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Efficient 5-hydroxymethylfurfural production in ChCl-based deep eutectic solvents using boric acid and metal chlorides

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Bio-based 5-hydroxymethylfurfural (5-HMF) production in DESs has garnered significant attention due to its effectiveness and environmental friendliness. In this study, acidic ChCl-based DESs and ChCl–fructose DES were compared in terms of 5-HMF production in the presence of four acids, namely boric acid, oxalic acid, citric acid, and *p*-toluenesulfonic acid. Simultaneously, two types of ChCl–fructose and ChCl–glucose DESs were explored in combination with boric acid for 5-HMF production respectively. The 5-HMF yield was optimized by varying parameters such as the mass ratio of ChCl to carbohydrate, catalyst usage, temperature, time, and water content. The results indicated that ChCl–fructose DES exhibits better performance in converting fructose to 5-HMF than acidic ChCl-based DES. A 5-HMF yield of 65.2% was obtained in ChCl–fructose DES (6 : 4 w/w) with 20% water and 80 mg boric acid at 120 °C for 120 minutes. Similarly, a 5-HMF yield of 33.7% from glucose was presented in ChCl–glucose DES (6 : 4 w/w) with 20% water, 120 mg boric acid, and 25 mg CrCl₃·6H₂O at 120 °C for 120 minutes. The addition of an appropriate amount of water is beneficial for promoting 5-HMF production in ChCl–fructose and ChCl–glucose DESs. The high viscosities of ChCl–fructose and ChCl–glucose DESs can be attributed to a strong intermolecular force, resulting in a large mass transfer resistance. Overall, this work provides an efficient and inexpensive approach for producing 5-HMF in ChCl–fructose and ChCl–glucose DESs.

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Introduction

5-Hydroxymethylfurfural (5-HMF), an important platform compound, has drawn significant attention from scientists as it can be used to produce levulinic acid, formic acid, 2,5-dimethylfuran, and furan compounds.^{1–3} Fructose and glucose are the main feedstocks for bio-based 5-HMF production. The industrial production of 5-HMF using fructose as a raw material has been achieved. However, the production cost is too high, resulting in a lack of market competitiveness. Therefore, more research focus is required on the glucose conversion to 5-HMF, considering the low cost and the structure similar to fructose.^{4,5} The stable molecular structure of glucose makes it challenging to achieve high yield and selectivity in converting it to 5-HMF.^{6,7} It's necessary to choose the effective solvents and catalysts for obtaining high-yield 5-HMF.

The conversion of glucose to 5-HMF usually undergoes two processes: the isomerization of glucose to fructose and the dehydration of fructose to 5-HMF, catalyzed by Lewis acid and Brønsted acid, respectively.⁸ The most commonly used

catalysts during the process of fructose to 5-HMF are still mineral acids such as HCl and H₂SO₄, but the high corrosivity and reusability issues of mineral acids in industry remain urgent problems that require attention.^{4,9} Metal salts such as CrCl₃·6H₂O and AlCl₃ are mainly used to catalyze glucose isomerization.^{10,11} Boric acid can simultaneously catalyze glucose isomerization and fructose dehydration and has non-toxic and non-corrosive properties as reported.^{12,13} The catalytic performance of catalysts varies in different solvents, especially in DESs, due to possible interactions between solvents, carbohydrates, and catalysts.¹⁴

Deep eutectic solvents (DESs) are regarded as a promising solvent for converting glucose to 5-HMF, because of the advantages of low-cost, non-toxic, easy preparation, recovery and environmental friendliness.^{15–17} The DESs composed of choline chloride (ChCl) and a hydrogen bond donor (HBD) exhibited their advantages in 5-HMF production from cellulosic biomass.^{16,18,19} The innovative application of DES in synergy with multiple technologies in biomass processing has provided new ideas for improving the conversion efficiency of biomass.²⁰ A 5-HMF yield of 72% from fructose was reported in the ChCl/carbon dioxide system, where carbon dioxide as a hydrogen bond donor provides easy product separation and ChCl recovery.¹⁶ ChCl–carboxylic acid DESs are the most common acidic DESs for producing 5-HMF from fructose, glucose, and cellulose, using citric acid, oxalic acid, maleic acid, formic acid,

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etc. as the hydrogen bond donor.^{21–26} However, excessive acid in ChCl–acid DESs may cause 5-HMF degradation to levulinic acid and formic acid.^{27,28}

