

Efficient and Environmental-Friendly Dehydration of Fructose to 5-HMF in Ultrasound Assisted Ionic Liquids / Deep Eutectic Solvents

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Research Article

Keywords: Ultrasound, Ionic liquids, Deep eutectic solvents, Fructose, Conversion, 5-HMF,

Posted Date: June 3rd, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-569903/v1>

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Abstract

5-Hydroxymethylfurfural (5-HMF) is one of the most significant intermediate platforms for the production of both chemicals and liquid fuel derived from biomass. This study aimed to assess the efficiency of ultrasound-assisted ionic liquids (ILs)/deep eutectic solvents (DES) in converting fructose to 5-HMF under milder conditions ($\leq 100^\circ\text{C}$). The reaction conditions for the two-step transformation of sugarcane bagasse (SCB) with metal chloride as a catalyst and ultrasonic-assisted DES were optimized. The results showed that under the best conditions for ultrasound-assisted ILs to convert fructose (ultrasonic frequency: 40 kHz, 80°C , 1 h, [Bmim]Cl, D001-cc: 100 mg, fructose addition: 100 mg), the yield of 5-HMF reached 65.29 mol%. In addition, the D001-cc catalyst maintained high catalytic activity after being reused 6 times, and the activated D001-cc basically achieved the initial fructose conversion effect. Under the optimal conditions of ultrasonic-assisted DES fructose conversion (ultrasonic frequency: 40 kHz, 100°C , 30 min, ChCl-OA (molar ratio: 1:2), water addition: 0.46 mL, DES addition: 1 g), the yield of 5-HMF reached 51.87 mol%. Under the best conditions of ultrasonic-assisted DES SCB conversion (ultrasonic frequency: 40 kHz, ultrasonic time: 1 h, DES: ChCl: OA, catalyst: $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, water addition: 0.46 mL, $130^\circ\text{C}/4\text{ h}$ ($150^\circ\text{C}/0.5\text{ h}$)), the yield of 5-HMF reached 47.43 mol%. The study initially showed that ultrasonic-assisted ILs/DES effectively converted fructose in one step. In addition, the synergy of DES and metal chloride can better convert lignocellulosic biomass. Simply stated, the ultrasound-assisted ILs/DES conversion of biomass has realized "physical driving chemistry". Thus, paving the way of high-value utilization of lignocellulose to become greener and economical.

1. Introduction

The persistent usage of traditional fossil fuels contributed to the global energy and chemical crises. Therefore, to achieve sustainable development, seeking a renewable natural resource to replace petrochemical energy has become the top priority of current research [1]. Biomass has the advantages of renewable, biodegradable, abundant reserves and low price on the earth, and can be used as a synthetic raw material for fuel oil and chemical intermediates. Among them, the monosaccharide is a promising renewable resource, and its basic unit is composed of 5 or 6 carbon atoms. Fructose is ubiquitous and has a wide range of sources. It can be easily extracted from honey, fruits and beets. Therefore, fructose is a universal resource for functional chemicals. The typical chemical transformation of fructose is to produce 5-HMF through a dehydration reaction [2]. Besides, the isomerization of fructose to glucose can also generate 5-HMF. The preparation of 5-HMF from sugars by the dehydration reaction is one of the most critical methods of converting biomass into useful chemicals.

5-HMF is a multifunctional biomass derivative building block, which can be converted to 2,5-dimethylfuran, 2,5-furandicarboxylic acid, 2,5-dimethyltetrahydrofuran, etc.[3]. These derivatives are widely used in the fields of plastic products, rubber and medicine. In addition, 5-HMF and its derivatives can prepare intermediates for the synthesis of various fine chemicals through esterification, halogenation, condensation and other reactions. They can synthesize resins, inks, plastic and rubber additives, lubricant additives and surface active agent [4]. Therefore, 5-HMF and its derivatives are considered to be a bridge

connecting biomass chemistry and petrochemistry, and have huge market value. However, because the active group of 5-HMF is highly unstable under high temperature and acidic conditions, rehydration reaction is prone to occur, which increases the production cost of 5-HMF. Therefore, the low efficiency in the synthesis process of 5-HMF and the serious side effects of the reaction system hinder its commercial production and application. In recent years, various catalysts have been researched and used to catalyze the dehydration of fructose to 5-HMF, and it has been proved that acid catalysts are suitable for this reaction. Homogeneous acid catalysts such as mineral acids (H_2SO_4 , HCl and HNO_3) and organic acids (lactic acid, FA and acetic acid) can achieve high yield production of 5-HMF. However, they are corrosive to reaction equipment, difficult to recycle and harmful to humans. Therefore, in order to achieve a green and sustainable environment, more and more heterogeneous catalysts (solid acid, ion exchange resin, H-type zeolite, metal phosphate) are utilized as catalysts in the fructose dehydration reaction [5]. The acidic ion exchange resin is a cost-efficient and convenient catalyst that has been used to catalyze fructose and biomass conversions into 5-HMF, including: Amberlyst-15, Amberlyst-36 [6, 7]. Pumrod et al. [8] used an ion exchange resin as a catalyst and obtained 84.92% 5-HMF at 120°C and 480 min. Qi et al. [9] used a cation exchange resin as a catalyst to catalyze the dehydration of fructose into 5-HMF in an acetone-water mixture, and finally obtained 70.3% of 5-HMF. Moreover, Lewis acid (such as metal chloride) can not only promote the fructose conversion to 5-HMF, but also can be used for the isomerization of glucose. There have been research efforts to combine metal chlorides with ionic liquids (ILs) to produce 5-HMF from biomass [10]. Yu et al. [11] used SnCl_4 as a catalyst to produce 4.0–8.1% of 5-HMF from starchy food waste. The study also showed that trivalent metal chlorides could provide a higher 5-HMF yield. Besides SnCl_4 , studies have also showed that catalysts like AlCl_3 and FeCl_3 are necessary for selectively increasing the yield of 5-HMF [12]. Li et al. [13] formed a catalytic system with acidic DES / CrCl_3 to convert fructose to 5-HMF; they concluded that the synergistic effect of CrCl_3 and DES is essential for the formation of 5-HMF. Acidic DES is used as Bronsted acid and metal chloride as Lewis acid in this system. The interaction between metal chloride and ILs promotes the chelation of oxygen atoms in sugar and enhances sugar conversion [14]. As an analogue of ILs, deep eutectic solvent (DES) is also widely used in the production of 5-HMF. The combination of acidic DES and metal chloride can improve the production efficiency of 5-HMF. Therefore, metal chloride, as a catalyst, can efficiently realize the biomass conversion to sugars. In addition, the solvent plays a vital role in the process of fructose conversion to prepare 5-HMF. Typical solvents for producing 5-HMF from fructose include dimethylsulfoxide (DMSO), dimethylformamide (DMF) and dimethylacetamide (DMA). However, these solvents have high boiling points, large toxic and side effects, and a strong affinity with 5-HMF, which pose a considerable challenge to the future effective, green and sustainable production of 5-HMF.

ILs are usually composed of organic cations and inorganic anions. Due to their low volatility, non-flammability, high polarity, designability, and easy separation from reactants and products. ILs become possible substitutes for organic solvents and have a wide range of uses as solvents and catalysts for biomass conversion. They have shown great potential in esterification reactions, and many biomass-related ILs materials have been identified [15]. Qi et al. [16] used 1-butyl 3-methylimidazole chloride ([Bmim]Cl) to catalyze inulin to obtain 82% of 5-HMF under mild conditions. Guo et al. [17] used hydrogen

sulfate ILs as a co-solvent and homogeneous catalyst to directly convert fructose into 5-ethoxymethylfurfural (5-EMF) in an ethanol solution. Li et al. [18] used N-methylimidazole bisulfate ([HMIM] HSO₄) to hydrolyze chitosan in the presence of acidic ILs to obtain 29.5 mol% of 5-HMF from 100 mg of chitosan. At present, the research on the sugar conversion to produce 5-HMF in ILs is mainly focused on acidic catalysts. Due to its large toxicity and difficulty in recovery and separation, it is necessary to study the relationship between the solid acid catalyst and fructose dehydration. In recent years, DESs have become a very promising reaction solvent. It is a salt that combines two or three components through hydrogen bonds and becomes molten at room temperature. The physical and chemical properties of DES are similar to traditional ILs, but it has attracted much attention because of its economical, green, and biodegradable characteristics. Hu et al. [19] realized the effective inulin conversion to 5-HMF in the DES based on oxalic acid. They adopted the ethyl acetate/DES biphasic system to improve the yield of the target product.

Lee et al. [20] used DES formed from choline chloride (ChCl) and dicarboxylic acid to produce 26.34% furfural from oil palm leaves. Zuo et al. [21] used AlCl₃•6H₂O as a catalyst and DES as a solvent. At 120°C for 5 h, the yields of 5-CMF and 5-HMF were 50.3 and 8.1%, respectively. In the above studies, the reaction system that uses DES to convert fructose to 5-HMF requires the addition of acidic catalysts, which is undesirable from the perspective of green chemistry. Therefore, the reaction system will be greener if the synthesized DES might be used as both a solvent and a catalyst. Assanosi et al. [22] used DES composed of ChCl and *p*-toluenesulfonic acid (*p*-TSA) for the dehydration of fructose to 5-HMF. The *p*-TSA used in this system is both the hydrogen bond donor (HBD) of DES and the dehydration of fructose. The reaction catalyst can produce 90.7% 5-HMF from fructose without adding a catalyst. Considering that many organic acids can be used as HBD to synthesize DES, the synthesis of acidic DES as both a catalyst and a solvent for biomass conversion will have a bright future.

Furthermore, DES has a strong delignification ability for lignocellulose. For example, after treating corn stover with ChCl-formic acid, 99% glucose yield can be achieved by enzymatic hydrolysis [23]. Therefore, acidic DES composed of ChCl and organic acids may also be a potential medium for efficiently converting fructose and biomass to 5-HMF. However, the high viscosity of ILs and DES, reduce their accessibility to substrates, resulting in incomplete reactions, and hence a decrease in the yield of the target products. Therefore, there is an urgent need to find a physical method capable of reducing the viscosity of the ILs and DES, and to achieve “physical driving of the chemistry”, thereby increasing the substrate permeability and speeding up the reaction.

