 2%. The reusability studies of [DBDIm]I as a solvent in glucose conversion were also conducted with five replications, and the experimental results had standard deviations below 2%.

3. Results and Discussion

3.1. Determination of Optimum Conditions for Glucose Conversion

Glucose conversion was conducted in [DBDIm]I-based IL, which has high hydrophobic properties due to its three butyl chains and three aromatic rings in its structure, as shown in Figure 1. The effects of [DBDIm]I as a solvent (also as a Lewis acid) and H_2SO_4 (Brønsted acid) in glucose conversion were observed at a temperature of 80 °C, with a reaction time ranging from 20 to 120 min. The results showed that a longer reaction time is essential for a better glucose conversion in [DBDIm]I (Figure 2a). The optimum reaction time of glucose conversion in [DBDIm]I supported by 1M H_2SO_4 was 120 min, which showed a yield of 76.3% HMF. The results also indicated that the glucose conversion in only water as a solvent without an acid catalyst at the same reaction conditions did not produce HMF. It is hard to dehydrate glucose in the presence of water; thus, it is also not feasible to form HMF in the absence of a dehydrating agent, such as Lewis acid or Brønsted acid catalysts. Nevertheless, the increase in temperature affected the HMF production, even in the system containing only glucose and water (Figure 2b). It was apparent that the higher temperature would promote the dehydration of glucose due to the vaporization of water.

The combination of a Lewis acid of [DBDIm]I and Brønsted acid of H_2SO_4 showed better glucose conversion than the Lewis acid or Brønsted acid alone. This study developed a strategy for integrating the sequential catalytic process for biomass transformation in a single-step reaction. The effect of temperature on glucose conversion was studied. The temperatures studied were with 5 °C increments from 80 to 105 °C, and the results are shown in Figure 2b. The % yield of HMF increased with increasing temperature. A high temperature was usually needed to promote the dehydration reaction of glucose; however, at the highest temperature tested, the HMF yield slightly decreased due to HMF transformation into LA and FA, as reported by others [8,34,41,45,46]. We conclude from this study that the optimum temperature for glucose conversion to HMF in [DBDIm]I with or without H_2SO_4 was 100 °C. The best glucose conversion conditions were the operating temperature of 100 °C and the reaction time of 120 min in [DBDIm]I as both the solvent and Lewis acid, and H_2SO_4 as a Brønsted acid catalyst. These conditions produced 82.2% HMF. Wang et al. [46] reported that the optimum temperature to convert lignocelluloses to HMF was 160°. Zhang et al. [41] reported the optimum temperature to convert lignocelluloses into HMF was 100 °C. This study showed notable improvement in the HMF yield compared to previously reported studies.

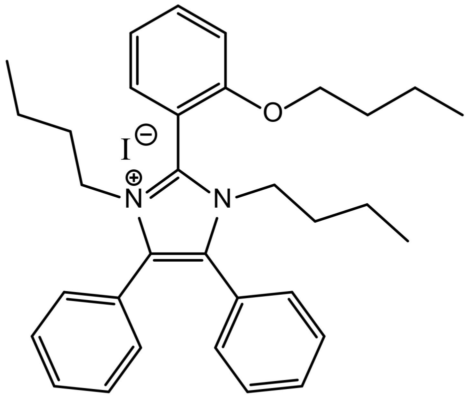
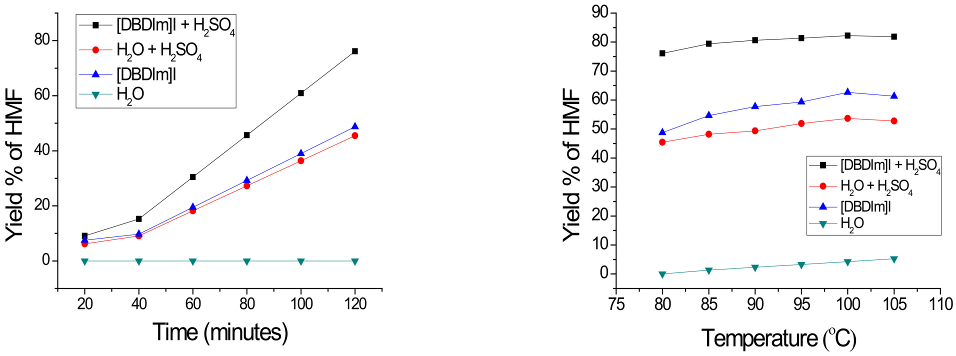