In consideration of acid usage and catalytic efficiency, ChCl–fructose DES and ChCl–glucose DES were explored for the production of 5-HMF and other downstream products using acid catalysts.^{9,29} These systems introduce fewer chemical reagents and facilitate easier 5-HMF separation compared to acidic ChCl-based DESs. Zuo *et al.*⁹ obtained an extremely high 5-HMF yield of 90.3% from fructose degradation with 1.2 mol% HCl as the catalyst in the DESs system, but a high HCl concentration led to a significant decrease in 5-HMF yield. Fructose and glucose were catalyzed to 5-HMF with yields of 91.3% and 60.1% by carbon solid acidic catalysts in ChCl–fructose and ChCl–glucose DES, respectively.²⁹ Additionally, a sucrose/fructose/glucose DES combined with a magnetically solid acid catalyst yields 75% 5-HMF in a solvent-free system.³⁰ The ChCl–CrCl₃·6H₂O DES was used to convert glucose and other carbohydrates to 5-HMF with a yield above 70%.³¹ Moreover, the biphasic system of DESs/organic solvents such as acetonitrile, tetrahydrofuran, and ethyl *N*-butyrate was also employed to improve the 5-HMF yield.^{32,33} Actually, more work is still needed to explore the suitable reaction system for 5-HMF production from glucose, including DESs and catalysts types.

In this study, acidic ChCl-based DESs and ChCl–fructose DES were studied for 5-HMF production from fructose. Here, some organic acids and boric acid were introduced for 5-HMF production in ChCl–fructose and ChCl–glucose DESs. Moreover, the impacts of process parameters on 5-HMF yield in ChCl–fructose DESs and ChCl–glucose DESs were investigated, including catalyst types and usage, the mass ratio of ChCl and carbohydrate, temperature, time, and water contents. Additionally, the viscosity of ChCl–fructose and ChCl–glucose DESs as a function of temperature was analyzed. Finally, the hydrolysis mechanism and the effect of DESs were also discussed. This work constructs a green reaction system for producing 5-HMF by combining boric acid with DESs.

Experimental

Chemicals

Fructose, glucose, 5-HMF, and choline chloride (99%) were procured from Sigma-Aldrich. Chemical reagents such as urea, citric acid, oxalic acid, *p*-toluenesulfonic acid, and boric acid were sourced from Guangfu Company in Tianjin. All other chemicals in this work are of analytical pure grade. Fructose, glucose, and 5-HMF (chromatographic pure) were employed to prepare samples for the standard curves.

The preparation of ChCl-based DESs

The DESs were prepared by mixing HBD and HBA according to the given ratio as presented in Table 1. The solid reagents were continuously stirred at 80 °C until a clear liquid was formed in a magnetic stirring reaction device. All reagents were dried in an oven prior to use. The formed DESs should be stored in a desiccator for subsequent use.

Table 1 The components of synthesized DESs

Entry	HBA	HBD	Molar ratio	DESs abbreviations
1	ChCl	Urea	1 : 1	ChCl–U
2	ChCl	Boric acid	1 : 1	ChCl–BA
3	ChCl	Citric acid	1 : 1	ChCl–CA
4	ChCl	Oxalic acid	1 : 1	ChCl–OA
5	ChCl	<i>p</i> -Toluenesulfonic acid	1 : 1	ChCl–TsOH
6	ChCl	Fructose	6 : 4 (w/w)	ChCl–F
7	ChCl	Glucose	6 : 4 (w/w)	ChCl–G

Dehydration of fructose and glucose in ChCl-based DESs

The hydrolysis experiments of fructose and glucose were carried out by magnetic stirring in a sealed glass bottle placed in an oil bath. According to the experiment design, the hydrolysis of fructose and glucose were conducted under specific conditions. The experiment flow was shown in Scheme 1.

In acidic ChCl-based DESs, the production of 5-HMF from fructose was carried out at a fructose concentration of 5 wt% at 120 °C after 120 minutes. In ChCl–fructose or ChCl–glucose DESs, 5-HMF was produced by adding catalyst under specific reaction conditions.

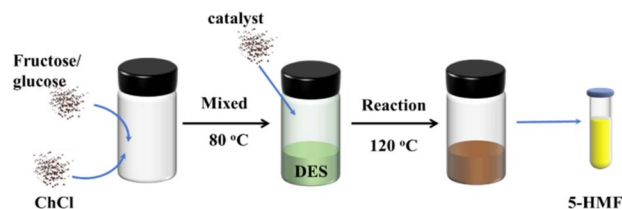
In a typical experiment, 600 mg of ChCl and 400 mg of fructose were mixed and stirred constantly at 80 °C until the liquid became clear. The synthesized DESs were preheated for 10 minutes at 120 °C in an oil bath, and then the catalyst boric acid of 100 mg was added to the reactors to initiate the hydrolysis reaction. The reaction was terminated by placing the reactor in an ice bath for 10 minutes. Subsequently, the liquid was collected by filtering the mixture, and then the volume of the liquid sample was adjusted to 25 mL with water. The samples were filtered through a 0.45 μm syringe filter, stored at 4 °C, and prepared for testing.