Ultrasound is a longitudinal wave with a frequency ranging between 16 kHz and 500 MHz [24]. Ultrasound has many unique properties and advantages and is widely used in various fields. The characteristics of ultrasound mainly include cavitation, mechanical and chemical effects. The acoustic cavitation is the process of vibration, expansion, contraction and collapse of the tiny bubbles existing in the liquid due to effects of sound waves. When the ultrasonic wave propagates in the medium, the average distance of the molecules in the liquid changes owing to the change in the molecular vibration. When it exceeds the critical molecular distance to keep up the liquid action, cavitation occurs. Powerful

shock waves or micro-jets follow cavitation. The micro-jets lead to a strong mechanical stirring effect locating, between the interfaces. This effect breaks through the laminar flow boundary limitation, thereby strengthening the transfer-process occurring between the interfaces in foods during processing. The chemical effect of ultrasound come from the local hot spots generated by cavitation. A large amount of energy releases when a bubble burst. This energy cannot be transferred to the surrounding environment immediately and forms a local high temperature. Accordingly, the extremely high temperature and pressure destroy the crystalline state of the substance, resulting in solid particles melting after colliding with each other. In recent years, there have been more and more applications of ultrasound in lignocellulosic biomass. Yu et al. [25] used ultrasonic ILs to pretreat bagasse, and the hydrolyzed glucose yield of sugarcane bagasse (SCB) was greatly increased. Ji et al. [26, 27] found that ultrasonic DES pretreatment can efficiently remove lignin and significantly increase the yield of reducing sugar after biomass hydrolysis. At present, the application of ultrasound in biomass is mainly embodied in pretreatment, that is, using the three effects of ultrasound to destroy the structure of biomass, remove lignin, and accelerate hydrolysis. However, there is no research report on applying ultrasonic-assisted ILs/DES to one-step fructose conversion reactions, so it is necessary to systematically study monosaccharide conversion reactions using such systems.

In this work, the one-stage fructose conversion to 5-HMF in an ultrasonic-assisted ILs / DES system was studied. The effects of ultrasonic frequency, type of ILs, mode and dose of solid acid, reaction period and number of times of solid acid reuse on the fructose conversion have been explained in ultrasonic ILs conversion process under relatively low temperature conditions. Furthermore, this study investigated the influences of the amount and type of DES applied, and the amount of water added to DES on fructose conversion to 5-HMF in the ultrasonic-DES system. This study also investigated the effects of using different HBD/HBA molar ratios of DES. Finally, in order to prove the feasibility of ultrasonic-assisted DES conversion system, SCB, as a raw material, was transformed into 5-HMF in two steps; first an ultrasonic treatment and then a catalytic conversion reaction. The effects of metal chloride type, DES type, water applied to the system, and reaction temperature and time on SCB conversion were examined.

2. Materials And Methods

2.1. Materials

SCB was obtained from the supermarket at Jiangsu University (Zhenjiang, China). SCB was dried in an oven set at 70°C to achieve constant weight, and then pulverized to pass through a 100-mesh sieve. The SCB contents of lignin, cellulose and hemicellulose ($19.60 \pm 0.82\%$, $36.40 \pm 0.54\%$ and $21.60 \pm 0.37\%$, respectively) were determined by the standard protocols of National Renewable Energy Laboratory (NREL) [28].

All chemicals used in this work were of analytical grade and used without further purification. 1-butyl-3-methylimidazolium acetate ([Bmim]OAc), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl), 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO₄), and 1-butyl-3-methylimidazole p-toluenesulfonate

([Bmim]TSO) were supplied by Chenjie Chemical Co., Ltd. (Shanghai, China) with purities of above 0.99 mass fraction. Ion-exchange resins, including D001-cc, D-72, 001-1.1, 001-7, 001-14.5 and Amberlyst-15, were purchased from the Chemical Plant of Nankai University (Tianjin, China). $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained from Tianjin Beichen Fangzheng Reagent Factory (Tianjin, China). Choline chloride (ChCl, 98%), fructose, levulinic acid, 5-hydroxymethyl furfural (5-HMF), glucose, xylose, cellobiose, oxalic acid (OA), lactic acid (LA), citric acid (CA), malic acid (MA), formic acid (FA), and acetic acid (AA) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Synthesis of DES

ChCl was dried at 80°C for six hours and cooled to room temperature in a desiccator before use. Compounds ChCl: OA, ChCl: CA, ChCl: LA, ChCl: FA, ChCl: MA and ChCl: AA were synthesized by mixing each of the target reagents (oxalic acid, citric acid, lactic acid, formic acid, malic acid and acetic acid) with ChCl at a specific molar ratio (1:1, 1:2, 1:3 and 1:4). The mixtures were heated at 70°C and constantly agitated (400 rpm) to create clear transparent liquids (DESs). The synthesized DESs were kept in a desiccator until use.

2.3. Ultrasound-assisted ILs catalyzed dehydration of fructose into 5-HMF

During a typical reaction, 0.1 g of fructose was put in a reaction tube, and known quantities of catalytic resin and ILs were added to the tube. The reaction mixture was agitated using an electromagnetic stirrer to keep the resin particles suspended at 80°C for the desired time in the ultrasound bath reactor. The ultrasonic equipment used in the experiment was shown in Fig. 1. Each sample was cooled and diluted with 10 g of ultra-pure water, followed by centrifugation to separate the catalyst. Then, the product yields were quantified by the high performance liquid chromatography system (HPLC).

2.4. Ultrasound-assisted DES catalyzed dehydration of fructose into 5-HMF

Fructose (0.1 g) and DES (1 g) were put in a 10 mL-reaction tube, then water was added at different volumes (0–1.0 mL). The reaction tube was stirred and then placed in the ultrasonic bath reactor. The mixture was left to react for a particular time and temperature. Ultrasonic power was controlled at 300 W. After the reaction, the reaction mixture was separated and filtered with a 0.22 μm syringe filter. Each sample was diluted with ultra-pure water prior to analysis.

2.5. Ultrasound-assisted DES two-step catalyzed SCB transformation into 5-HMF

First, SCB (0.1 g), DES (1 g) and metal chloride catalyst (0.1 g) were put in a 10 mL-reaction tube with 0–1.0 mL of water. The reaction tube was stirred uniformly and put in an ultrasonic bath reactor. The

mixture was sonicated (40 kHz, 300 W) for 30 min at room temperature to enable the DES to penetrate the SCB entirely. After the sonication, the reactants were heated in an oil bath (80–150 ° C; 0.5–4 h). The reaction mixture was subjected to centrifugation to separate the supernatant. The supernatant was filtered by a 0.22 µm membrane filter and diluted with ultra-pure water before analysis.

2.6. Product analysis

Quantitative analysis of the product was carried out using an Agilent series 1260 HPLC system (Agilent Technologies, CA, USA), equipped with Aminex HPX-87H ion exclusion column (300 × 7.8 mm i.d., BIO-RAD), a G1362A differential refractive index detector and G1329B autosampler. A 5 mM H₂SO₄ aqueous solution was used as a mobile phase at a flow rate of 0.6 mL/min. The detective temperature and the column temperature were 50 and 60°C, respectively. The injection volume of the sample and standard was 20 µL. Product peaks were identified with reference to standards. The fructose conversion rate (FCR) and fructose conversion products were determined using Eqs. (1) and (2). The yields of glucose, xylose, furfural, FA, levulinic acid, and 5-HMF from SCB were determined using Eq. (3).

$$FCR_{fructose}(\%) = \left(1 - \frac{C \times V}{M}\right) \times 100\%$$

(1)

$$Y_{5-HMF,LA,FA,FUR}(\%) = \frac{V \times C \times W}{126 \times M} \times 100\%$$

(2)

$$Product \quad yield \quad (mol\%) \quad) = \frac{Conc_p(mg \ ml^{-1}) \times Vol(ml) / M_p}{M_{scb}(mg) \times N(\%) \times T(\%) / M_p} \times 100\%$$

(3)

Where *V* is the diluted volume (mL), *C* is the concentration of HPLC detectable product (mg/mL), *W* is the molecular mass of the corresponding product; 126 is the molecular masses of fructose; *M* is the mass of fructose (mg); *Conc_p* is the concentration of HPLC detectable products, i.e., glucose, xylose, furfural, FA, levulinic acid, and 5-HMF; *M_p* represents molecular mass of the corresponding product; *M_{scb}* represents the mass of SCB; *N* represents the cellulose or hemicellulose content in the SCB; *T* represents 1 mg of cellulose or hemicellulose being converted into the theoretical mass of the corresponding product.

3. Results And Discussion

3.1. The effect of ultrasound-assisted ILs on fructose conversion

3.1.1. Determination of the reaction system

Figure 2a shows the results of the effect of ultrasonic-ILs on the fructose conversion reaction system. As seen, when using [Bmim]Cl as a reaction solvent, the FCR and the 5-HMF yield (65.29 mol%) were significantly higher than [Bmim]OAc, [Bmim]HSO₄ and [Bmim][TfO]. This might be related to differences in the acid strength of the different IL anions. However, a study has revealed that the yield of 5-HMF has a great relationship to the carbon chain length of the IL cation. The longer the carbon chain, the stronger the aggregation, and the lower the 5-HMF yield [29]. Besides, the hydrophilicity and hydrophobicity of ILs also affect the yield of 5-HMF. The better the hydrophilicity of the IL, the better the dissolution of fructose in the IL. Such conditions speed-up the contact between fructose molecules and the ion exchange resin, and hence increases the 5-HMF yield. In addition, the lower viscosity of [Bmim]Cl and the stronger hydrogen bond formed connecting Cl⁻ ions and fructose molecules led to a stronger interaction between [Bmim]Cl and fructose [29]. FA, levulinic acid, furfural and other by-products were also detected in the reaction solution, which indicated that the 5-HMF obtained by the dehydration of fructose was partially rehydrated. Among them, there was no significant difference between the yields of FA and levulinic acid produced by the four investigated ILs.

