INTRODUCTION

Along with the fast growth of global economy, every country in the world needs more and more fossil fuels. For the purpose of achieving sustainable development of economy in a long period of time, we are in urgent need for seeking a novel and renewable alternative energy resource. Lignocellulosic biomass is an important renewable energy resource, because it can be converted into various kinds of green chemicals and liquid fuels via different thermochemical technologies. Typical composition of lignocellulosic biomass includes three main components, namely cellulose, hemicellulose, and lignin, and xylose is a representative sugar unit that makes up the largest proportion in hemicellulose structure. Although great progress has been made for the conversion of biomass to chemicals and fuels in recent years, how to produce targeted products with high yields in a green and economic manner still remains as a challenge. Furfural is a bio-based platform chemical from the thermochemical conversion of biomass hemicellulose, and it is extensively applied in the production of solvent, pharmaceuticals, liquid fuels, etc. Especially, aldol condensation reactions between furfural and carbonyl compound with active α-H could produce oxygenated precursors with certain
carbon numbers, and the precursors could further undergo hydrodeoxygenation reactions to give long-chain liquid alkanes that are able to be directly used as vehicle fuels and aviation fuels.\textsuperscript{11,12} Conventional hydrothermal technologies for furfural production can achieve about 50% of theoretical furfural yield, but they pose problems like high energy consumption, high cost, equipment corrosion, and environmental pollution caused by acidic waste water and residues.\textsuperscript{13} Therefore, researchers have developed plenty of innovative catalytic reaction systems in these years, aiming at the high-efficiency production of furfural. The superiority over conventional systems mainly concentrated on the optimization for solvents and catalysts.

The catalysts used during the hydrothermal decomposition of biomass carbohydrates can be divided into two categories, namely homogeneous and heterogeneous catalysts. The latter has been the focus of much attention because of its characteristic of easy recycling. For example, Bruce et al\textsuperscript{14} conducted the conversion of xylose in γ-valerolactone-water solvent mixture using micropore zeolite SAPO-34 as the catalyst, and they obtained 40% yield of furfural, while catalyst deactivation was not observed during 3-time recycling test. Homogeneous catalyst can spread in the reaction system adequately, and therefore, they can closely interact with reactants, leading to much better carbohydrates conversion results than heterogeneous catalysts. Zhao et al\textsuperscript{15} chose pressurized CO\textsubscript{2} as the acidic catalyst and perform the catalytic conversion of xylose, arabinose and xylan in isopropanol-water solvent mixture for furfural production, and a maximum furfural yield of 69% was achieved from xylose. Le Guenic et al\textsuperscript{16} carried out the xylose dehydration reaction catalyzed by FeCl\textsubscript{3} in the cyclopentyl methyl ether-water biphasic solvent with NaCl as an additive and achieved 75% yield of furfural.

Solvent configuration also has significant effects on furfural production, because the distribution and activities of sugar conformers differ in different kinds of solvent. Moreover, the solvent molecules may combine with reactants or intermediates, which could affect the stabilization of intermediates and transition states.\textsuperscript{17,18} The most common solvent systems consist of three different types including single-phase solvent, biphasic solvent and ionic liquid. Recently, single-phase solvent system made up of water and organic solvent has been found to hinder side reactions to a certain degree and to raise furfural yields notably. The reason was that the organic solvent altered the distribution of sugar conformers and replaced the active water molecules near the target products to prevent the products from secondary reactions like hydration and fragmentation.\textsuperscript{18,19} Ionic liquid has superior ability in biomass solvation, so it has been widely utilized as an advanced solvent in the hydrothermal conversion of biomass.\textsuperscript{20} However, the potential of ionic liquid in practical application was restricted due to its much higher cost than traditional organic solvent.