For the experiment of glucose conversion, 600 mg of ChCl and 400 mg glucose was mixed at 80 °C and formed the ChCl–glucose DES. In the typical experiment, the catalysts boric acid (120 mg) and CrCl₃·6H₂O (100 mg) were added to catalyze glucose hydrolysis at 120 °C for 2 h. In the optimization experiment, the reaction condition were adjusted according to the experimental design.

For the experiments on the effect of water content on 5-HMF yield, different amounts of water, namely 10 wt%, 20 wt%, 30 wt%, 40 wt%, and 50 wt%, were added respectively to the formed DESs.

The measurement of ChCl-based DES viscosity

The viscosities of ChCl–fructose and ChCl–glucose DESs were measured using a rotation viscometer, and the solvent



Scheme 1 The experimental flowchart of fructose/glucose dehydration in ChCl–fructose and ChCl–glucose DESs.



temperature was maintained in a water bath device to achieve temperature changes.

Products analysis

The hydrolysis products were analyzed by high performance liquid chromatography (HPLC). Fructose, glucose, and 5-HMF were quantified on a Flexar LC-Chromera HPLC using a PerkinElmer instrument from the US, equipped with a Shodex SH1011 column (8.0 × 300 mm) and a refraction-differential detector (RID). The mobile phase was 0.005 mol per L H₂SO₄. The samples were measured at a flow rate of 0.6 mL min⁻¹ at a column temperature of 50 °C, and the sample injection volume was 10 μL.

The calculation of 5-HMF yield from fructose and glucose was as following:

$$\text{Yield}_{5\text{-HMF}} = \frac{\text{Moles of 5-HMF}}{\text{Initial moles of carbohydrate}} \times 100\%$$

Results and discussion

Comparison of acidic ChCl-based DESs and ChCl-fructose DES in the conversion of fructose to 5-HMF

Due to the dual functions of acidic ChCl-based DESs as solvents and catalysts, an increasing number of studies have focused on carbohydrate hydrolysis in acidic ChCl-based DESs.¹⁸ Some investigations have also been conducted to explore the possibility of saccharide conversion in ChCl-saccharide DESs.^{9,29} Here, the production of 5-HMF from fructose was compared in acidic ChCl-acid DESs and ChCl-fructose DES as depicted in Fig. 1. For acidic ChCl-based DESs, four types of ChCl-acid DESs were prepared according to Table 1, with boric acid (BA), oxalic acid (OA), citric acid (CA), and *p*-toluenesulfonic acid (TsOH) as HBDs, and ChCl-urea DES served as a control. As shown in Fig. 1 (left), 5-HMF was detected after hydrolysis in four acidic DESs without any additional catalyst. The yields of 28.4%, 38.9%, and 30.9% corresponded to the HBDs of BA, OA, and CA, respectively. However, a very low yield of 5-HMF was

obtained in the ChCl-TsOH DES under the same conditions, even 5-HMF was not detected in the ChCl-urea DES as the control. The lower yield is mainly related to the acidity of TsOH in the DES system. The strong acidity of TsOH can promote the excessive decomposition or polymerization of fructose. This phenomenon leads to a significant augmentation in the generation of by-products, thereby resulting in a notable reduction in the yield of 5-HMF.

The results showed that the acidic environment in DES was necessary for the production of 5-HMF, and the type and content of acidic HBD have a significant impact on the yield.

In comparison, the above four acids were used as catalysts in ChCl-fructose DES to produce 5-HMF from fructose. As shown in Fig. 1 (right), a remarkably high yield of 5-HMF was exhibited in ChCl-fructose DES, with values of 54.4%, 55.5%, 60.6%, and 22.0% by BA, OA, CA, and TsOH, respectively. Evidently, a stronger acidity of the catalyst leads to a higher yield of 5-HMF. Nevertheless, when the strongest acid TsOH is employed as the catalyst, the yield of 5-HMF is unexpectedly the lowest value. The results reveals a significant advantage of ChCl-fructose DES over acidic ChCl-based DESs. Similarly, the low yield of 5-HMF in acidic DESs may also be related to the acid types and content. That is, strong acids or excessive acids in the hydrolysis system may lead to serious side reactions, which is consistent with previous studies.^{9,34}

In ChCl-fructose DES, fructose forms a unique hydrogen-bonding network with ChCl. Hydroxyl groups of fructose interact with choline chloride's chloride ions and choline cation's nitrogen atom, stabilizing intermediates in fructose to 5-HMF conversion.³⁵ Conversely, in acidic DESs, acidic components interact with reactants *via* proton donation. High-acidity causes non-selective reactions like over-dehydration or side reactions, forming humins and by-products, reducing 5-HMF yield.³⁶ ChCl-fructose DES has a different solvation effect on fructose than acidic DESs. In ChCl-fructose DES, the solvation shell around fructose controls reaction-group orientation, promoting 5-HMF forming intramolecular dehydration.^{14,37} In acidic DESs, strong acidity disrupts fructose solvation, leading to unregulated reactions and lower 5-HMF yield.