As noticed in Fig. 2b, as the catalyst dosage increased from 50 to 250 mg, the yield of fructose converted to 5-HMF increased first, then decreased. While the FA and levulinic acid yields gradually increased with increasing the catalyst amount. At D001-cc dosage of 100 mg, the highest yield of 5-HMF was obtained (65.62 mol%); the corresponding FA and levulinic acid yields were 3.85 and 1.06 mol%, respectively. This was attributed to the increase in the catalytic sites as the dosage of the catalyst increased, which enhanced the dehydration of fructose and thus the 5-HMF yield increased. When D001-cc was gradually increased to 250 mg, the 5-HMF yield began to decrease steadily. This was possibly because the excessive catalyst amount accelerated both the fructose dehydration reaction and side reactions. In addition, the excessive catalyst in the reaction system impedes the mass transfer process, thereby limiting the contact between the catalyst and fructose [30]. Li et al [6] proved that the D001-cc resin has an excellent catalytic performance when used for the fructose dehydration reaction.

Figure 2c illustrates the effect of different catalyst types on fructose dehydration. Strong macroporous acid ion-exchange resins (D001-cc, D072 and Amberlyst-15) showed higher catalytic activity than gel strong acid ion-exchange resins (001* 7, 001* 1.1, 001* and 14.5). In particular, D001-cc resin displayed the highest catalytic performance resulting in the highest FCR and the maximum 5-HMF yield (65.03 mol%). In comparison with the gel ion exchange resin, the macroporous strong acid resin has a larger internal pore size and a larger surface area, which will accelerate the ion exchange capacity and enable fructose to enter the resin quickly [31]. Furthermore, the macroporous resin, belongs to the styrene-DVB resin type, with sulfonic acid functional groups, has a higher acid strength than the gel resin. In addition, the structure and performance of ion exchange resin have a significant effect on the dehydration of fructose.

The results of the effect of fructose loading on its conversion are shown in Fig. 2d. When the fructose loading increased from 50 to 100 mg, the yield of 5-HMF increased from 57.15 to 65.29 mol%, then gradually decreased due to the gradual increase in the fructose loading to 250 mg. This might be caused

by the interaction between 5-HMF and fructose to form a polymer. Also, the increase in fructose loading > 250 mg did not significantly change the yields of 5-HMF, FA and levulinic acid. This indicated that ILs have abilities to inhibit humins formation during the fructose conversion process [32]. At the fructose loading of 50–250 mg, the FCR was above 95%, which was due the strong acidity effect of the D001-cc resin that can fully convert fructose in a short reaction process. The strong acidity of D001-cc resin also promotes rehydration reactions of 5-HMF, producing some by-products.

3.1.1. The effect of ultrasonic frequency on fructose conversion

The effect of ultrasonic frequency on the fructose conversion was studied in a ILs-D001-cc system, results are shown in Fig. 3. In Fig. 3a and b, the 5-HMF yield and the FCR gradually increased due to the increase in the ultrasonic frequency and the reaction time. The fructose conversion at 40 kHz, 80°C and 100 min yielded 65.84 mol% of 5-HMF, which decreased to 58.53 mol% at 60 kHz. The high-frequency ultrasound can increase the release rate and cavitation efficiency of a single bubble, thus speeding up the dissolution of fructose by ILs [33]. The cavitation of ultrasound causes fructose molecules to enter the interior of the D001-cc resin quickly and combines with the acidic sites in the resin to undergo dehydration reaction, thereby generating 5-HMF. However, the excessively high frequency makes active cavitation challenging to occur, resulting in rapid attenuation of the sound energy in ILs [34]. In a high-frequency ultrasound, the bubble size to become smaller and the existence time is shorter, which will cause fewer fructose molecules to enter the high-energy bubbles, correspondingly reducing the binding of fructose molecules with the acidic groups of the D001-cc resin, thereby weakening the fructose dehydration reaction. The fructose conversion by-products have also been seen when using various ultrasound frequencies and reaction times (Fig. 3c-e). As the reaction time increased, the yields of FA and levulinic acid also increased. Combined with the analysis of Fig. 3a, it noticed that at least two reaction types proceed simultaneously during the ultrasound-assisted ILs fructose dehydration process. On one hand, fructose was continuously dehydrated to generate 5-HMF under the catalysis of the D001-cc resin. On the other hand, the generated low-stable 5-HMF underwent rehydration led to the appearance of by-products. The FA yield was not significantly different when using 20, 40 and 60 kHz. After fructose conversion reaction at 20 kHz for 100 min, the yield of levulinic acid was significantly higher than other frequencies. This might be due to that the cavitation produced by a low-frequency ultrasound stimulated the 5-HMF rehydration reaction.

3.1.2. Effect of catalyst reuse on the fructose conversion to 5-HMF

The effect of the reuse of D001-cc resin on the fructose conversion reaction was studied. After reusing the D001-cc resin six times in the fructose conversion system, it still maintained high catalytic activity, and the 5-HMF yield reached > 60 mol% (Fig. 4). In addition, the numbers of the catalyst reuse had no significant effect on the yield of by-products. After activating the reused D001-cc resin, its catalytic

activity could reach the activity of the original resin. Therefore, D001-cc resin has a better effect on fructose dehydration and can be reused, thus making the fructose conversion system greener.

3.2. The effect of ultrasound-assisted DES on fructose conversion

3.2.1. The effect of DES molar ratio on fructose conversion

The effect of the molar ratio of the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) in DES on fructose conversion was studied. In the ChCl-OA system (Fig. 5a), as the ratio of HBA/HBD increased, the yield of 5-HMF from fructose conversion increased. At a molar ratio of 1:2, the 5-HMF yield was the highest (49.42 mol%) compared with the other molar ratios. When the molar ratio was increased, the yield of 5-HMF decreased, and the yields of FA and levulinic acid were 9.47 and 7.52 mol%, respectively. When the molar ratio of the ChCl-MA system increased (Fig. 5b), the 5-HMF yield and FCR first increased, then decreased. Moreover, the fructose yield gradually decreased, and the yields of FA and levulinic acid steadily increased. At the HBA/HBD molar ratio of 1:2, the 5-HMF yield was 42.78 mol%, and the FCR was 97.76%. In the ChCl-FA system (Fig. 5c), as the molar ratio increased, the 5-HMF yield gradually increased. At the molar ratio of 1:2, the 5-HMF yield and FCR were the highest, while the yield of levulinic acid was lower. Compared with the other acid DESs, the DES-FA system had significantly higher FA yields; most of the FA amount was derived from DES, while the remaining amount was derived from the side reactions existed in the course of the conversion process. In the ChCl-AA system (Fig. 5d), the 5-HMF yield and the FCR increased with increasing the molar ratio. At the molar ratio of 1:2, the 5-HMF yield tended to stabilize, suggesting that isomerization and dehydration reactions of fructose happened simultaneously, resulting in an increase in the FCR while the 5-HMF yield unchanged. In the ChCl-LA system (Fig. 5e), the yields of 5-HMF, FA and levulinic acid increased, but with insignificant magnitudes, with increasing the molar ratio, which indicated that the LA amount in DES had little influence on the fructose conversion process. In the ChCl-CA system (Fig. 5f), the yields of 5-HMF, FCR, FA and levulinic acid decreased with increasing the molar ratio. At a molar ratio of 1:1, the yields of 5-HMF and FCR were 40.41 mol% and 94.69%, respectively. The above phenomenon could be related to the viscosity of CA. The greater the viscosity of DES, the weaker the interaction force between it and fructose. Therefore, when the CA concentration was higher, the DES would have higher viscosity, which in turn weakened the mass transfer process between the DES and fructose; thereby hindered the fructose dehydration and as a result 5-HMF yield decreased.

In the light of the above results, the higher the content of acidic HBD in the DES system, the more acidic sites were provided, which would accelerate the dehydration reaction of fructose. Therefore, as the molar ratio increased, the fructose yield and FCR in most DES systems gradually decreased. However, the higher the molar ratio of ChCl-LA in pretreatment of biomass, the lower the yield of reducing sugars obtained from the pretreated biomass [35]. This indicated that the efficiency of cellulose hydrolysis can improve by using a higher molar ratio of ChCl-LA. However, fructose is more exposed to hydrolysis under acidic

conditions; so the higher molar ratio of ChCl-LA can accelerate the dehydration reaction of fructose. In addition, the yields of FA and levulinic acid also increased with the increase in the molar ratio, illustrating the simultaneous enhancement of both the fructose rehydration and the fructose dehydration. However, the increase in the yield of by-products in the system was undesirable. Therefore, taking into consideration of the yields of 5-HMF and by-products, the optimal molar ratio of HBA and HBD in ChCl-OA, ChCl-MA, ChCl-FA, ChCl-AA, and ChCl-LA system was 1:2.

3.2.2. Determination of ultrasonic DES reaction system

The effect of different types of DES on fructose conversion was studied; results are presented in Fig. 6a. Among all the DES systems investigated, the ChCl-OA system showed the highest 5-HMF yield from the fructose dehydration (51.83 mol%). In the ChCl-AA system, the yield of fructose was the largest and the FCR was the lowest; the yields of FA and levulinic acid were also minimal. In the ChCl-FA system, the yield of FA in the reaction residue was 17.64 mol%. In the ChCl-MA and ChCl-CA systems, the yield of fructose converted to 5-HMF was the lowest. This was because the DESs composed of ChCl-MA and ChCl-CA have larger viscosities, which was not conducive to the penetration of fructose into DES. There are specific differences in the fructose conversion by the different DESs, which was related to the nature and composition of the HBD. Among them, OA is a strong acid ($pK_{a1} = 1.25$, $pK_{a2} = 4.14$), FA is a simplest carboxylic acid ($pK_{a1} = 3.75$), AA is a mild weak acid ($pK_{a1} = 4.75$), and LA is a medium-strong acid ($pK_{a1} = 3.86$). The acid dissociation constant of MA is $pK_{a1} = 3.46$, $pK_{a2} = 5.10$, and CA is $pK_{a1} = 3.14$. Fructose dehydration is greatly affected by the acid dissociation constant of the HBD in DESs. The pK_a values of DES acids decreased followed the order: ChCl-AA > ChCl-LA > ChCl-FA > ChCl-MA > ChCl-CA > ChCl-OA. Except for ChCl-MA and ChCl-CA, all DESs led to an increase in the yield of 5-HMF from the fructose dehydration, following a reverse order compared to that of the pK_a values. In addition, a study has shown that the performance difference between DESs mainly depends on the number of -COOH groups. In the DES, the -COOH groups of HBD can form more hydrogen bonds with HBA [36]. In this context, the interaction between DES and fructose depends on the strength and stability of the hydrogen bond interaction between the HBA and the HBD [37]. Among all HBDs, FA, AA and LA are monobasic acids, OA and MA are dibasic acids, and CA is tribasic acid. Moreover, the carboxylic acid groups in dibasic acid and tribasic acid DESs can form dimer chains, thereby limiting the migration of solvent molecules [38]. Therefore, the fluidity of DES is poor, and the low rate of mass-transfer between solvent molecules might weaken the interaction with fructose and hindered the dissolution of fructose, thereby reducing the yield of 5-HMF. Although OA is a dibasic acid, due to its strong acidity, the yield of 5-HMF from fructose is still high.