In the past few years, studies have shown that some ionic liquids were able to catalyze the biomass dehydration reaction, while they were still responsible for biomass solvation. Consequently, researchers employed a little amount of ionic liquid as a homogeneous catalyst, and satisfying furfural yields as well as reduced reaction cost were achieved from biomass feedstocks.\textsuperscript{21} For example, Serrano-Ruiz et al\textsuperscript{22} used Brønsted acidic ionic liquid catalysts for furfural production from xylose in tetrahydrofuran-water and 85% yield of furfural was achieved. Wang et al\textsuperscript{23} developed a Lewis acidic ionic liquid catalyst for the same reaction and 80% yield of furfural was obtained in γ-valerolactone-water solvent mixture. Nevertheless, the number of studies concerning furfural production from biomass carbohydrates catalyzed by ionic liquid catalysts was still limited, and the related catalytic reaction pathways remain unclear, especially regarding the function of different components in ionic liquid catalysts. In this work, we take advantage of both the high affinity toward biomass from the Brønsted acidic [bmim]Cl-containing ionic liquid and the outstanding catalytic performance from Lewis acidic metal chlorides for biomass dehydration reaction to produce furfural, and developed several ionic liquid catalysts including [bmim]Cl/FeCl\textsubscript{3} as a representative for furfural production from xylose. The main idea was to investigate the influence of metal chloride component and imidazole component in ionic liquid catalyst on the formation rules of furfural. Butanone-water solvent mixture was chosen as the reaction media. Butanone is commonly recognized as a green solvent that can be directly synthesized from biomass resources.\textsuperscript{24,25}

2 | MATERIAL AND METHODS

2.1 | Materials

Xylose, xylulose, furfural, AlCl\textsubscript{3}·6H\textsubscript{2}O, FeCl\textsubscript{3}·6H\textsubscript{2}O, CuCl\textsubscript{2}·2H\textsubscript{2}O, and CrCl\textsubscript{3}·6H\textsubscript{2}O were purchased from Aladdin Industrial Corporation. Butanone was purchased from Sinopharm Chemical Reagent. [bmim]Cl/FeCl\textsubscript{3} (1-butyl-3-methylimidazolium chloroferrate), [emim]Cl/FeCl\textsubscript{3} (1-ethyl-3-methylimidazolium chloroferrate), [bmim]Cl/AICl\textsubscript{3} (1-butyl-3-methylimidazolium chloroaluminate), [bmim]Cl/CuCl\textsubscript{2} (1-butyl-3-methylimidazolium chlorocuprate), and [bmim]Cl/CrCl\textsubscript{3} (1-butyl-3-methylimidazolium chlorochromate) were synthesized by Shanghai Chengjie Chemical Corporation. Especially, [bmim]Cl/FeCl\textsubscript{3} was manufactured by mixing [bmim]Cl (1-butyl-3-methylimidazolium chloride) and FeCl\textsubscript{3} with specified mole ratios to form 4 different ionic liquids labeled IL1, IL2, IL3, and IL4. The mole fractions of FeCl\textsubscript{3} (\(\chi(\text{FeCl}_3)\)) were set to 0.33, 0.5, 0.67, and 0.75, respectively. In other words, the number of moles of [bmim]Cl to that of FeCl\textsubscript{3} were 2:1, 1:1, 1:2, and 1:3 for IL1,
IL2, IL3, and IL4, respectively. As for other ionic liquids, the mole fractions of the metal chlorides were 0.5.

### 2.2 Ionic liquid catalyst characterization

Raman spectra were recorded using dispersive Raman spectrometer DXR SmartRaman (Thermo Scientific) equipped with 532 nm laser and CCD detector. Spectra were obtained with 5 cm⁻¹ resolution, using 10 × 5 seconds time of exposures, and laser power was set at 5.8 mW.

The critical characteristic structures in ionic liquid were determined by ESI-MS spectra using an Agilent 6500 series accurate-mass quadrupole time-of-flight system (Agilent), and the fragmentor voltage was set to 180 V. The MS samples were prepared by diluting the ionic liquid in water with a concentration of about 5 mg/mL. MS data were acquired and analyzed by Agilent Mass Hunter software version B.09.00 (B9044.0).

Lewis/Brønsted acidity of the ionic liquid catalyst was verified by pyridine-adsorbed Fourier Transform Infrared Spectroscopy (Py-FTIR). The results were described in Supporting Information.