The advantage of ChCl-fructose DES lies in that it allows for the free selection of the type and amount of acid catalyst as required. However, for acidic DESs, both solvent formation and catalytic efficiency need to be considered simultaneously. Therefore, the combination of ChCl-fructose DES and acid catalyst is an effective method for 5-HMF production. In terms of acid catalyst selection, boric acid would be intensively investigated due to its advantages in catalytic activity, isomerization ability, non-corrosiveness, and eco-friendliness. In reported works, a nearly 60% yield of 5-HMF was achieved with 100 g per L boric acid (B(OH)₃) and 50 g per L sodium chloride at a highly concentrated 30% fructose in H₂O/methyl isobutyl ketone (MIBK) solvents.³⁸ In this work, a slightly low yield of 5-HMF was obtained using boric acid without an extraction solvent in ChCl-fructose DESs. A higher yield of 5-HMF is expected through process optimization. Boric acid would be further studied for 5-HMF production in ChCl-fructose and ChCl-glucose DESs in the following experiments.

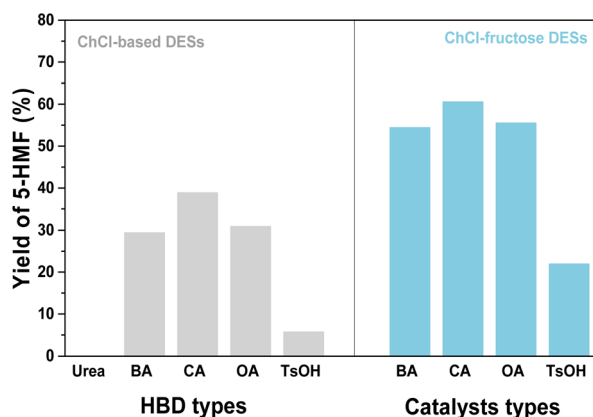


Fig. 1 The 5-HMF yields from fructose in ChCl-acid DESs and ChCl-fructose DES at 120 °C after 120 min.



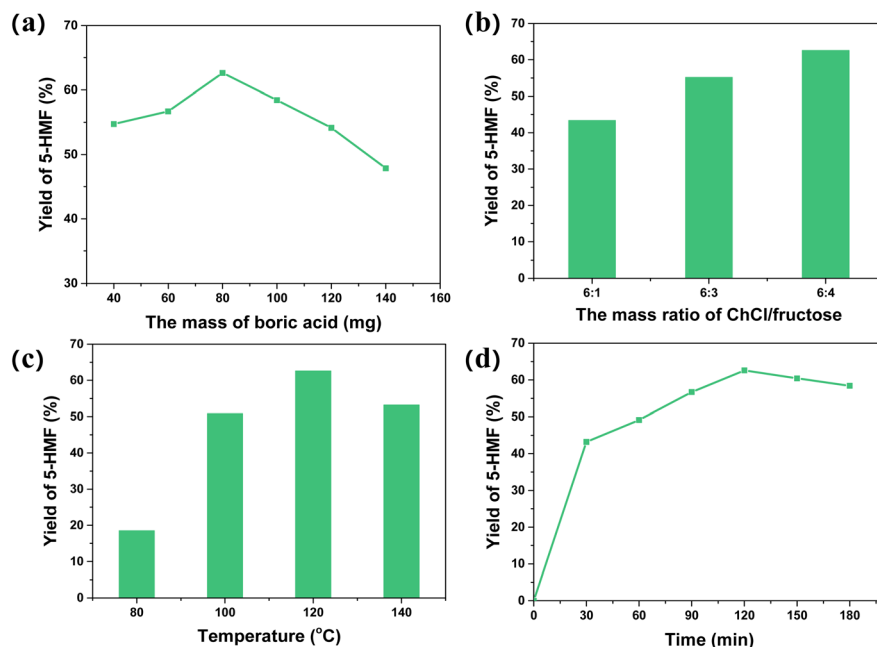


Fig. 2 The change in 5-HMF yield from fructose in ChCl–fructose DES with the reaction condition (a) boric acid usages (b) ChCl–fructose mass ratios (c) temperature (d) reaction time.