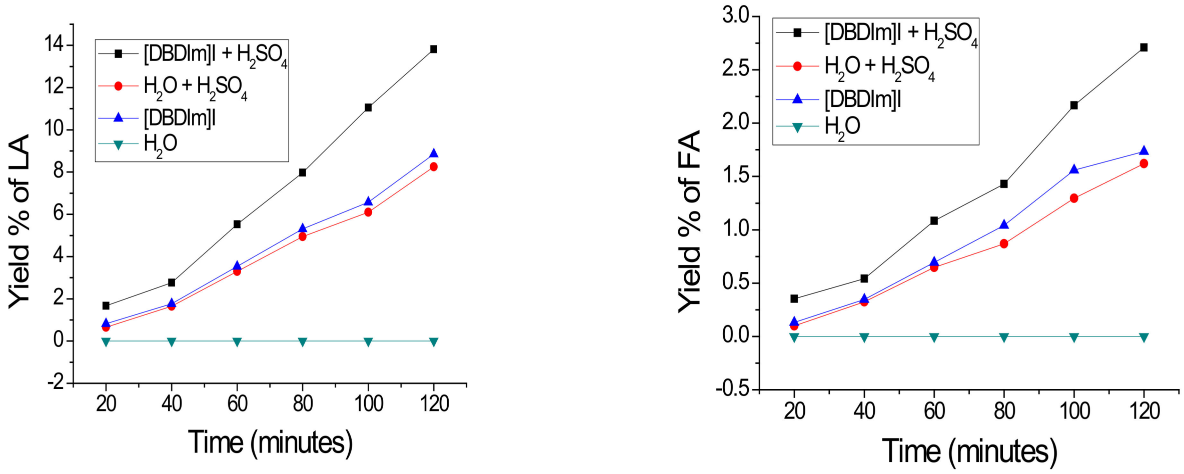
Figure 1. Structure of [DBDIm]I.



(**a**) (**b**)

Figure 2. (**a**) HMF percentage yield from glucose conversion in water or [DBDIm]I as a solvent, with or without H_2SO_4 at 80 °C; and (**b**) effect of temperature on glucose conversion.

There were few reports available on the sugar conversion to HMF. Fructose conversion to HMF supported by metal halides as a Lewis acid within 3 h gave a 70.0% HMF yield [16]. HMF from cellulose conversion reported by Xiao et al. [24] produced a yield of 54.9% within 9 h at 150 °C in [BMIm]Cl-based IL. Cellulose conversion in [BMIm]Cl supported by $TiOSO_4$ catalyst at 100 °C for 3 h produced 38.0% HMF [28,44–46]. Wang et al. [46] reported a yield of 43.7% HMF from cellulose in the presence of tetrabutylammonium-chloride (TBAC) and chromium(III) trichloride ($CrCl_3{\cdot}6H_2O$) catalyst at a 140 °C and 90 min reaction time. These reports showed lower HMF yields with relatively longer reaction times at higher temperatures compared to our study. The other glucose conversion products in [DBDIm]I or water at 80 °C with and without the addition of H_2SO_4 were LA and FA, as presented in Figure 3. The highest %mole yield of LA and FA were 13.8% and 2.7%, respectively. The results showed that the rehydration of HMF to LA and FA was also possible.



(**a**) (**b**)

Figure 3. HMF rehydration at 80 °C to LA (**a**) and FA (**b**) in [DBDIm]I or water, with or without H_2SO_4.

3.2. Performance of [DBDIm]I as a Solvent for Glucose Conversion

The performance of [DBDIm]I as a solvent in glucose conversion was studied further at optimum conditions. All products of glucose conversion were analyzed using HPLC. High glucose conversion to HMF (82.2%) was observed in the system with [DBDIm]I and 1M H_2SO_4. A low yield of HMF (5.2%) from glucose was observed in the control system with only glucose and water. The addition of H_2SO_4 in the control has improved the glucose conversion to HMF, with a yield of 49.1%. The glucose conversion results in [DBDIm]I or water, with or without H_2SO_4 at optimum conditions, are shown in Table 1.