### 2.3 Procedure of xylose conversion

In a typical experiment for furfural production, 1 mL water and 4 mL butanone were added to a glass pressure reactor (15 mL, Synthware), and then, 0.15 g xylose and 0.5 mmol ionic liquid catalyst were charged into the solvent mixture. The reactor was put into an oil bath preheated to 140°C, and the magnetic stirring rate was maintained at 600 rpm. When the reaction time reached preset values, the glass reactor was taken out from the oil bath and was cooled by air flow. The solution in the glass reactor was filtered through a 0.22-μm syringe filter and diluted tenfold with water prior to high-performance liquid chromatography (HPLC) analysis. Each experiment was repeated three times, and the resulting mean value and standard deviation are shown in the figures.

### 2.4 Analytical methods

The filtered solution was analyzed on an UltiMate 3000 HPLC system (Thermo Scientific). A Bio-Rad Aminex HPX-87H column was used to quantify furfural whose retention time was 43.85 minutes, while a Bio-Rad Aminex HPX-87C column was used to quantify xylose and xylulose whose retention time was 10.97 and 13.28 minutes, respectively. An RI 2000 refractive index detector (Schambeck SFD GmbH) was used for signal collection with a sample cell temperature at 40°C. H₂SO₄ solution (pH 2.5) was used as the mobile phase, and its flow rate and corresponding column temperature were kept at 0.6 mL/min and 60°C, respectively. The concentrations of xylose, xylulose, and furfural were determined by comparison against standard calibration curves. The conversion rate of xylose and the yield of xylulose and furfural were calculated as follows:

\[
\text{xylose conversion} = \frac{\text{moles of xylose reacted}}{\text{moles of starting xylose}}
\]

\[
\text{xylulose yield} = \frac{\text{moles of xylulose formed}}{\text{moles of starting xylose}}
\]

\[
\text{furfural yield} = \frac{\text{moles of furfural formed}}{\text{moles of starting xylose}}
\]

Other liquid-phase products were analyzed by DSQ II gas chromatography-mass spectrometry (GC-MS) system (Thermo Scientific) equipped with a DB-wax capillary column (30 m × 0.25 mm × 0.25 mm). Helium (99.999%) at a flow rate of 1 mL/min was used as carrier gas. The GC oven temperature was programmed to increase from 40°C (1 minute) to 240°C (20 minute) at 8°C/min heating rate. The MS detector was operated in electron ionization (EI) mode (70 eV) with a scan range of m/z 35-450 and an ion source temperature set to 200°C. All detected chemicals were identified by comparison with the NIST (National Institute of Standards) MS library.

The distribution of xylose conformers in butanone-water and pure water was measured by 13C-NMR. Details can be found in Supporting Information.

### 3 RESULTS AND DISCUSSION

#### 3.1 Catalyst structure

During the synthesis process of [bmim]Cl/FeCl₃ ionic liquid catalysts, equivalent molar amount of FeCl₃ and [bmim]Cl reacted with each other to form a homogeneous and stable ionic liquid, in which [bmim]Cl⁺ and FeCl₄⁻ existed as the main ion species. When excessive FeCl₃ was added, heavier anions like Fe₃Cl₇⁻ and Fe₃Cl₁₀⁻ may be formed. However, previous studies selected pure ionic liquids as samples for characterization. In order to identify the structures of [bmim]Cl/FeCl₃ existing in the proposed butanone-water solvent mixture in our study, a small amount of ionic liquid was dissolved into the butanone-water solvent mixture to form a homogeneous solution, and the Raman spectra for the solution containing IL1, IL2, IL3, and IL4 were recorded, respectively. As shown in Figure 1, main features of [bmim]Cl/FeCl₃ appear at 111, 138, 301, 335, 389, and 411 cm⁻¹. The most intensive peak observed at 335 cm⁻¹ along with the peaks at 111, 138, and 389 cm⁻¹ is attributed to the characteristic vibration frequencies of FeCl₄⁻, while the feature at 411 cm⁻¹ comes from the vibration of [bmim]⁺. For the purpose of identifying the source of vibration at 301 cm⁻¹, we
collected the Raman spectrum of supercooled [bmim]Cl liquid at 20°C, and a broad band appears at 301 cm⁻¹, representing a characteristic vibration frequency from [bmim]Cl. Compared with other studies, a notable difference in this work is that complex anions like Fe₂Cl₇⁻ and Fe₃Cl₁₀⁻ were not detected from Raman spectra. The reason could be the highly diluted ionic liquid in butanone-water solvent mixture, and therefore, it was less possible for free FeCl₃ and FeCl₄⁻ in solution to form dimeric anions or higher coordination.