The conversion of fructose to 5-HMF catalyzed by boric acid in ChCl–fructose DES

The conversion of fructose catalyzed by boric acid in ChCl–fructose DES was optimized by varying process parameters such as boric acid usage, the mass ratio of fructose to ChCl, temperature, and reaction time. The effect of boric acid content on the production of 5-HMF from fructose was examined within the range of 40–140 mg at 120 °C after 120 minutes. As shown in Fig. 2a, under the aforementioned reaction conditions, the yield of 5-HMF initially increased and then declined with the increase of boric acid content, reaching a peak at 80 mg of boric acid.

The mass ratio of ChCl–fructose affects the properties of DESs, fructose solubility, and catalytic efficiency. The yield of 5-HMF from fructose was investigated at ChCl–fructose mass ratios of 6:1, 6:3, 6:4, 6:5, and 6:6. The experimental phenomenon showed that as the fructose content in the system increases, the formation of DESs becomes more and more difficult, accompanied by the continuous increase in viscosity. Even the ChCl–fructose mixture appears too viscous to form a clarified DES at mass ratios of 6:5 and 6:6. From Fig. 2b, there is an upward trend in the 5-HMF yield from 43.4% to 62.6% as the ChCl–fructose mass ratio decreases from 6:1 to 6:4. The highest 5-HMF yield of 62.6% is exhibited at a mass ratio of 6:4 with 80 mg of boric acid at 120 °C after 120 minutes.

The yield of 5-HMF from fructose was studied in ChCl–fructose DES at temperatures ranging from 80 to 140 °C after 120 min. As shown in Fig. 2c, the yield of 5-HMF increased with the increase of hydrolysis temperature from 80 to 120 °C. Subsequently, the 5-HMF yield began to decline at 140 °C. The highest 5-HMF yield was obtained at 120 °C from fructose in this process. These results indicate that the conversion of fructose to

5-HMF strongly depends on the reaction temperature in the ChCl–fructose DES. The effect of time on the 5-HMF yield was also studied from fructose during 0–180 minutes in ChCl/fructose of 6:4 (w/w) with 80 mg of boric acid at 120 °C. From Fig. 2d, the 5-HMF yield showed a change trend of initial increase followed by a slightly decrease from 0 to 180 min. The highest 5-HMF yield of 62.6% was obtained from fructose after 120 minutes at 120 °C. Subsequently, the 5-HMF yield began to decrease with the prolongation of time, which can be attributed to the degradation or polymerization of 5-HMF at longer times.³⁹

In summary, the highest 5-HMF yield of 62.6% from fructose was obtained in ChCl–fructose DES (6:4 w/w) with 80 mg of boric acid at 120 °C for 120 minutes.

The conversion of glucose to 5-HMF catalyzed by boric acid and CrCl₃ in ChCl–glucose DES

The conversion of glucose to 5-HMF in ChCl–glucose DES was investigated. The impact of various reaction factors on 5-HMF yield was analyzed, including catalysts, the mass ratio of glucose to ChCl, temperature, and reaction time.

The 5-HMF yields in ChCl–glucose DES were compared with various catalysts BA, OA, CA, TSOH to screen for the optimal catalysts. Evidently, boric acid exhibited the most optimal catalytic performance, which was far higher than that of other catalysts (Fig. 3a). This can be attributed to the isomerization of boric acid. To further improve the catalytic efficiency, the catalytic effect of the combined catalysts composed of boric acid and metal chlorides were also investigated, such as CrCl₃, AlCl₃, FeCl₃, CuCl₂. The catalyst combination of boric acid and CrCl₃ displayed the maximum 5-HMF yield among all catalyst systems (Fig. 3a).