Table 1. Results of glucose conversion at optimum conditions (100 °C for 2 h) *.

Solvent	Catalyst	%Mole Yield of Product			Remark
		HMF	Levulinic Acid	Formic Acid	
[DBDIm]I H_2O	Non Catalyst	52.1 ± 1.0 4.3 ± 0.1	9.6 ± 0.3 0.8 ± 0.1	1.9 ± 0.1 0.2 ± 0.1	[DBDIm]I gives better performance as a solvent
[DBDIm]I H_2O	H_2SO_4	82.2 ± 2.1 49.1 ± 1.4	14.9 ± 0.4 8.9 ± 0.4	2.9 ± 0.1 1.8 ± 0.1	[DBDIm]I performance as a solvent increased with the addition of H_2SO_4

* The results are the average of five replications with SD.

The main product in glucose conversion was HMF. However, LA and FA were also formed as side products after the decomposition reaction due to the more reactive glucose in the presence of [DBDIm]I as both solvent and Lewis acid catalyst. According to many reported studies, the acidic catalyst promotes water formation in the glucose dehydration process [7,11,20,26,47–49]. [DBDIm]I increased the –OH group's reactivity in glucose (stretch out the –OH bonding) for the easier release of water molecules and produced HMF. The use of [DBDIm]I as a solvent in glucose dehydration increased the HMF production in the acid catalyst due to the synergistic effect between the $[DBDIm]^+$ cation of IL and H^+ to make a more selective reaction. Furthermore, [DBDIm]I made an easier separation of HMF and side products from the trace glucose and impurities due to its property as a surfactant. The use of water as a solvent system without a catalyst showed its incapability to produce any products. These results supported the ability of [DBMIm]I to catalyze the glucose dehydration reaction, as well as being the better medium compared to water. The hydrophobicity of [DBDIm]I supported the selectivity of HMF capturing in the biphasic system (aqueous–organic (IL)) after completion of the reaction; thus, the separation of the product became easier. All of the glucose conversion products can be separated easily from IL due to the hydrophilic nature of HMF, LA, and FA. The IL can be recycled in the process.

The proposed mechanism of glucose dehydration in [DBDIm]I is shown in Figure 4. In the first step, the pyranose-ring-opening of glucose occurred to form the first intermediate molecule (b). The protonation of the anomeric –OH group within the intermediate molecule (b) by Brønsted acid led to the next intermediate species (c). The I^- anion of the IL deprotonated the –OH group of the intermediate species (c) to form a furanose ring (d). This intermediate was further oxidized assisted by the $[DBDIm]^+$ cation to produce the following molecule (e). At the last step, HMF (f) production occurred through the second dehydration supported by [DBDIm]I at 100 °C. Kassaye et al. [23] reported that the chloride (Cl^-) ion size has a small effect on the hydrolysis process. At the same time, [Bmim]Cl has the potential for cellulose degradation assisted by metal catalysts (sulfated zirconia), with a maximum HMF yield of 57.0% [23]. Tyagi et al. [3] reported a maximum HMF yield of 69.9% in 2 h using [Bmim]Cl as solvent. The iodide anion's role is relatively significant in increasing glucose dehydration. The I^- anion is larger and more polarized than Cl^-, which enhances the hydrolysis and pyranose-ring-opening of glucose.