Regarding the effect of ultrasound frequency on fructose conversion, the fructose yield gradually decreased with increasing the ultrasound frequency (Fig. 6b). Under similar conditions, the 5-HMF yield and FCR increased first and then decreased, while the yields of FA and levulinic acid did not change. Compared with no ultrasound, the yield of 5-HMF after ultrasound was increased significantly. At 40 kHz, the 5-HMF yield was 50.03 mol%. This was because the cavitation of ultrasound accelerated the interaction of DES with fructose molecules, promoted the combination of fructose and acid sites in DES,

and hence accelerated fructose dehydration. The yield of 5-HMF declined at 60 kHz, indicating that the cavitation effects produced at different ultrasonic frequencies were different. The higher the ultrasonic frequency, the greater the required sound intensity and the weaker the cavitation, that is, the cavitation decreased with increasing the ultrasonic frequency. Consequently, the ultrasonic frequency of 40 kHz has the best effect on fructose conversion.

Figure 6c displayed the results of the effect of acidic DES loading on fructose conversion. From the figure, it has been showed that as the DES loading increased, the fructose and 5-HMF yield gradually decreased, while the yields of FA and levulinic acid gradually increased. When the loading of DES was 1 g, the 5-HMF yield and FCR were the highest (49.20 and 97.51%, respectively). This illustrated that the ratio of fructose and DES in the system has a great influence on the yield of 5-HMF. A proper amount of DES in the system can get a higher 5-HMF, and an excessive amount of DES will induce rehydration or polymerization of 5-HMF, so reducing the yield of 5-HMF. Therefore, the selected optimal loading amount of DES for the ultrasonic-DES fructose conversion system that maximized the 5-HMF yield and minimized the by-products yield was 1 g.

The results of the effect of the amount of water added in DES on the fructose conversion process are shown in Fig. 6d. As illustrated in the figure, when the amount of water added to DES increased, the FCR and the 5-HMF yield first increased, and then decreased; while the fructose yield gradually decreased, and the yields of FA and levulinic acid gradually increased. When adding 0.46 mL of water to the DES, the highest 5-HMF yield was obtained (49.38 mol%). Simultaneously, amounts of FA and levulinic acid were produced (7.91 and 3.54 mol%, respectively). The addition of water can improve the viscosity of DES, thereby increasing the mass transfer process, resulting in better penetration of DES into fructose molecules. New et al. [39] found that adding water to DES helps to increase the recovery rate of hemicellulose and xylose, while improving the mass transfer. However, a study has revealed that adding excessive water to DES generates hydrogen bonding between water molecules and ChCl, thereby reducing the stability and strength of the hydrogen bond interaction between ChCl and the HBD, as a result the DES structure destroyed [40]. This will weaken the catalytic effect of DES and hinder the interaction between DES and fructose. Therefore, when the amount of water added was greater than 0.46 mL, the yield of 5-HMF gradually decreased. At the same time, the increase in water content of the system can accelerate the occurrence of side reactions. This is because water is a polar aprotic solvent, which can enhance side reactions and promote the rehydration of 5-HMF, thereby decreasing the yield of 5-HMF [41]. However, adding proper amount of water to DES can inhibit the formation of humins. Lee et al. [20] found that adding a certain amount of water to DES can cause a decrease in the furfural yield. The above research shows that the presence of water in DES is essential to improve the characteristics of the reaction system and increase the yield of the product. Adding 0.46 mL of water to DES will facilitate fructose conversion.

In the ultrasound-assisted DES system, we investigated the effect of different reaction times on the fructose conversion process at 80 and 100°C (Fig. 6e-f). At 80°C, the yields of 5-HMF, FA, and levulinic acid decreased owing to the increase in the reaction time. The yield of 5-HMF was 50.24 mol% after 60 min, which remained levelled-off after prolonging the reaction time longer than 60 min. At 100°C, the yield

of 5-HMF increased first with increasing the reaction time, and then decreased. Moreover, the FCR, the FA yield and the levulinic acid yield gradually increased, and the fructose yield gradually decreased. In the reaction period of 10–20 min, the dehydration rate of fructose at 100°C was higher than 80°C, which demonstrated that the high temperature was beneficial to fructose conversion.

When fructose reacted at 100°C for 30 min, the yield of 5-HMF was 51.87 mol%. As the reaction time increased, the yield of 5-HMF began to decrease, while the yield of FA began to increase significantly, and rehydration reaction occurred at this time. This is consistent with the results of Lee et al. [20]. Under the same reaction time, the yield of reaction by-products at 100°C was higher than 80°C. This indicated that high temperature accelerated the side reaction. In addition, the fructose dehydration and 5-HMF rehydration occurred simultaneously.

3.3. The effect of ultrasound-assisted DES on SCB conversion

3.3.1. Effects of metal catalysts, HBD and water on the conversion reaction

The effect of metal chlorides on SCB conversion to 5-HMF in a two-step ultrasonic-assisted DES system was studied. As seen in Fig. 7a, the yield of 5-HMF in the ChCl-OA system was significantly improved after adding metal chlorides to the system. This was because the Lewis acidic sites in metal chlorides promote SCB hydrolysis by attacking the oxygen atoms of SCB glycosidic bonds [42]. At the same time, the supramolecular complex formed by the competition between the anionic hydrogen bond in DES and the ligand of metal chloride can cleave the hydrogen bond in SCB [43], which can effectively remove lignin from SCB, and generate hydrolysis of SCB cellulose. The subsequent sugar conversion provided favorable conditions. The 5-HMF yields produced in the different DES/catalyst systems follow the order: ChCl-OA-SnCl₄ > ChCl-OA-CrCl₃ > ChCl-OA-CuCl₂ > ChCl-OA-AlCl₃ > ChCl-OA-FeCl₃. The highest yield of 5-HMF in the ChCl-OA-SnCl₄ system was 45.44 mol%. However, the acid strength of metal chlorides has a great relationship with the acid hydrolysis constant (pKa). The acid hydrolysis constants of Sn⁴⁺ (-0.6), Cr³⁺ (4.0), Cu²⁺ (3.8), Al³⁺ (5.0) and Fe³⁺ (2.2) are significantly different. So, the lower the acid hydrolysis constant, the higher the yield of 5-HMF. Also, DESs containing metal chlorides with higher acid hydrolysis constants have better pretreatment effects on biomass [26]. In addition to metal chlorides, the OA in DES can also play a catalytic role as a Brønsted acid. The sugars and by-products in the different reaction systems were also determined. It was found that the yields of glucose, xylose and cellobiose in ChCl-OA-FeCl₃ and ChCl-OA-CrCl₃ systems were higher than that in other reaction systems, while the yields of levulinic acid in ChCl-OA-SnCl₄, ChCl-OA-FeCl₃ and ChCl-OA-CuCl₂ systems were higher than that in other systems. This assumes the simultaneous occurrence of cellulose hydrolysis, glucose dehydration, and 5-HMF rehydration during SCB conversion. In addition, DES combined with metal chlorides and interacted with SCB at different sites, thus, the conversion effect on SCB was also different.

DESs containing OA and FA as HBD had the best performance during SCB conversion, which conformed to the results of the fructose conversion (Fig. 7b). Under the catalysis of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, the yields of 5-HMF from SCB conversion in ChCl-OA and ChCl-FA systems were 47.43 and 44.69 mole%, respectively. This was related to the effect of the acid dissociation constant of the HBD in DES, which has been analyzed in Sect. 3.2.2. The results demonstrated that the ChCl-OA- SnCl_4 system was crucial to SCB conversion. The SCB conversion system containing acidic DESs and SnCl_4 , which has a better catalytic effect, performed the dual purpose of pretreatment and conversion. The Cl^- anions in DES and SnCl_4 could form hydrogen bonds with the lignin in SCB, leading to the dissolution of lignin. The remaining cellulose and hemicellulose were hydrolyzed into sugars under acidic conditions, and the sugars would be converted to form 5-HMF. On one hand, the SnCl_4 added to DES acted as Lewis acid catalyst for SCB hydrolysis and conversion reactions, and on the other hand, Cl^- anions in DES cooperated with ChCl in DES to deconstruct SCB. The results of the influence of the amount of water in DES on SCB conversion are shown in Fig. 7c. The gradual increase in the amount of water in DES led to an increase first in the 5-HMF yield and then a decrease, but with no significant difference between the samples. When the amount of water added in DES was 0.46 mL, the 5-HMF yield was at the highest level (45.44 mol%). Moreover, the yields of glucose, xylose, cellobiose and levulinic acid did not affect by the change in the amount of water added to DES.