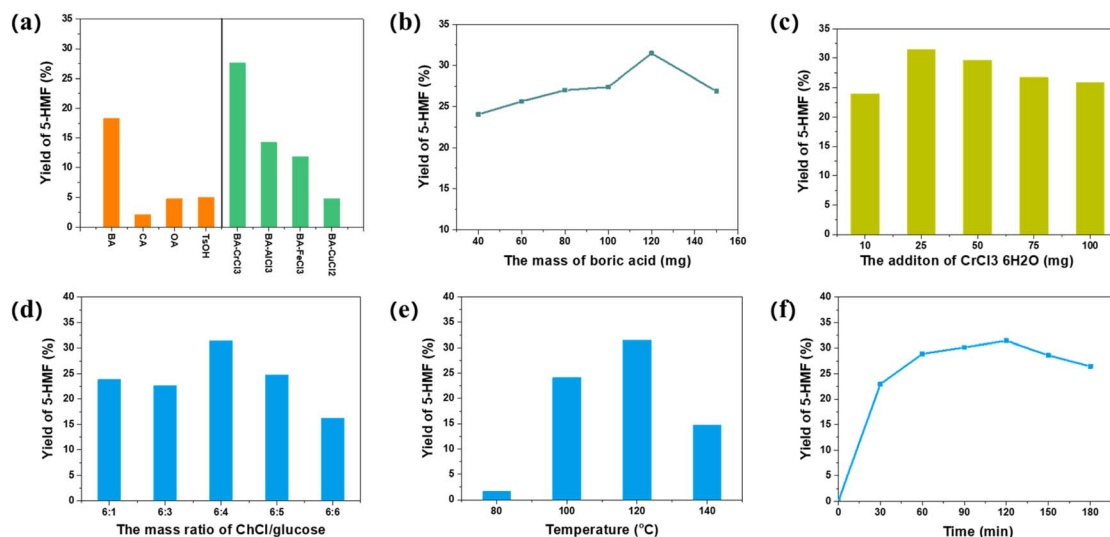


Fig. 3 The change in 5-HMF yield from glucose in ChCl–glucose DES with the reaction condition (a) catalysts types (b) boric acid usages (c) $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ usages (d) ChCl–glucose mass ratios (e) temperature (f) reaction time.

The conversion of glucose to 5-HMF was conducted in ChCl–glucose DES with 100 mg CrCl_3 and boric acid, the change in 5-HMF yield were shown in Fig. 3b and c with the usage of boric acid and CrCl_3 . As the boric acid content increased from 40 mg to 140 mg, the yield of 5-HMF first rose and then fell, reaching the maximum at a boric acid addition of 120 mg. When the addition of CrCl_3 in the system was 10, 25, 50, 75, or 100 mg, the maximum 5-HMF yield was achieved with 25 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ addition as depicted in Fig. 3c. The results indicated that an appropriate catalyst dosage is essential for achieving a high yield of 5-HMF. And the highest 5-HMF yield emerged in ChCl–glucose DES with 25 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 120 mg boric acid.

The effect of ChCl to glucose mass ratios on 5-HMF yield was investigated with 120 mg boric acid and 25 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at 120 °C after 120 minutes at the mass ratio of 6 : 1, 6 : 3, 6 : 4, 6 : 5, and 6 : 6. In this range, the mixture of ChCl and glucose can form a clear and transparent solution. The viscosity of ChCl–glucose DES is notably lower than that of ChCl–fructose DES. The highest 5-HMF yield of 31.5% was exhibited at a mass ratio of 6 : 4. As the mass ratio of ChCl to glucose was 6 : 5 and 6 : 6, the 5-HMF yield decreased to 24.8% and 16.3% (Fig. 3d). The high viscosity of ChCl–glucose DES at high glucose contents may be an important factor for the reduced 5-HMF yield. Because it blocks mass transfer and inhibits the hydrolysis reaction.⁴⁰ The high 5-HMF yield at elevated glucose contents also corresponds to a high 5-HMF concentration, which is beneficial for industrial production due to reduced product separation costs.

The effect of temperature on 5-HMF yield from glucose was studied at 80, 100, 120, 140 °C (Fig. 3e). When the temperature is set at 120 °C, the highest yield of 5-HMF was obtained at 120 °C. Only a negligible amount of 5-HMF was produced at 80 °C. As the temperature increased from 80 °C to 120 °C, the yield of 5-HMF increased along with the increase in temperature. However, a significant decrease in the yield was observed as the temperature

was further elevated to 140 °C. In general, high temperature can enhance the thermal motion of molecules and promote the conversion of glucose to 5-HMF.⁴¹ However, polymerization reactions at high temperature may occur to form humins, reducing the 5-HMF yield and selectivity. Besides, excessive temperature may destroy the DESs structure and have an adverse effect on the catalytic reaction.⁴² The conversion of glucose to 5-HMF was carried out within 0 to 180 minutes. The highest 5-HMF yield of 31.5% was obtained from glucose at 120 °C after 120 minutes (Fig. 3f). In the initial 30 min, the yield of 5-HMF increased rapidly with the increase of time, then it continued to increase at a slow rate until 120 min. After that, the yield of 5-HMF decreased instead with the prolong of time, which can be attributed to 5-HMF degradation or polymerization at longer times.³⁹ All in all, the highest 5-HMF yield of 31.5% from glucose was produced in ChCl–glucose DES (6 : 4 w/w) with 120 mg boric acid and 25 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at 120 °C for 120 minutes.