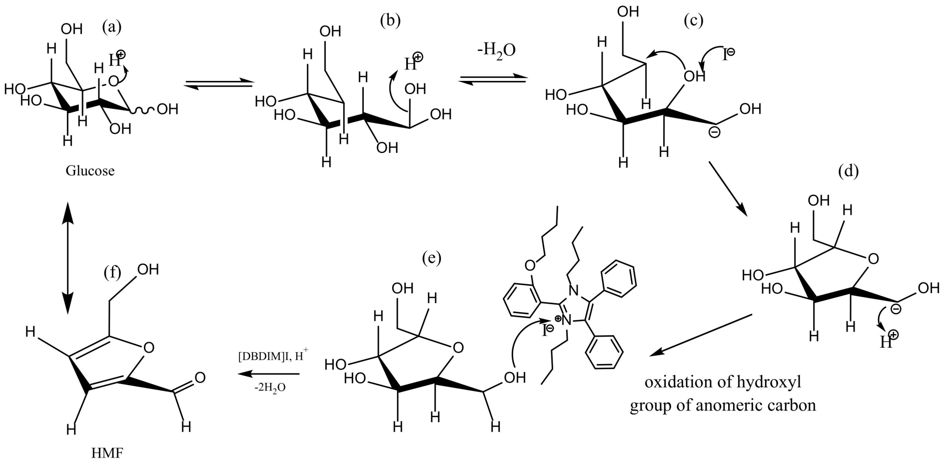
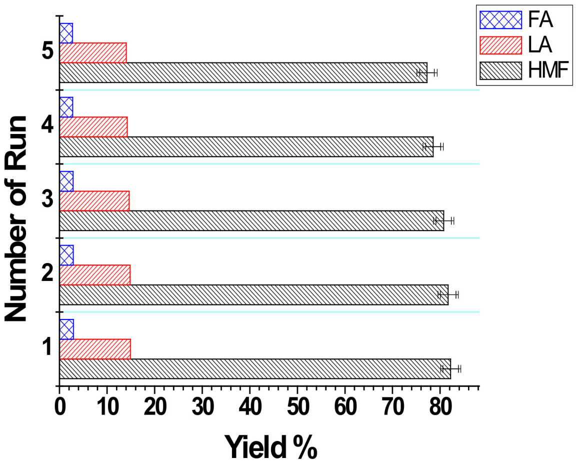


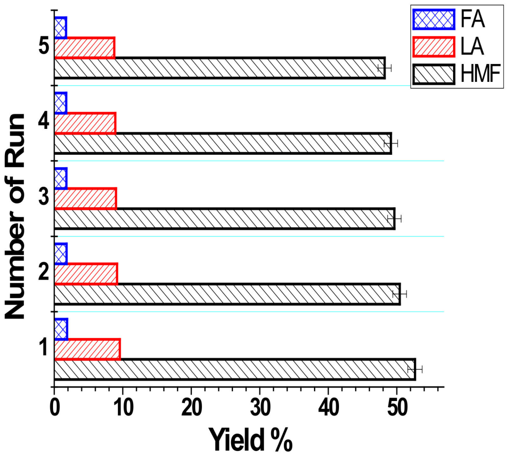
Figure 4. Proposed mechanism of glucose dehydration in [DBDIm]I as a solvent in the presence of a Brønsted acid catalyst. Note: (**a**) hydrolyze glucose with acid; (**b**) ring opening of glucose (dehydration); (**c**) closing pentacyclic; (**d**) de-carbanion; (**e**) oxidation of anomeric carbon; (**f**) HMF.

3.3. Recovery and Reusability of [DBDIm]I in Glucose Conversion

The HMF, LA, and FA were easily separated from the aqueous phase due to their difference in polarity, which is significantly different from [DBDIm]I. The efficient extraction of HMF requires a suitable solvent that should have low miscibility with water and lead to a high partition coefficient for each compound [24,43,46,50]. Therefore, [DBDIm]I can be used as a potential solvent. The conversion products in the [DBDIm]I phase can be easily separated by extracting in demineralized water. This advantage has led to the recycling and reuse of [DBDIm]I several times. Thus, the recovered [DBDIm]I can be reapplied for the next glucose conversion to the HMF process. The extraction of products was carried out using the mixtures of toluene and water (4:1, v/v) by liquid–liquid extraction to separate the HMF from LA and FA. After washing twice, the recycled [DBDIm]I was further used in the conversion process of 0.5 g of glucose with or without the addition of 0.5 mL 1 M H_2SO_4 at 100 °C for 2 h in an oven, for up to five cycles. The results are shown in Figure 5. The %mole yield trend of the glucose conversion products (HMF, LA, and FA) in the presence of H_2SO_4 decreased in each subsequent cycle, resulting in lower yields of products after the fifth cycle: 77.2% HMF, 14.0% LA, and 2.8% FA. Similarly, the use of recycled IL for glucose conversion in the absence of H_2SO_4 produced a lower %mole yield of HMF, LA, and FA, which were 48.2%, 8.8%, and 1.7%, respectively.