3.3.2. Effect of reaction temperature and time on SCB conversion

The effect of reaction time on the conversion of SCB was studied at different temperatures (Fig. 8). It can be seen from the figure that as the reaction time increased, the yields of glucose and xylose in the reaction system gradually decreased. While the cellobiose yield did not significantly affect by increasing the reaction time. The yield of levulinic acid increased, but the increase was not significant. At the reaction temperature of 80–130°C, the yield of 5-HMF increased with increasing the reaction time, and reached the maximum level in 4 h. At 130 and 140°C, the 5-HMF yield reached the maximum level in 0.5 h, and then gradually decreased due to the increase in the reaction time. In addition, the levulinic acid yield at 130 and 140°C was significantly higher than at 80–100°C. After reacting at 80, 90, 100, 110, 120, 130, 140 and 150°C for 0.5 h, 7.57, 8.12, 9.06, 18.68, 24.39, 33.46, 42.38 and 44.14 mol% of 5-HMF were obtained. The 5-HMF yield was basically the same after 4 h reaction time at 120–130°C and 0.5 h reaction time at 140–150°C (≥ 40 mol%). Under the reaction conditions of 80–110°C, the yield of 5-HMF was low due to the negative impacts of the partially-dehydrated intermediates. As the reaction temperature increased, the intermediates decreased and the reaction accelerated, thus led to an increase in the 5-HMF yield. The above research once again showed that the yield of 5-HMF was greatly affected by the high temperature, which was conducive to the formation of 5-HMF. However, after reaching a certain temperature, the yield of by-products gradually increased, indicating that high temperature accelerated the reaction rate. Under harsh reaction conditions, the generated 5-HMF and intermediates might undergo polymerization to large fragments or humic substances, thereby the 5-HMF yield

decreased [13]. In addition, when the temperature was lower than 110°C, the yields of intermediates (glucose and xylose) were higher, reaching 20.47 and 6.75 mol%, respectively. However, when the reaction temperature was above 110°C, the yields of glucose and xylose decreased significantly. This showed that the reaction rate of sugar-dehydration was greatly accelerated at 110°C. Based on the above analysis, 140 and 150°C, 0.5 h were selected as the best reaction conditions for SCB conversion.

3.4. Comparison with past studies

In order to measure the conversion effect of ultrasonic-ILs/DES on fructose and SCB, the results of this study were compared with the corresponding results of other solvent-catalyst systems (Table 1). All the subsequent studies where to obtain 5-HMF from fructose: Ji et al. [28] used supercritical CO₂ and ILs to react at 90°C for 30 min to obtain 27.73% of 5-HMF. Qi et al. [9] used an ion exchange resin as a catalyst and microwave heating under the conditions of acetone-water biphasic reaction system to obtain 70.3% 5-HMF from fructose hydration at 150°C for 10 min. Körner et al. [44] used water as a solvent and FA as a catalyst for fructose rehydration at 200°C for 10 min to obtain 56% of 5-HMF. Phuong et al. [45] and Cao et al. [46] used sulfonated amorphous carbon silica and ethylenediaminetetraacetic acid (EDTA) as catalysts to obtain 67 and 89% of 5-HMF, respectively. Compared with the reaction system that has been studied, the ultrasonic-assisted ILs/DES system is greener and safer. The acidic ion-exchange resin as a catalyst was used in the ultrasonic ILs system to convert fructose, and 65.29 mol% of 5-HMF was obtained. In the ultrasonic DES (ChCl-OA) system, without using any catalyst, 51.87 mol% of 5-HMF was obtained from fructose after reacting at 100°C for one hour. Among them, the carboxylic acid in DES played a dual role, which makes the reaction system greener. In addition, a previous report demonstrated that the ultrasound-assisted IL has a synergistic effect on the SCB conversion reaction, and clarified the effectiveness of ultrasonic in the pretreatment and conversion of SCB [47]. 65.72 % 5-HMF was obtained under the conditions of ultrasound-assisted IL at 140°C, 25 min, and an ion-exchange resin catalyst. In this study, the reaction solvent used in SCB conversion was DES, which is more economical compared with ILs, and the catalyst used was SnCl₄•5H₂O. This system generated 44.14 mol % 5-HMF after a reaction time of 30 min at 150°C, which was much higher than the 5-HMF yield obtained by Iryani et al. [48]. The comparison of the above studies confirmed that the ultrasonic ILs/DES system is very effective in converting fructose and SCB to 5-HMF, and also confirmed that the D001-cc ion-exchange resin and acidic DES have excellent catalytic activity when used in the one-step fructose conversion reaction. In addition, employing metal chlorides in DES created favorable conditions for the pretreatment and conversion of SCB.

Table 1
Comparison of the yield of fructose and sugarcane bagasse converted to 5-HMF.

Substrate	Reaction system	Conditions	Catalyst	5-HMF yield	Refs
Fructose	Supercritical/carbon dioxide-[Bmim]OAc	90°C, 30 min	Supercritical/carbon dioxide	27.73%	[27]
Fructose	Acetone–water reaction media	150°C, 10 min	Cation exchange resin	70.3%	[9]
Fructose	Water	200°C, 10 min	Formic acid	56%	[43]
Fructose	Deep eutectic solvent (ChCl:OA)	110°C, 4 h	Sulfonated amorphous carbon–silica	67%	[44]
Fructose	Water-MIBK biphasic system Containing polyvinylpyrrolidone and 2-butanol	160°C, 2 h	Ethylenediaminetetraacetic acid (EDTA)	89%	[45]
Fructose	Ultrasound-assisted [Bmim]Cl	80°C, 1 h	Ion-exchange resin catalyst, D001-cc	65.29 mol%	This study
Fructose	Ultrasound-assisted DES(ChCl:OA)	100°C, 1 h	No	51.87 mol%	This study
Sugarcane Bagasse	Hot compressed water	270°C, 10 min	No	3.09 wt%	[47]
Sugarcane Bagasse	Ultrasound-assisted [Bmim]OAc	140°C, 25 min	Ion-exchange resin catalyst, D001-cc	65.72%	[46]
Sugarcane Bagasse	Ultrasound-assisted DES (ChCl:OA)	150°C, 30 min	SnCl ₄ ·4H ₂ O	44.14 mol%	This study
Note: [Bmim]OAc: 1-butyl-3-methylimidazolium acetate; ChCl: Choline chloride; OA: Oxalic acid; MIBK: Methyl isobutyl ketone; [Bmim]Cl: 1-butyl-3-methylimidazolium chloride.					

4. Conclusions

This work demonstrated a greener and safer method to efficiently produce 5-HMF from fructose/SCB using ultrasonic ILs/DES systems. In the ultrasonic-ILs and D001-cc system, a higher yield of 5-HMF was obtained, and the D001-cc resin still maintained higher catalytic activity after being reused six times. In the ultrasonic DES system, the carboxylic acid used as HBD in the composition of DES efficiently catalyzed fructose conversion. On this basis, ultrasonic DES combined with metal chloride were used to transform SCB in two steps, the reaction system was optimized. At optimum conditions, more than 44 mol% of 5-HMF obtained from SCB conversion. This study showed that ultrasound could significantly improve the mass transfer between ILs/DES and fructose/SCB, and promote their interaction to increase

the yield of 5-HMF. Ultrasound is a low-energy, low-pollution physical method. Combine it with ILs/DES to achieve “physical driving chemistry”, thereby achieving efficient decomposition and transformation of biomass. The reaction system established in this research could give a breakthrough for realizing a high-efficiency conversion and high-value utilization of monosaccharides, carbohydrates and even woody biomass.

Declarations

CRediT authorship contribution statement

Qinghua Ji: Supervision, Validation, Conceptualization, Writing - review & editing, Writing - original draft, Methodology, Software. **Xiaojie Yu:** Resources, Data Curation. **Abu ElGasim A. Yagoub:** Writing - Review & Editing. **Li Chen:** Funding acquisition. **Cunshan Zhou:** Supervision, Validation, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful for the support provided by the National Natural Science Foundation of China (32072174), Social development of Jiangsu Province – General Project (BE2020776).

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Figures

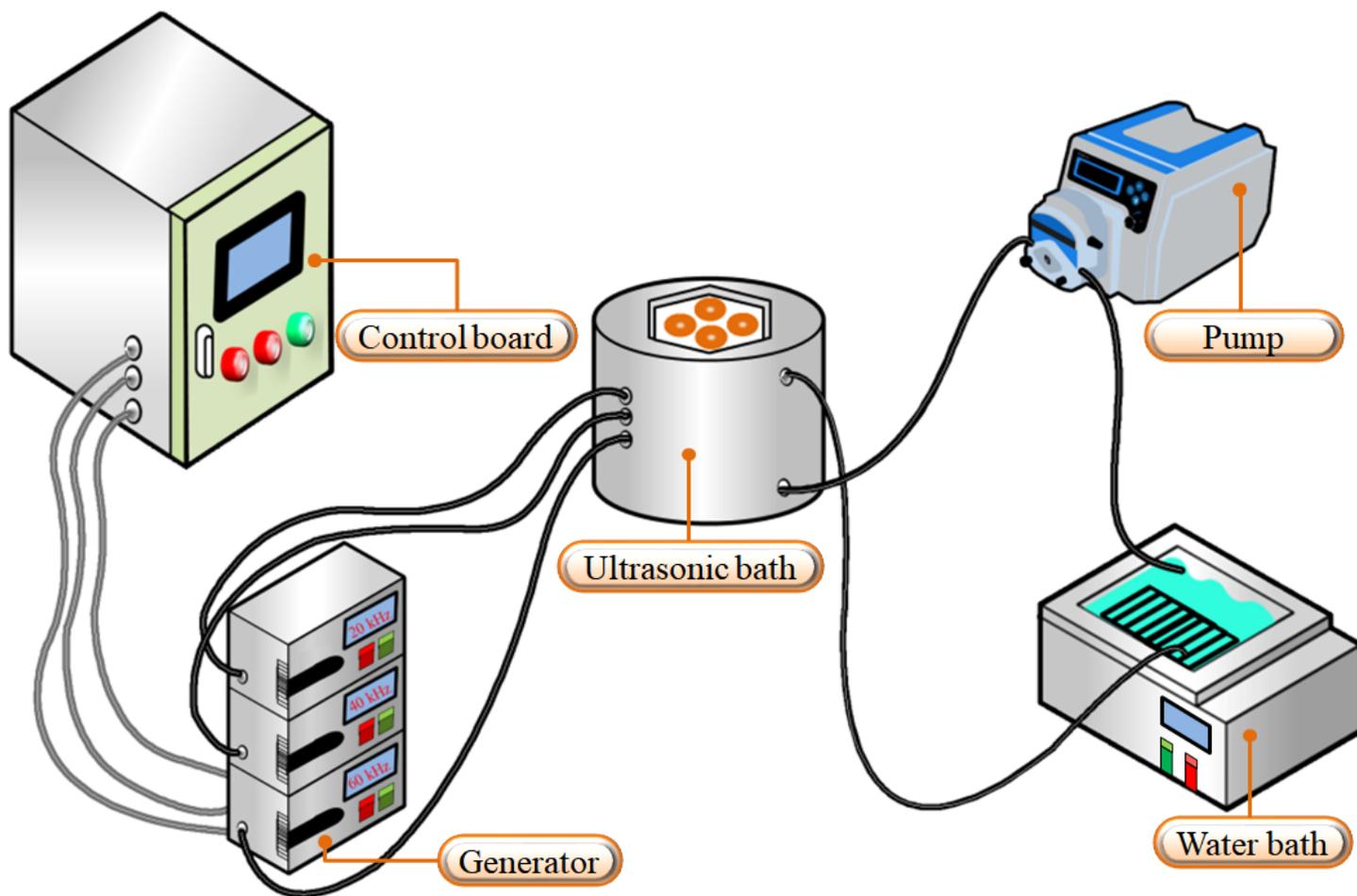


Figure 1

Schematic diagram of ultrasound equipment.