The physicochemical properties of ChCl–fructose and ChCl–glucose DESs

Considering the effect of viscosity on DES properties and mass transfer efficiency, the viscosities of ChCl–fructose and ChCl–glucose DESs were measured using a rotational viscometer within the temperature range of 298–358 K. As shown in Fig. 4, the viscosities of ChCl–fructose DES and ChCl–glucose DES were 5.3437×10^4 and 7.937×10^3 mPa s at 298 K, then gradually decreased to 576 and 388 mPa s at 358 K with the increase of temperature. Both of them meet the characteristics of Newton fluid. Evidently, the viscosity of ChCl–fructose DES was far higher than that of ChCl–glucose DES, which was in accordance with the formation of DES at a high fructose content. The decreased viscosity of DESs at high temperatures also promote the catalytic reaction and increase 5-HMF yield, which can be explained by the improved mass transfer efficiency and catalytic activity.⁴⁰ In comparison, a significantly higher viscosity of



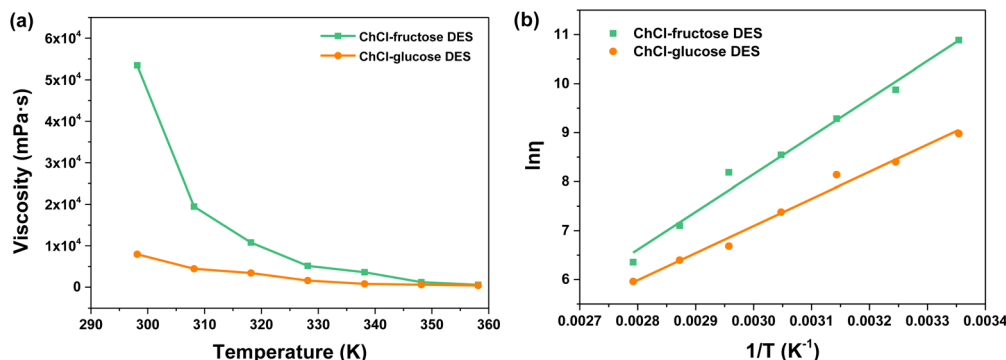


Fig. 4 (a) The temperature dependence of the viscosity of ChCl–fructose and ChCl–glucose DESs. (b) The relationship between viscosity of ChCl-based DESs and $1/T$.

ChCl–fructose and ChCl–glucose DESs was found compared to acidic ChCl-based DESs in our previous work,³⁵ far exceeding the viscosity of water and organic solvents. Obviously, high-viscosity solvents are unfavorable for the conversion of fructose and glucose, which is consistent with the reported drawback of DESs.

The relationship between viscosity and temperature was also fitted by the Arrhenius model in Fig. 4b, presenting a good linear fitting for the data with high correlation coefficient values ($R^2 = 0.98$). The activation energy values (E_a) were 64.07 and 46.04 kJ mol⁻¹ for ChCl–fructose and ChCl–glucose DESs, indicating that choline chloride and fructose created a stronger intermolecular force than that of glucose. The high viscosity of these two DESs can be attributed to a large number of hydrogen bonds and the high molecular weight of choline chloride, fructose, and glucose.

Effect of water content on 5-HMF yield in ChCl–fructose and ChCl–glucose DESs

During the conversion of saccharides to 5-HMF, a small amount of water is inevitable due to the hydrophilicity and hygroscopicity of DESs and the release of water as a product during the hydrolysis process.⁴² However, the effect of water on 5-HMF production in ChCl–fructose and ChCl–glucose DESs remains complex and unclear, potentially affecting solvent viscosity, properties, and reaction pathway.^{40,43}

Here, the 5-HMF yield is presented with water contents of 10, 20, 30, 40, and 50 wt% in two DESs under the optimal reaction condition. As shown in Fig. 5, the 5-HMF yield had a slight improvement as the water content increased from 0 to 20 wt% for both of ChCl–fructose DES and ChCl–glucose DES. Afterwards, the yield presented a dramatic decrease. In ChCl–fructose DES, the 5-HMF yield increased from 62.6% to 65.2% as the water content increased 20 wt%, and decreased to 22.2% with 50 wt% water content. In ChCl–glucose DES, the similar 5-HMF yields of 31.5%, 32.8%, and 33.7% were obtained with water contents of 0, 10, 20 wt%, and then it gradually decreases to 17.0% with 50 wt% water content.

The slight improvement in 5-HMF yield at low water content can be explained by the improved hydrolysis efficiency and 5-

HMF stability. On one hand, the addition of proper water reduces the viscosity of DESs and mass transfer resistance, leading to improved hydrolysis efficiency.¹² On the other hand, the chloride ion in ChCl-based DESs can stabilize 5-HMF by forming strong hydrogen bonds among them, further reducing side reactions and increasing the 5-HMF yield. However, at high water content in DES maybe had an adverse effect on catalytic hydrolysis. Excessive water may destroy the structure of DES by replacing the hydrogen bonding between HBD and HBA with water–DES and water–water interactions.⁴⁴ The high content of water also promotes side reactions, such as 5-HMF degradation and polymerization, resulting in lower product yield.