(**a**)



(**b**)

Figure 5. Results of glucose conversion in recycled [DBDIm]I at 100 °C for 2 h with H_2SO_4 (**a**) and without H_2SO_4 (**b**).

This study showed that [DBDIm]I has potential as a solvent and catalyst for glucose conversion. The yields of HMF, LA, and FA decreased during each cycle because [DBDIm]I was consumed during the reaction. The recycled [DBDIm]I supported by H_2SO_4 presented a relatively good performance, with an HMF yield higher than 70.0%, for up to five cycles, as shown in Figure 5. Zhao et al. [16] showed that the HMF from fructose conversion supported by metal halides as a Lewis acid was under 70.0% when reacted for 3 h. Leng et al. [14] used [BMIm]Cl and $CrCl_3$–$AlCl_3$ as catalysts in glucose conversion for 2 h at 120 °C, producing approximately 54.7% HMF. Zhang et al. [15] also reported the yield of 31.2% HMF when cellulose was used as a substrate with [EMIm]Cl and ATP–SO_3H–Cr(III) as catalysts. Our study showed that [DBDIm]I is a more effective medium due to its recyclability and its capability to retain its catalytic property in glucose conversion up to the five cycles.

The use of imidazolium-based IL, such as [DBDIm], has some advantages, such as being environmentally friendly, non-toxic, and easy to be produced on an industrial scale [25,51–53]. Other reports showed the use of [BMIm]Cl and [HMIm]HSO_4 as eco-friendly Lewis acid imidazolium-based ILs in cellulose conversion, with the addition of a metal ion catalyst, was more effective and efficient compared to other methods [3,40]. Wang et al. [45] reported that the tetrabutylammonium-chloride (TBAC) and chromium(III) trichloride ($CrCl_3 \cdot 6H_2O$) catalysts have significantly accelerated the conversion process of cellulose to HMF. However, this ammonium-based IL is more toxic to the environment than the imidazolium-based IL [25,51–53]. The present study showed the versatility of [DBDIm]I, which acts as a catalyst and as a solvent, in improving the glucose dehydration to HMF.

4. Conclusions

A [DBDIm]I-based IL has successfully converted glucose to HMF, LA, and FA, with high yields at 100 °C for 120 min, supported by H_2SO_4 as a Brønsted acid catalyst; these yields were 82.2% HMF, 14.9% LA, and 2.9% FA. [DBDIm] has potential as both a solvent and catalyst for glucose conversion. It can be recycled and reused in glucose conversion until the fifth cycle, with yields of 70.0% HMF, 10.0% LA, and 2.0% FA.

Supplementary Materials: The following are available online at https://www.mdpi.com/2076-3417/11/3/989/s1. Supplement File contains HPLC chromatograms.

Author Contributions: Conceptualization, M.Z., D.W., B., and B.B.; methodology, M.Z.; software, M.Z.; validation, M.Z. and B.B.; formal analysis, M.Z., and D.W.; investigation, M.Z.; resources, M.Z.; data curation, M.Z.; writing—original draft preparation, M.Z.; writing—review and editing, M.Z., D.W., I.G.W., and R.B.; visualization, M.Z., D.W., I.G.W., and R.B.; supervision, D.W., B., and B.B.; project administration, M.Z. and D.W.; funding acquisition, M.Z., D.W., B. and B.B. All authors have read and agreed to the published version of the manuscript.