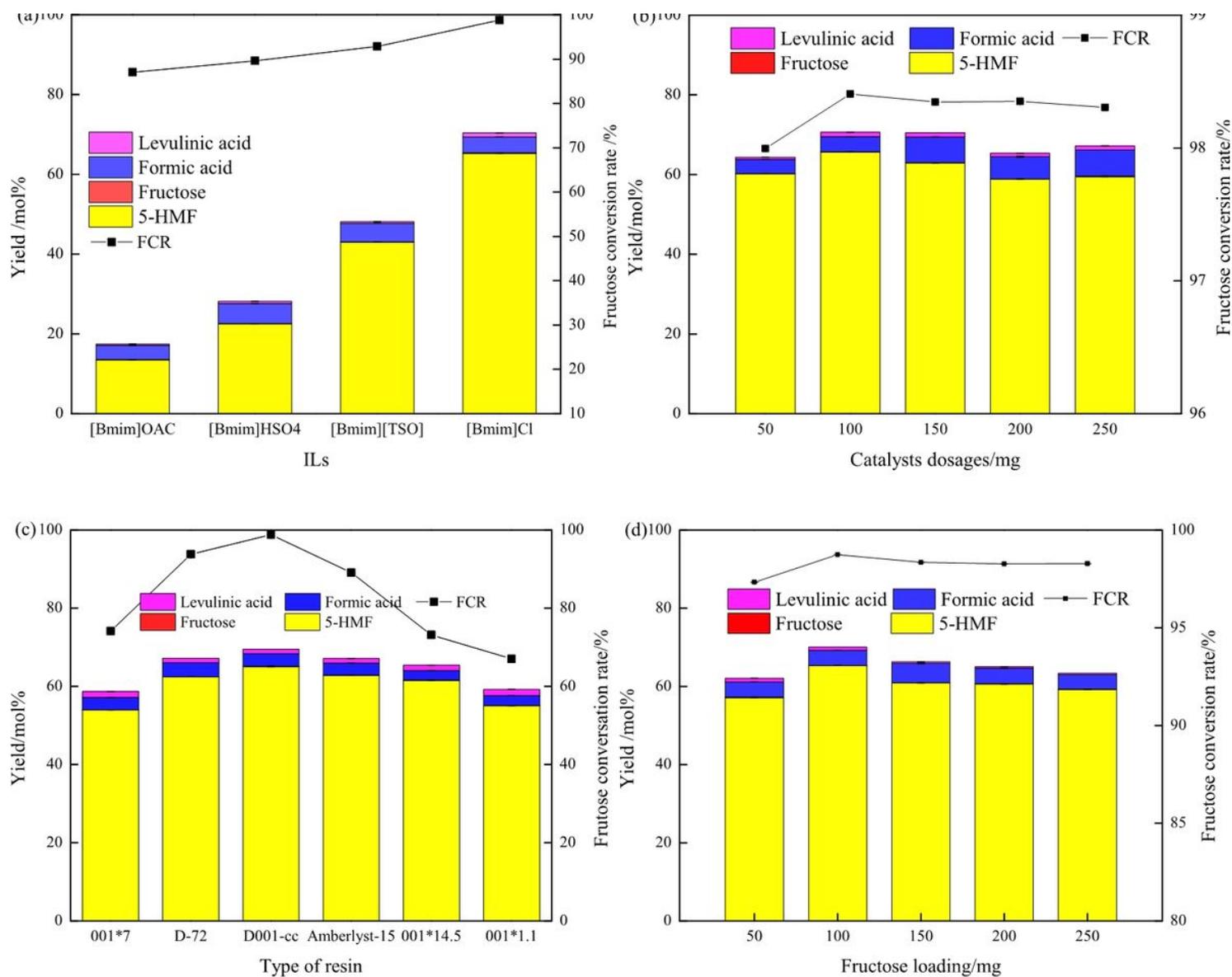


Figure 2

The effect of ultrasound-assisted ILs on fructose conversion. (a) Types of ionic liquid (Fructose: 0.1 g, ILs: 1 g, D001-cc: 0.1 g, ultrasonic 300 W, 40 kHz, 80 °C, 1 h); (b) Catalyst dosage (Fructose: 0.1 g, [Bmim]Cl: 1 g, D001-cc: 50-250 mg, ultrasonic 300 W, 40 kHz, 80 °C, 1 h); (c) Catalyst type (Fructose: 1g, [Bmim]Cl: 1g, Catalyst: 0.1g, ultrasonic 300 W, 40 kHz, 80 °C, 1 h); (d) Fructose loading (Fructose: 1 g, ILs: 1 g, D001-cc: 1 g, ultrasonic 300 W, 40 kHz, 80 °C, 1 h).

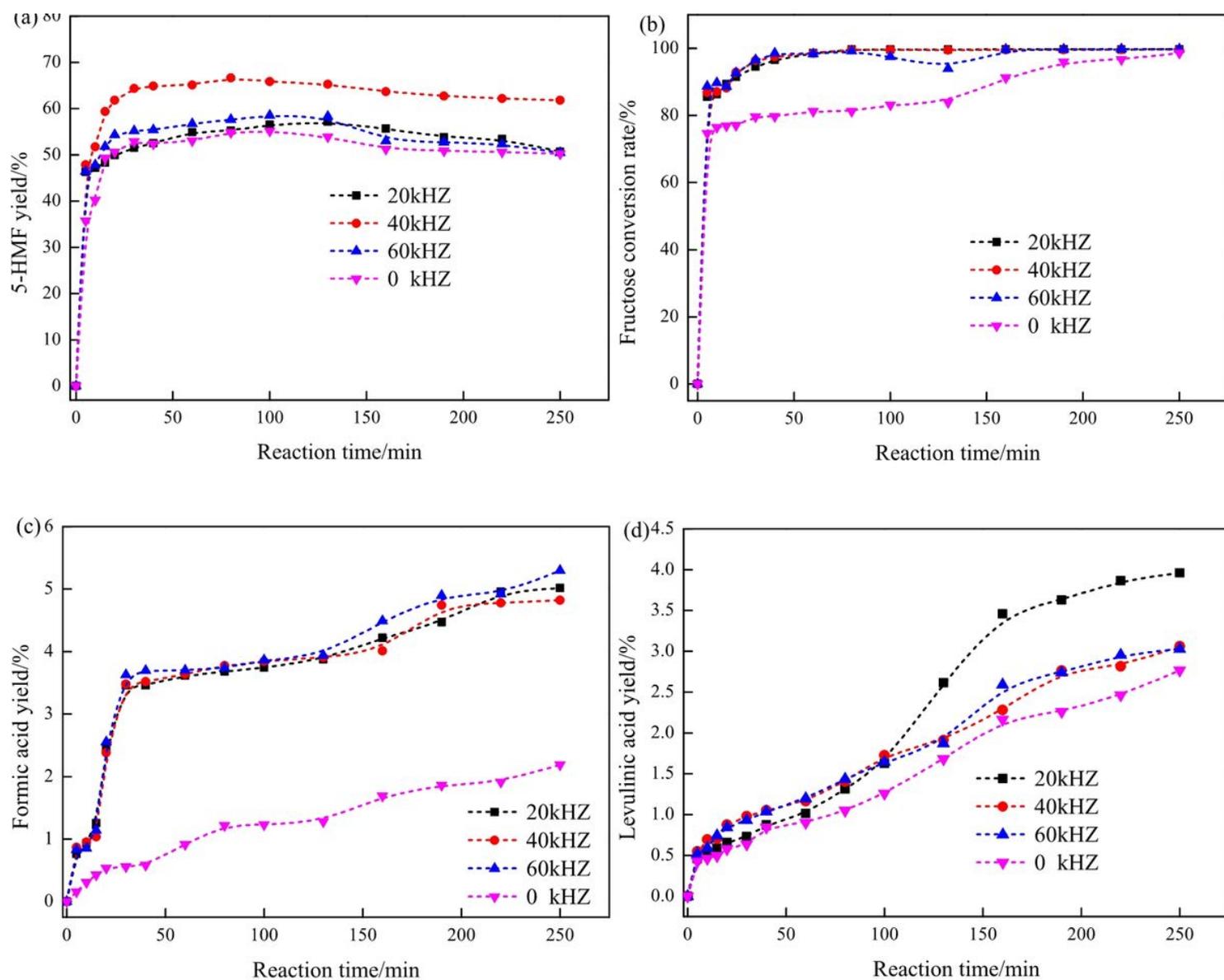


Figure 3

The effect of ultrasonic frequency on fructose conversion. (a) 5-HMF; (b) Fructose conversion rate; (c) Formic acid; (d) levulinic acid. (Fructose: 0.1 g, [Bmim]Cl: 1 g, D001-cc: 0.1 g, ultrasonic 300 W, 80 °C).