The possible mechanism of glucose dehydration to 5-HMF in ChCl–glucose DESs by boric acid and CrCl₃·6H₂O

In this study, the combined catalysts composed of boric acid and CrCl₃·6H₂O were employed to convert glucose to 5-HMF in ChCl–glucose DES. When only boric acid was used to catalyze glucose conversion, a certain amount of 5-HMF was produced in ChCl–glucose DES, indicating that boric acid can efficiently catalyze glucose isomerization and fructose dehydration, which is in accordance with its catalytic activity reported previously.⁴⁵ The addition of co-catalysts boric acid and CrCl₃·6H₂O further

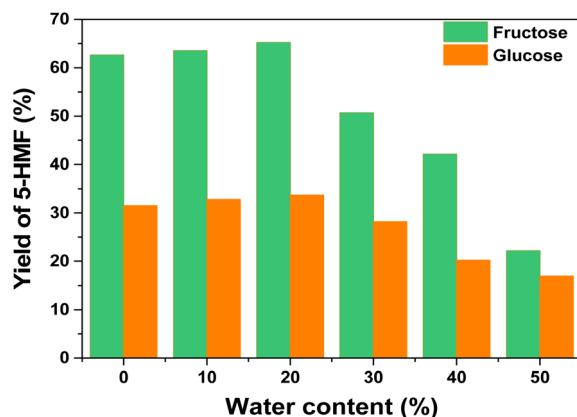
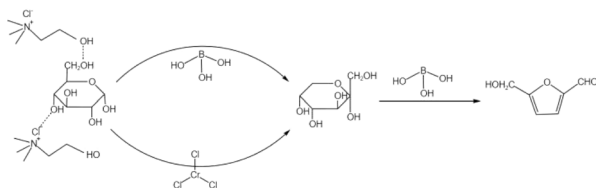


Fig. 5 The effect of water contents on 5-HMF yield in ChCl–fructose and ChCl–glucose DESs under the optimized condition.



Scheme 2 The simplified mechanism for glucose to 5-HMF in ChCl-glucose DES by boric acid and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

promotes 5-HMF production as shown in Fig. 3. The possible mechanism for this conversion is illustrated in Scheme 2. Here, both of boric acid and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ could catalyze the glucose isomerization to fructose. In this reaction system, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ can enhance glucose isomerization efficiency, leading to a high 5-HMF yield. Besides, boric acid played dual roles in reducing the reaction energy barrier and increasing the exothermicity of the overall isomerization.³⁸ Also, the existence of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ maybe promote to form fructose-borate or glucose-borate complexes, facilitating the conversion of glucose to fructose.⁴⁶ As for ChCl-glucose DES, it not only serves as a reaction medium but also improves 5-HMF stability and water tolerance due to the interactions among ChCl, boric acid, glucose, and 5-HMF. The presence of a large number of hydrogen bonds inhibits more side effects and increases the final 5-HMF yield. But to date the possible mechanism remains unclear due to the complexity of the reaction, more work needs to be done to verify the complexes formation by experiment and DFT calculation. And we would further explore the mechanism in the following research.

Conclusions

In summary, a comparison was made between the efficacy of acidic ChCl-based DESs and ChCl-fructose DES in converting fructose to 5-HMF in the presence of four acids, namely boric acid, oxalic acid, citric acid, and *p*-toluenesulfonic acid. Moreover, two types of ChCl-fructose and ChCl-glucose DESs were respectively explored in combination with boric acid for 5-HMF production. The results demonstrated that ChCl-fructose DES was more effective than acidic ChCl-based DESs. Process optimization experiments showed that a 5-HMF yield of 65.2% was obtained in ChCl-fructose DES (6 : 4 w/w) with 20% water and 80 mg boric acid at 120 °C for 120 minutes. There was a 5-HMF yield of 33.7% in ChCl-glucose DES (6 : 4 w/w) in addition of 20% water with 120 mg boric acid and 25 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ at 120 °C for 120 minutes. Furthermore, the effect of water content in ChCl-fructose and ChCl-glucose DESs was investigated, revealing that a water content lower than 20% in DESs slightly enhanced the 5-HMF yield. Both of these two DESs exhibited high viscosity at room temperature. A higher viscosity of ChCl-fructose DES was found compared to that of ChCl-glucose DES, even far surpassing general solvents. The corresponding activation energies E_a are 64.07 and 46.04 kJ mol^{-1} , implying a stronger intermolecular force and a larger mass transfer resistance. This work has provided an efficient and inexpensive

approach for producing 5-HMF from fructose and glucose in ChCl-fructose and ChCl-glucose DESs using boric acid. However, further efforts are required to improve the 5-HMF yield, ranging from optimizing the properties of DESs to enhancing the catalysts.

Data availability

The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of interest

There are no conflicts to declare.

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