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References

1. Tong, X.; Ma, Y.; Li, Y. Biomass into chemicals: Conversion of sugars to furan derivatives by catalytic processes. *Appl. Catal. A Gen.* **2010**, *385*, 1–13. [CrossRef]
2. Wang, K.; Liu, Y.; Wu, W.; Chen, Y. Production of Levulinic Acid via Cellulose Conversion Over Metal Oxide-Loaded MOF Catalysts in Aqueous Medium. *Catal. Lett.* **2020**, *150*, 322–331. [CrossRef]
3. Tyagi, U.; Anand, N.; Kumar, D. Synergistic effect of modified activated carbon and ionic liquid in the conversion of microcrystalline cellulose to 5-Hydroxymethyl Furfural. *Bioresour. Technol.* **2018**, *267*, 326–332. [CrossRef] [PubMed]
4. Boisen, A.; Christensen, T.; Fu, W.; Gorbanev, Y. Process integration for the conversion of glucose to 2,5-furandicarboxylic acid. *Chem. Eng. Res. Des.* **2009**, *87*, 1318–1327. [CrossRef]
5. Bozell, J.J.; Petersen, G.R. Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy's "Top 10" revisited. *Green Chem.* **2010**, *12*, 539–554. [CrossRef]
6. Menegazzo, F.; Ghedini, E.; Signoretto, M. 5-Hydroxymethylfurfural (HMF) production from real biomasses. *Molecules* **2018**, *23*, 2201. [CrossRef] [PubMed]
7. Zakrzewska, M.E.; Bogel-Łukasik, E.; Bogel-Łukasik, R. Ionic liquid-mediated formation of 5-hydroxymethylfurfural—A promising biomass-derived building block. *Chem. Rev.* **2010**, *111*, 397–417. [CrossRef]
8. Kuster, B. 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture. *Starch Stärke* **1990**, *42*, 314–321. [CrossRef]
9. Rosatella, A.A.; Simeonov, S.P.; Frade, R.F.; Afonso, C.A. 5-Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. *Green Chem.* **2011**, *13*, 754–793. [CrossRef]
10. Hu, L.; Zhao, G.; Hao, W.; Tang, X. Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals via furanic aldehydes. *RSC Adv.* **2012**, *2*, 11184–11206. [CrossRef]
11. Chheda, J.N.; Román-Leshkov, Y.; Dumesic, J.A. Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono-and poly-saccharides. *Green Chem.* **2007**, *9*, 342–350. [CrossRef]
12. Kim, Y.; Mittal, A.; Robichaud, D.J.; Pilath, H.M. Prediction of Hydroxymethylfurfural Yield in Glucose Conversion through Investigation of Lewis Acid and Organic Solvent Effects. *ACS Catal.* **2020**, *10*, 14707–14721. [CrossRef]
13. Grande, P.M.; Bergs, C.; Domínguez de María, P. Chemo-Enzymatic Conversion of Glucose into 5-Hydroxymethylfurfural in Seawater. *ChemSusChem* **2012**, *5*, 1203–1206. [CrossRef] [PubMed]
14. Leng, E.; Mao, M.; Peng, Y.; Li, X. The Direct Conversion of Cellulose into 5-Hydroxymethylfurfural with $CrCl_3$ Composite Catalyst in Ionic Liquid under Mild Conditions. *ChemistrySelect* **2019**, *4*, 181–189. [CrossRef]