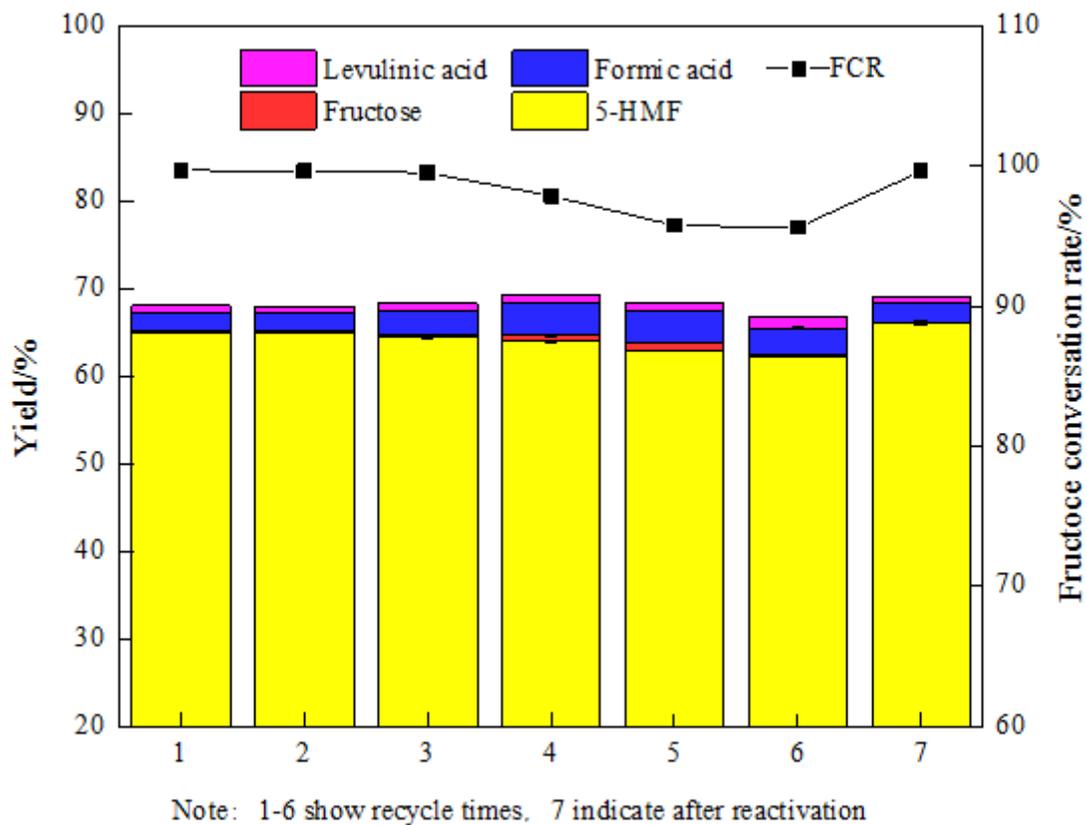


Figure 4

Effect of catalyst reuse on the conversion of fructose to 5-HMF. (Fructose: 0.1 g, [Bmim]Cl: 1 g, D001-cc: 0.1 g, ultrasonic 300 W, 80 °C, 1 h).

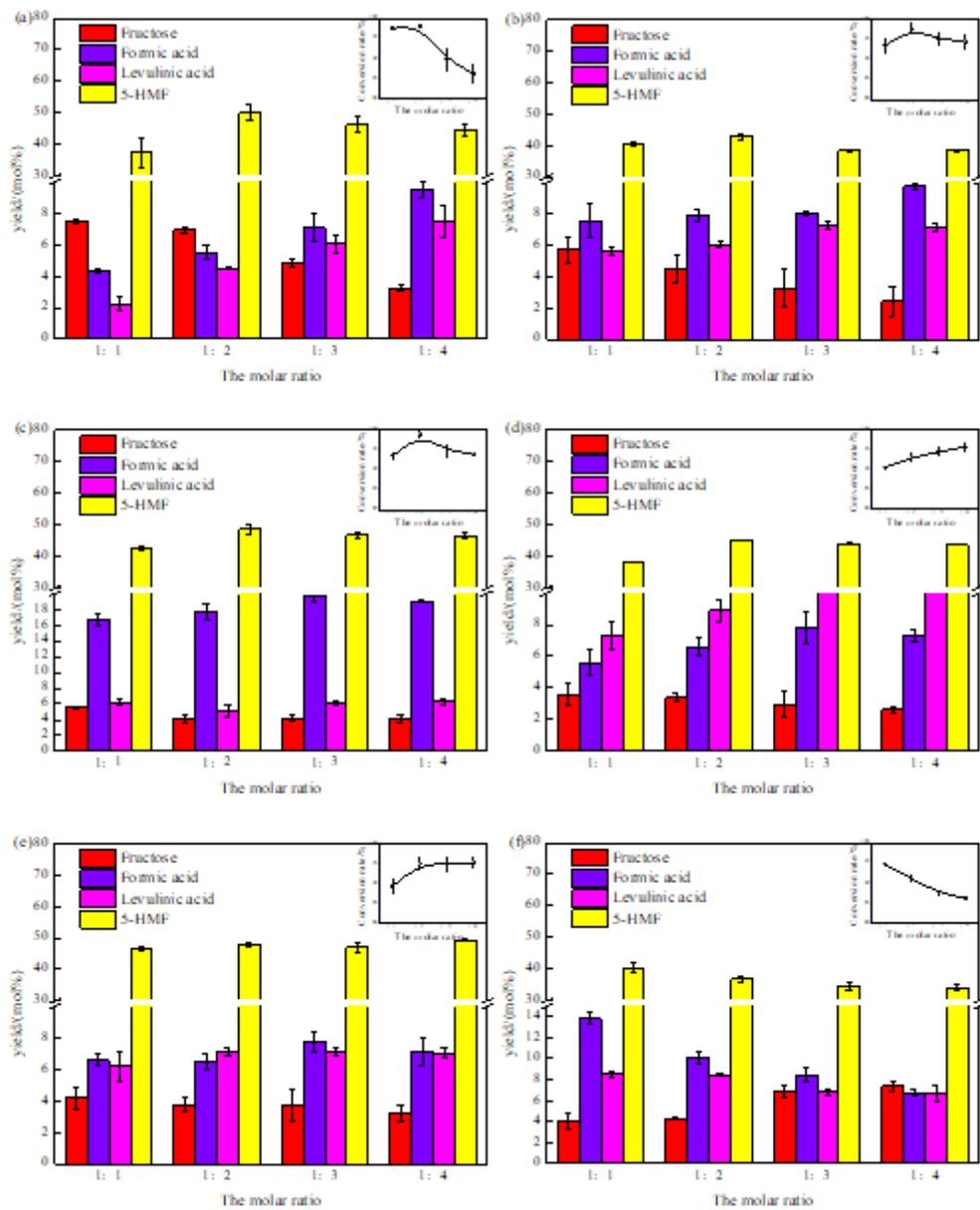


Figure 5

The effect of DES molar ratio on fructose conversion. (a) Oxalic acid; (b) Malic acid; (c) Formic acid; (d) Acetic acid; (e) Lactic acid; (f) Citric acid. (Fructose: 0.1 g, DES: 1 g, ultrasonic 300 W, 100 °C, 1 h).