For further confirming the structure of ionic liquid in the proposed solvent system, ESI-MS spectra were recorded for the solution of IL4. As depicted in Figure 2, the existence of [bmim]⁺, FeCl₄⁻, and FeCl₃ is strongly ascertained with molecular formula calculation scores higher than 94. Complex anions such as Fe₂Cl₇⁻ and Fe₃Cl₁₀⁻ still do not turn up in the spectrum, which is in accordance with the Raman spectra in Figure 1. It could be inferred that excessive FeCl₃ existed as free molecules in the solution, and most of them offered Lewis acidity, while some of them would undergo hydrolyzation reactions to provide Brønsted acidity.³²

3.2 | Effects of catalyst composition on xylose conversion and furfural yield

Xylose dehydration reactions were carried out using ionic liquid catalysts with different χ(FeCl₃), and the time-varying xylose conversion and furfural yield were shown in Figure 3. It is obvious that all the four catalysts have similar catalytic performance for the catalytic conversion of xylose, and when the reaction lasted for 90 minutes, all the xylose conversions reached over 90%. The catalytic activity ranking from high to low is as follows: IL3 > IL4>IL2 > IL1, which suggested that FeCl₃ might be more responsible for rapid xylose conversion than [bmim]Cl. On the contrary, considerable differences could be found in the time-varying furfural yield with different ionic liquids as catalysts. IL1 exhibited the worst catalytic performance, and only 38% yield of furfural was obtained even though the reaction lasted for 180 minutes. When catalyzed by IL2, IL3, and IL4, furfural yield could arrive at the maximum value (56%, 47%, and 41%, respectively) within the first 90 minutes. Afterward, furfural yields showed a steep drop at longer reaction times. One possible reason was that furfural underwent condensation reactions with xylose or xylulose to form byproducts like humins.³³,³⁴ The furfural yield ranking catalyzed by the 4 different ionic liquids at 90 min from high to low was as follows: IL2 > IL3>IL4 > IL1. Sun et al studied the acidity of [bmim]Cl by ¹H-NMR, and the result suggested that the signal of 2-H on the imidazole ring totally disappeared after KOH titration. The formation of water was also confirmed by Fourier Transform infrared spectroscopy (FTIR) after titration, which firmly demonstrated the Brønsted acidity of [bmim]Cl.³⁵ The pH values of 0.1 mol/L FeCl₃ solution and [bmim]Cl/FeCl₃ solution were measured to be 2.03 and 1.92, respectively. The corresponding H⁺ concentrations were 0.009 and 0.012 mol/L, respectively. By comparison of H⁺ concentrations, Brønsted acidity of FeCl₃ was dominant for xylose dehydration. Excessive amount of Lewis acidity from FeCl₃ or Brønsted acidity could result in secondary reactions including retroaldolization.³⁶-³⁸ Therefore, appropriate χ(FeCl₃) should be chosen to achieve fast formation of furfural and inhibited occurrence of side reactions.
It has been demonstrated that during furfural production from xylose dehydration, the reaction would choose to go along two different paths according to the acid type existing in the reaction system. If the catalyst mainly possessed Lewis acidity, xylose would first undergo isomerization reaction to produce xylulose, followed by dehydration of xylulose for furfural formation. If the catalyst showed Brønsted acidity, xylose would lose three water molecules straightly to produce furfural. In order to understand the dehydration mechanism of xylose, the time-varying xylulose yield in the presence of different ionic liquid catalysts was obtained by HPLC. As shown in Figure 4, with catalyst IL1 the highest xylulose yield during the whole reaction process was only about 5%. This indicated a relatively weak Lewis acidity of IL1, and most of xylose directly dehydrated to produce furfural. Comparatively, 11% yield of xylulose was achieved at 30 minutes when the reaction was catalyzed by IL2, and therefore, a stronger Lewis acidity of IL2 than IL1 was evidenced, leading to more xylose being selectively isomerized to xylulose. Within the first 30 minutes, the order of xylulose yield from high to low is as follows: IL2 > IL3 > IL4, suggesting that xylulose yield would decrease with relatively high \( \chi(\text{FeCl}_3) \) of ionic liquid catalyst. This could be due to the strengthened Lewis acidity, because xylulose might undergo side reactions with furfural when catalyzed by Lewis acid catalysts. 