15. Zhang, Y.; Pan, J.; Gan, M.; Ou, H. Acid–chromic chloride functionalized natural clay-particles for enhanced conversion of one-pot cellulose to 5-hydroxymethylfurfural in ionic liquids. *RSC Adv.* **2014**, *4*, 11664–11672. [CrossRef]
16. Zhao, H.; Holladay, J.E.; Brown, H.; Zhang, Z.C. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. *Science* **2007**, *316*, 1597–1600. [CrossRef]
17. Qi, X.; Watanabe, M.; Aida, T.M.; Smith, R.L. Synergistic conversion of glucose into 5-hydroxymethylfurfural in ionic liquid–water mixtures. *Bioresour. Technol.* **2012**, *109*, 224–228. [CrossRef]
18. 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. [CrossRef]
19. Yang, Y.; Liu, W.; Wang, N.; Wang, H. Effect of organic solvent and Brønsted acid on 5-hydroxymethylfurfural preparation from glucose over $CrCl_3$. *RSC Adv.* **2015**, *5*, 27805–27813. [CrossRef]
20. Su, Y.; Brown, H.M.; Huang, X.; Zhou, X.-d. Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical. *Appl. Catal. A Gen.* **2009**, *361*, 117–122. [CrossRef]
21. Tan, M.; Zhao, L.; Zhang, Y. Production of 5-hydroxymethyl furfural from cellulose in CrCl2/Zeolite/BMIMCl system. *Biomass Bioenergy* **2011**, *35*, 1367–1370. [CrossRef]
22. Despax, S.; Estrine, B.; Hoffmann, N.; Le Bras, J. Isomerization of d-glucose into d-fructose with a heterogeneous catalyst in organic solvents. *Catal. Commun.* **2013**, *39*, 35–38. [CrossRef]
23. Kassaye, S.; Pant, K.K.; Jain, S. Synergistic effect of ionic liquid and dilute sulphuric acid in the hydrolysis of microcrystalline cellulose. *Fuel Process. Technol.* **2016**, *148*, 289–294. [CrossRef]
24. Xiao, S.; Liu, B.; Wang, Y.; Fang, Z. Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide-ionic liquid mixtures. *Bioresour. Technol.* **2014**, *151*, 361–366. [CrossRef]
25. Zunita, M.; Wahyuningrum, D.; Bundjali, B.; Wenten, I.G.; Boopathy, R. The Performance of 1, 3-Dipropyl-2-(2-propoxyphenyl)-4, 5-diphenylimidazolium Iodide based Ionic Liquid for Biomass Conversion into Levulinic Acid and Formic Acid. *Bioresour. Technol.* **2020**, *315*, 123864. [CrossRef]
26. Makertihartha, I.; Zunita, M.; Rizki, Z.; Dharmawijaya, P. Solvent extraction of gold using ionic liquid based process. *AIP Conf. Proc.* **2017**, *1805*, 030008.
27. Makertihartha, I.; Zunita, M.; Dharmawijaya, P.; Wenten, I. Supported ionic liquid membrane in membrane reactor. *AIP Conf. Proc.* **2017**, *1788*, 040003.
28. Makertihartha, I.; Rizki, Z.; Zunita, M.; Dharmawijaya, P. Dyes removal from textile wastewater using graphene based nanofiltration. *AIP Conf. Proc.* **2017**, *1840*, 110006.
29. Chiappe, C.; Rodriguez Douton, M.J.; Mezzetta, A.; Pomelli, C.S. Recycle and extraction: Cornerstones for an efficient conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids. *ACS Sustain. Chem. Eng.* **2017**, *5*, 5529–5536. [CrossRef]
30. Zunita, M.; Wahyuningrum, D.; Bundjali, B.; Wenten, I.G.; Boopathy, R. Corrosion Inhibition Performances of Imidazole Derivatives-Based New Ionic Liquids on Carbon Steel in Brackish Water. *Appl. Sci.* **2020**, *10*, 7069. [CrossRef]
31. Kamavaram, V.; Reddy, R.G. Thermal stabilities of di-alkylimidazolium chloride ionic liquids. *Int. J. Therm. Sci.* **2008**, *47*, 773–777. [CrossRef]
32. Huddleston, J.G.; Willauer, H.D.; Swatloski, R.P.; Visser, A.E. Room temperature ionic liquids as novel media for 'clean'liquid–liquid extraction. *Chem. Commun.* **1998**, 1765–1766. [CrossRef]
33. Huang, L.; Zhai, M.; Peng, J.; Xu, L. Synthesis of room temperature ionic liquids from carboxymethylated chitosan. *Carbohydr. Polym.* **2008**, *71*, 690–693. [CrossRef]
34. Hou, Q.; Zhen, M.; Liu, L.; Chen, Y. Tin phosphate as a heterogeneous catalyst for efficient dehydration of glucose into 5-hydroxymethylfurfural in ionic liquid. *Appl. Catal. B Environ.* **2018**, *224*, 183–193. [CrossRef]
35. Zhang, Z.; Zhao, Z.K. Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. *Bioresour. Technol.* **2010**, *101*, 1111–1114. [CrossRef]
36. Hsu, W.-H.; Lee, Y.-Y.; Peng, W.-H.; Wu, K.C.-W. Cellulosic conversion in ionic liquids: Effects of H_2O/cellulose molar ratios, temperatures, times, and different ILs on the production of monosaccharides and 5-hydroxymethylfurfural (HMF). *Catal. Today* **2011**, *174*, 65–69. [CrossRef]
37. Earle, M.J.; Seddon, K.R. Ionic liquids. Green solvents for the future. *Pure Appl. Chem.* **2000**, *72*, 1391–1398. [CrossRef]
38. Plechkova, N.V.; Seddon, K.R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150. [CrossRef]
39. Ståhlberg, T.; Sørensen, M.G.; Riisager, A. Direct conversion of glucose to 5-(hydroxymethyl) furfural in ionic liquids with lanthanide catalysts. *Green Chem.* **2010**, *12*, 321–325. [CrossRef]
40. Tiong, Y.W.; Yap, C.L.; Gan, S.; Yap, W.S.P. Kinetic and thermodynamic studies of oil palm mesocarp fiber cellulose conversion to levulinic acid and upgrading to ethyl levulinate via indium trichloride-ionic liquids. *Renew. Energy* **2020**, *146*, 932–943. [CrossRef]
41. Román-Leshkov, Y.; Dumesic, J.A. Solvent effects on fructose dehydration to 5-hydroxymethylfurfural in biphasic systems saturated with inorganic salts. *Top. Catal.* **2009**, *52*, 297–303. [CrossRef]
42. Zhang, K.; Pei, Z.; Wang, D. Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemicals: A review. *Bioresour. Technol.* **2016**, *199*, 21–33. [CrossRef]
43. Bicker, M.; Hirth, J.; Vogel, H. Dehydration of fructose to 5-hydroxymethylfurfural in sub-and supercritical acetone. *Green Chem.* **2003**, *5*, 280–284. [CrossRef]