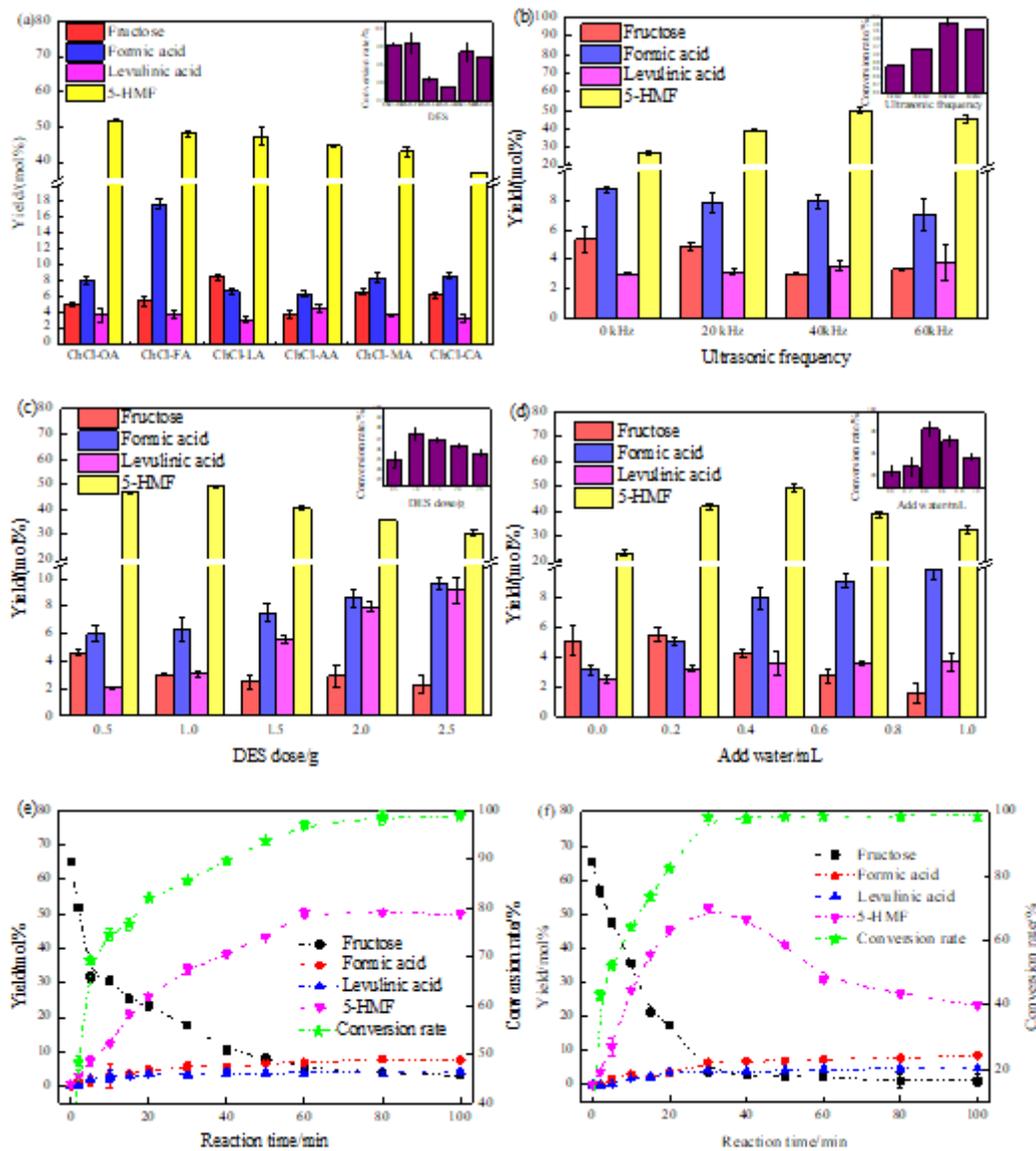


Figure 6

The effect of ultrasound-assisted DES on fructose conversion. (a) Types of DES (Fructose: 0.1 g, DES: 1 g, water: 0.46 mL, ultrasonic 300 W, 40 kHz, 100 °C, 1 h); (b) Ultrasonic frequency (Fructose: 0.1 g, (ChCl:OA): 1 g, water: 0.46 mL, ultrasonic 300 W, frequency: 0, 20, 40, 60 kHz, 100 °C, 1 h); (c) DES loading (Fructose: 0.1 g, (ChCl:OA): 0.5-2.5 g, water: 0.46 mL, ultrasonic 300 W, 40 kHz, 100 °C, 1 h); (d) The amount of water added in DES (Fructose: 0.1 g, (ChCl:OA): 1 g, water: 0-0.92 mL, ultrasonic 300 W, 40 kHz, 100 °C, 1 h). (e-f) Reaction time (Fructose: 0.1 g, (ChCl:OA): 1 g, water: 0.46 mL, ultrasonic 300 W, 40 kHz, 80 and 100 °C, 0-100 min).

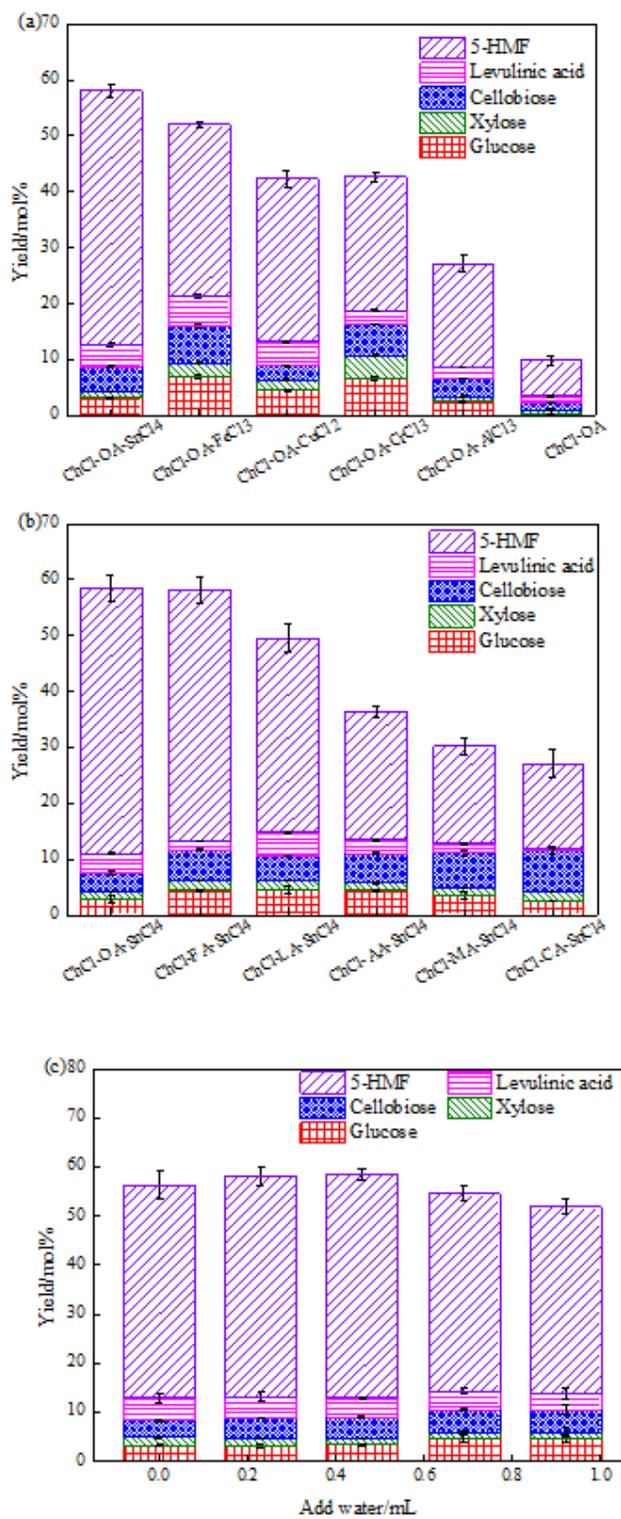


Figure 7

The effect of ultrasound-assisted DES on SCB conversion. (a) Types of metal chloride (SCB: 0.1 g, (ChCl:OA): 1 g, metal chloride: 0.1 g, water: 0.46 mL, pretreatment condition: ultrasonic 300 W, 40 kHz, 80 °C, 30min, reaction condition: 130 °C, 4 h); (b) Types of DES (SCB: 0.1 g, DES: 1 g, SnCl₄·5H₂O: 0.1 g, water: 0.46 mL, pretreatment condition: ultrasonic 300 W, 40 kHz, 80 °C, 30 min, reaction condition: 130

°C, 4 h); (c) The amount of water added in DES (SCB: 0.1 g, DES: 1 g, SnCl₄·5H₂O: 0.1 g, water: 0-0.92 mL, pretreatment condition: ultrasonic 300 W, 40 kHz, 80 °C, 30min, reaction condition: 130 °C, 4 h).

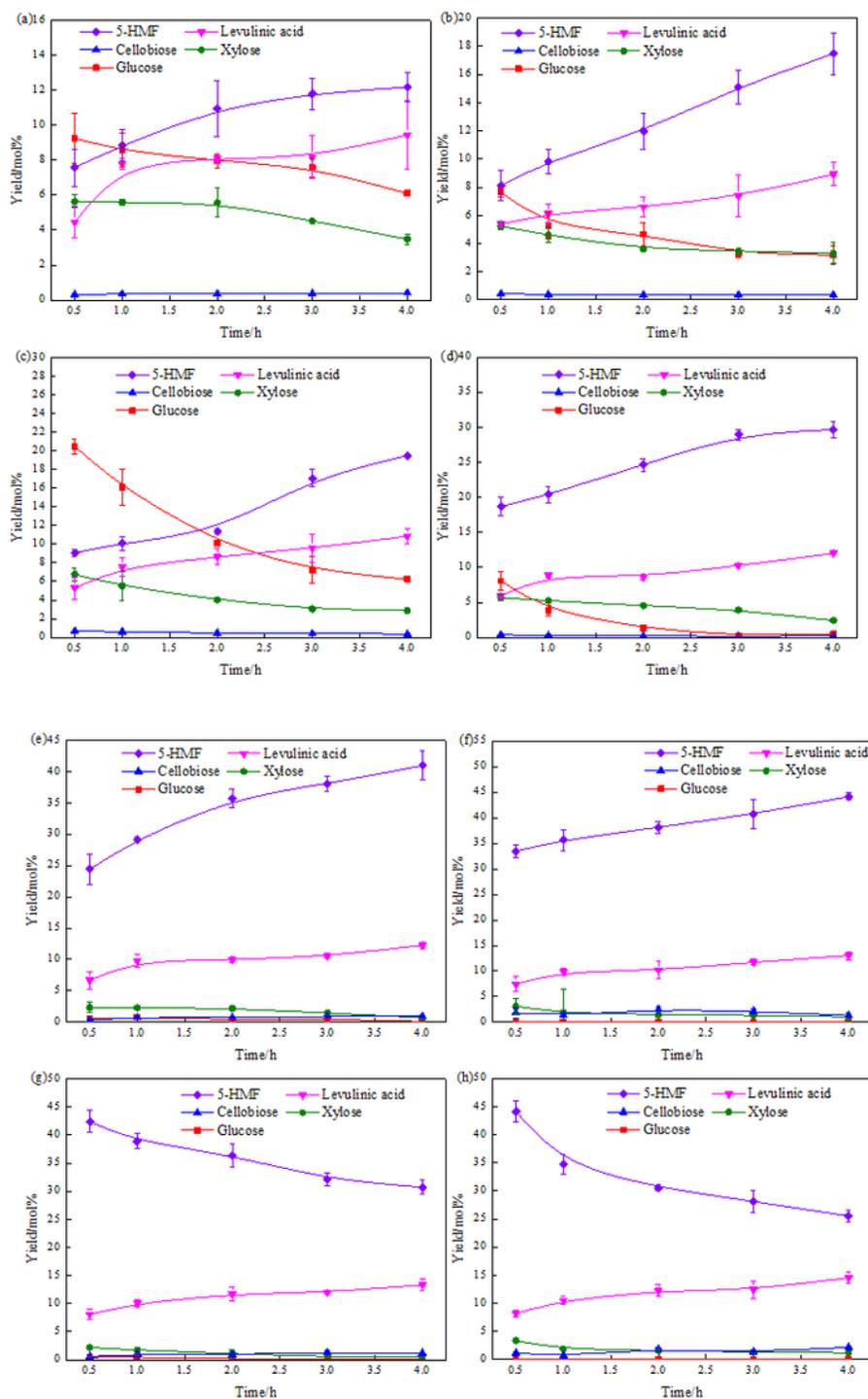


Figure 8

Effect of reaction temperature and time on SCB conversion. (a) 80 °C; (b) 90 °C; (c) 100 °C; (d) 110 °C; (e) 120 °C; (f) 130 °C; (g) 140 °C; (h) 150 °C. (SCB: 0.1 g, DES: 1 g, SnCl₄·5H₂O: 0.1 g, water: 0.46 mL, pretreatment condition: ultrasonic 300 W, 40 kHz, 80 °C, 30min, reaction condition: 80-150 °C, 0.5- 4 h).

Supplementary Files

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