Through comprehensive consideration of both Figures 3 and 4, the low furfural yield catalyzed by IL1 might result from its weak Lewis acidity. Although a little xylose went through isomerization-dehydration reaction pathway with relatively low apparent activation energy than direct dehydration, the dominating route was still the direct dehydration that needs high apparent activation energy. The order of furfural yield catalyzed by IL2, IL3, and IL4 from high to low was the same as the order of xylulose yield, and therefore, xylulose was proven to be a key intermediate during furfural production. Overall, IL2 showed the most satisfying catalytic performance. When [bmim]Cl held a predominant position (IL1), the dehydration of xylose was hard to occur because of high apparent activation energy. Besides, furfural tended to be involved in secondary reactions in the presence of Bronsted acid. If FeCl\(_3\) made up a large proportion in the catalyst, it would be easier for the occurrence of xylose conversion through isomerization-dehydration reaction due to low activation energy barriers. Consequently, for the sake of achieving the best xylose conversion and furfural yield, the content of FeCl\(_3\) and [bmim]Cl in ionic liquid should be synergistically optimized to obtain an appropriate acidity distribution.

In order to further verify the performance of the catalyst, control experiments were carried out in pure water and pure
butanone solvent. The results showed that the dehydration reaction could hardly occur in pure butanone. The reason might be that the catalyst could not hydrolyze in butanone to provide necessary acidity. In water, the highest xylose conversion and furfural yield were 35% and 9% at 240 minutes, respectively. Thus, an appropriate amount of butanone had a positive organic solvent effect on xylose dehydration.

3.3 Effects of catalyst composition on liquid-phase product distribution

In order to gain a deep insight into the effect of catalysts with different catalyst composition on the dehydration of furfural, the liquid-phase products were investigated by GC-MS and the product distribution corresponding to each catalyst was shown in Figure 5. The soluble products from xylose conversion were divided into three main categories, namely oxygenated aliphatics, furans, and cyclohexenones. Furfural (1) was a primary compound in the liquid-phase products, and it made up 38%, 94%, 90%, and 74% of the furans corresponding to IL1-IL4, respectively. Other furan products from xylose conversion mainly included 3-(2-furanyl)-3-penten-2-one (2), 5-hydroxy-4,5-dimethyl-2,5-dihydrofuran-2-one (3), and 5-methyl-2(5H)-furanone (4), and all the furans account for over 73% of the soluble products (2) could come from the aldol condensation reaction between (1) and pentanone intermediates from retroaldolization of xylose.42 Furanone (3) and (4) might be the hydration products of hydroxyl-rich acids from the ring opening of xylose.43 Oxygenated aliphatics mainly consisted of acetic acid (5), 2-ethyl-hexenal (6), 5-methyl-4-hepten-3-one (7), 3,4-dimethyl-3-hexen-2-one (8), and 4-hydroxy-4-methyl-2-pentanone (9), and they comprised 2%-14% of the soluble products. The byproduct (5) primarily resulted from the retroaldolization of xylose in the presence of Brønsted acid.44,45 C6-C8 aldehydes and ketones (6) (7) (8) (9) were likely to be formed by the aldol condensation reactions between the solvent molecule (butanone) and other small molecules from the retroaldolization of xylose.46-48 However, this reaction could not have profound effect on furfural production. Control experiments were carried out under the same conditions using tetrahydrofuran-water solvent mixture, which is a common solvent configuration that is much less possible for the occurrence of side reactions between furfural and solvent. A low furfural yield of 44% was achieved. Cyclohexenones were mainly made up of 6-methyl-3-(1-methylthyl)-2-cyclohexen-1-one (10), 2-hydroxy-3-methyl-6-(1-methylthyl)-2-cyclohexen-1-one (11), and 4-hydroxy-2-methyl-5-(1-hydroxy-1-isopropyl)-2-cyclohexen-1-one (12), and they constituted 5%-19% of the soluble products. The origin of cyclohexenones might be the cyclization of the chain intermediates.49