44. Chiappe, C.; Pieraccini, D. Ionic liquids: Solvent properties and organic reactivity. *J. Phys. Org. Chem.* **2005**, *18*, 275–297. [CrossRef]
45. Shen, Y.; Zhang, Y.; Chen, Y.; Yan, Y. Combination of Brønsted and Lewis Polymeric Catalysts for Efficient Conversion of Cellulose into 5-Hydroxymethylfurfural (HMF) in Ionic Liquids. *Energy Technol.* **2016**, *4*, 600–609. [CrossRef]
46. Wang, S.; Du, Y.; Zhang, W.; Cheng, X. Catalytic conversion of cellulose into 5-hydroxymethylfurfural over chromium trichloride in ionic liquid. *Korean J. Chem. Eng.* **2014**, *31*, 1786–1791. [CrossRef]
47. Wang, P.; Yu, H.; Zhan, S.; Wang, S. Catalytic hydrolysis of lignocellulosic biomass into 5-hydroxymethylfurfural in ionic liquid. *Bioresour. Technol.* **2011**, *102*, 4179–4183. [CrossRef]
48. Makertihartha, I.; Dharmawijaya, P.; Zunita, M.; Wenten, I. Post combustion CO_2 capture using zeolite membrane. *AIP Conf. Proc.* **2017**, *1818*, 020074.
49. Chun, J.A.; Lee, J.W.; Yi, Y.B.; Hong, S.S. Direct conversion of starch to hydroxymethylfurfural in the presence of an ionic liquid with metal chloride. *Starch Stärke* **2010**, *62*, 326–330. [CrossRef]
50. Lewkowski, J. Synthesis, chemistry and applications of 5-hydroxymethyl-furfural and its derivatives. *Arkivoc* **2001**, *1*, 17–54. [CrossRef]
51. Zunita, M.; Wahyuningrum, D.; Buchari, B.B. Investigation of corrosion inhibition activity of 3-butyl-2,4,5-triphenylimidazole and 3-butyl-2-(2-butoxyphenyl)-4, 5-diphenylimidazole toward carbon steel in 1% NaCl solution. *Int. J. Electrochem. Sci.* **2012**, *7*, 3274–3288.
52. Handy, S.T.; Okello, M. The 2-position of imidazolium ionic liquids: Substitution and exchange. *J. Org. Chem.* **2005**, *70*, 1915–1918. [CrossRef] [PubMed]
53. Liu, W.; Cheng, L.; Zhang, Y.; Wang, H. The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: Database and evaluation. *J. Mol. Liq.* **2008**, *140*, 68–72. [CrossRef]