Through comparison of liquid-phase products between different ionic liquid catalysts, it could be obviously found that IL2 and IL3 promoted the production of furans, while IL1 and IL4 had poor selectivity for furans. Furans accounted for 84%, 91%, 92%, and 73% of the soluble products corresponding to IL1-IL4, respectively, and furfural made up large proportions of the furans. It could be inferred that both Lewis acid and Brønsted acid favored the formation of furans concerning dehydration, ring opening, aldol condensation, hydration, etc. IL4 showed the worst furan selectivity among all the four catalysts, which was consistent with the lowest furfural yield at 180 minutes in Figure 3, because strong Lewis acidity from excessive FeCl3 facilitated the occurrence of side reactions involving furfural consumption at long reaction times.37,38 When compared with IL3 and IL4 that had larger proportion of FeCl3, IL1 and IL2 had higher selectivity for oxygenated aliphatics. Therefore, [bmim]Cl could accelerate the retroaldolization reaction. The selectivity ranking of cyclohexenones corresponding to different catalysts from low to high is as follows: IL1 < IL2 ≈ IL3 < IL4, indicating that large content of FeCl3 would be beneficial for the cyclization reaction, which agreed with the experimental results from our previous study.50

According to the above discussion about liquid-phase product, we proposed a reaction network for xylose conversion catalyzed by bifunctional catalyst [bmim]Cl/FeCl3 with different content of [bmim]Cl and FeCl3, as shown in Figure 6. The primary reaction path involved three stages, namely ring opening, isomerization, and dehydration, among which the dehydration reaction was catalyzed by Brønsted acid while ring opening and isomerization reaction were catalyzed by Lewis acid.51 Xylose could also undergo direct dehydration reaction to lose three molecules of water leading to furfural formation when the reaction was only catalyzed by Brønsted acid, though it has been illustrated that this route

![Figure 5](image-url)
needed high activation energy and would hardly occur in the presence of Lewis acid. Various chain intermediates would be formed during the reaction, and they further went through side reactions like cyclization, retroaldolization, condensation, and hydration to form certain byproducts.

### 3.4 Catalytic performance of different metal chlorides and imidazolium ionic liquids

For the purpose of demonstrating the superiority of the ionic liquid catalysts developed in this work over conventional inorganic salt catalysts, four common Lewis acidic homogeneous catalysts, namely FeCl₃, AlCl₃, CuCl₂, and CrCl₃, as well as the ionic liquids prepared by mixing these four salts and [bmim]Cl at 1:1 mole ratio, were selected as the catalysts for the catalytic conversion of xylose. The corresponding xylose conversion and furfural yield were described in Figure 7. Apparently, the ionic liquid catalyst [bmim]Cl/FeCl₃ had even better catalytic performance than FeCl₃, and it could achieve higher xylose conversion and furfural yield in the same reaction condition. Hence, the newly formed ions such as FeCl₄⁻ and [bmim]⁺ derived from the newly synthesized ionic liquid catalyst were much more effective for promoting the whole reaction process than the original FeCl₃. For further verification, control experiments were carried out with [bmim]Cl as the only catalyst. The results suggested that xylose was not reacted, and therefore, [bmim]Cl itself was not able to provide necessary acidity for xylose conversion in the proposed butanone-water solvent mixture. However, along with the increasing χ(FeCl₃), 2-H in [bmim]Cl was easier to leave the imidazole ring and become H⁺ owing to the anti-shielding effect of FeCl₃, ensuring sufficient Brønsted acidity for the occurrence of xylose dehydration reaction.

Among all the tested metal chloride catalysts, AlCl₃ showed the best catalytic performance. Nevertheless, the cost of AlCl₃ was much higher than FeCl₃, and the magnetic characteristic of [bmim]Cl/FeCl₃ enabled its potential in easy recovery and industrial application, which was not possible for [bmim]Cl/AlCl₃. The catalytic activity ranking for the four metal chlorides from good to bad is as follows: AlCl₃ > CrCl₃ > FeCl₃ > CuCl₂. Pearson listed the absolute electronegativity of a large number of cations, among which Al³⁺ > Fe³⁺ ≈ Cr³⁺ > Cu²⁺, and generally, high electronegativity represented strong Lewis acidity. Thus, it could be ascertained that metal chlorides with strong Lewis acidity would favor furfural production from xylose dehydration considerably. Once the metal chlorides were mixed with [bmim]Cl to form ionic liquid catalysts, the conversion from xylose to furfural would also be greatly facilitated. For instance, when [bmim]Cl/FeCl₃ took the place of FeCl₃, furfural yield showed a remarkable ascent from 41% to 56%. One main reason could be the formation of active ions like FeCl₄⁻ in each ionic liquid. Other ionic liquid including [emim]Cl (1-butyl-3-methylimidazolium chloride), [Hmin] Cl (1-methylimidazole hydrochloride), and [HDmim]Cl (1,2-dimethylimidazolium hydrochloride) could also combine with metal salts to form ionic liquid catalysts. [Emim]Cl/FeCl₃ was tested in this study, and the optimum furfural yield was 62%. So far some researchers have already employed this kind of ionic liquid in the production from C5 carbohydrates, and similar conversion results were achieved like in this work. However, most of the previous work used ionic liquid as both solvent and catalyst, leading to potential risks.
including high cost and environmental pollution. The catalytic reaction system proposed in this work is composed of butanone-water mixture as a green solvent system and ionic liquids as catalysts, and therefore, it introduces some excellent aspects such as low ionic liquid dosage and environmentally friendly solvent.

From a practical point of view, the reusability of the ionic liquid catalyst would be a challenge because of its special physicochemical characteristics compared with traditional homogeneous and heterogeneous catalysts. For example, ionic liquids usually had low volatility and high viscosity. Researchers have developed some technologies for the recycle of ionic liquid, such as induced phase separation, distillation, adsorption, and extraction. Hayashi et al. found that [bmim]Cl/FeCl₃ showed a large magnetic susceptibility that offered opportunities for easy recycling, though a large amount of the ionic liquid might be required. However, the large-scale utilization of these technologies was still restricted due to some unresolved disadvantages. Besides, a general criterion for ionic liquid recycling is still absent, and therefore, comprehensive study will be carried out in the future to develop an efficient method for evaluating the ionic liquid catalysts used in this work.

We previously employed [bmim]Cl/AlCl₃ as a catalyst in the production of furfural from xylose in γ-valerolactone-water solvent mixture, and 80% yield of furfural was achieved from xylose. When γ-valerolactone was replaced with butanone, the furfural yield slightly decreased to 75%. Therefore, the two solvents had similar performance. However, the market price of γ-valerolactone was much higher than that of butanone. Although butanone may have some toxicity issues, it has been evaluated and listed as a green and recommended solvent. Besides, butanone-water mixture is biphasic at room temperature, which enables the low-cost extraction and separation of furfural. Hence, the proposed reaction system had great potential for the production of furfural from biomass carbohydrates.

4 | CONCLUSIONS

In this research, several ionic liquid catalysts made up of [bmim]Cl and different metal chlorides were developed for the catalytic conversion of xylose in butanone-water solvent mixture to produce furfural. After catalyst optimization, 75% yield of furfural was achieved at 140°C. [Bmim]Cl/FeCl₃ catalysts with content of [bmim]Cl and FeCl₃ were prepared by altering χ(FeCl₃), and the effects of catalyst composition on the distribution of liquid-phase products were investigated. The results indicated that FeCl₃ promoted the isomerization reaction from xylose to xylulose, while excessive amount of FeCl₃ or [bmim]Cl would result in the occurrence of side reactions. These reactions could include the cyclization of chain intermediates to form cyclohexenones and the condensation reactions between furfural and intermediates, resulting in decreased furfural yield. Comparison between various catalysts suggested that the ionic liquid catalysts developed in this work gained substantial improvement in the catalytic performance when compared with crude metal chlorides and [bmim]Cl. The main reason was that new types of anions with strong catalytic activities were formed during ionic liquid catalyst preparation. Efficient catalytic conversion of xylose with relatively low apparent activation energy was achieved by employing the catalyst with both Lewis acidity and Brønsted acidity, and the primary reaction pathway followed ring opening, isomerization, and dehydration reactions, leading to high-efficiency production of furfural. Nevertheless, in order to optimize the xylose conversion process, the catalyst composition was supposed to be further adjusted by applying an appropriate mole ratio of metal chloride to [bmim]Cl.

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CONFLICT OF INTEREST

The authors declare that they have no competing interests.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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