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Ionic liquids: Efficient solvent and medium for the transformation of renewable lignocellulose

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Received April 5, 2012; accepted May 6, 2012; published online July 13, 2012

Carbon-enriched lignocelluloses are regarded as the perfect alternative for nonrenewable fossil fuel, and have a great potential to alleviate the increasing energy crisis and climate change. However, the tightly covalent structure and strong intra and inter-molecular hydrogen bonding in lignocellulose make it high recalcitrance to transformation due to the poor solubility in water or common organic solvents. Dissolution and transformation of lignocellulose and its constituents in ionic liquids have therefore attracted much attention recently due to the tunable physical-chemical properties. Here, ionic liquids with excellent dissolving capability for biomass and its ingredients were examined. The technologies for lignocellulose biorefining in the presence of ionic liquid solvents or catalysts were also summarized. Some pertinent suggestions for the future catalytic conversion and unitization of this sustained carbon-rich resource are proposed.

ionic liquids, lignocellulose, dissolution, biorefinery

1 Introduction

Society currently has a serious dependence on a finite supply of nonrenewable fossil-fuel-based hydrocarbons, which are used in almost every synthetic material and as an energy supply in the economy. This dependence results in an increasing energy shortage, environmental pollution, unstable social and political conditions, and then harms to the health and well-being of society and ecosystems [1]. The growth in energy demand is projected to continue, and the cumulative impact of burning fossil fuels to meet this demand raises serious concerns.

Lignocellulose is a readily abundant, widely distributed, carbon-neutral sustainable resource worldwide. It has been regarded as an attractive alternative to petroleum-derived fuels and energy carriers, and has a great potential to alleviate the increasing energy crisis and green-house effect [2, 3].

Therefore, efficient transformation of lignocellulose has attracted increasing attention in the last few decades. It is well known that green biomass is composed of a tight matrix of covalently linked and hydrogen bonded carbohydrate polymers (cellulose and hemicellulose) and phenolic polymers (lignin), which results in insolubility in water and common solvents. Limited organic and inorganic hybrid solvents, such as DMAc/LiCl, DMF/N₂O₄, NMNO, DMSO/TBAF, and some molten salt hydrates such as LiClO₄·3H₂O and LiSCN·2H₂O, were reported to be promising for dissolution of cellulose. However, use of those solvents may be precluded by cost, toxicity, instability and recyclability issues [4]. Therefore, development of alternative solvents for the efficient dissolution and transformation of lignocellulose into energy carriers and value-added biochemical is necessary.

Room-temperature ionic liquids (ILs) have attracted increasing attention in many fields, including organic chemistry, electrochemistry, catalysis, physical chemistry, and engineering due to their distinctive and tunable

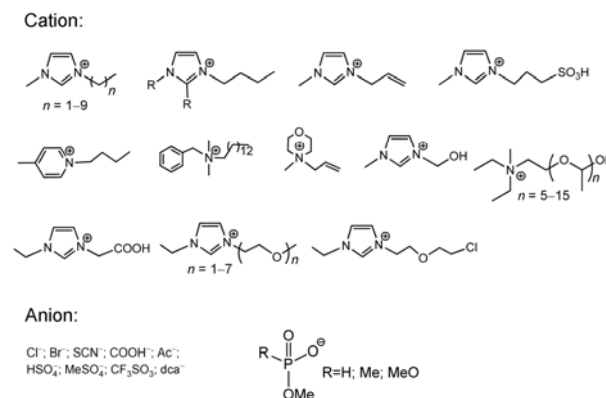
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properties [5–7]. They have been widely used in green chemistry for applications such as CO₂ capture and utilization [8–10] and the dissolution and transformation of cellulosic biomass [2]. In 2002, Rogers first reported that alkyl-imidazolium ILs can dissolve cellulose efficiently, and a solubility of 10 wt% was achieved in 1-butyl-3-methyl imidazolium chloride ([bmim]Cl) at 100 °C [11]. High-resolution ¹³C NMR characterization revealed that the polysaccharide is disordered in IL solution [12], which greatly facilitates further modification and utilization of this renewable resource. In addition, it is the most important that the dissolved cellulose can completely regenerate in water, alcohol, and acetone without a significant change in the degree of polymerization or polydispersity. Inspired by these significant findings, lots of ILs with Cl[−] and other strong hydrogen bond-accepting cations or anions such as an allyl group or −COOH have been explored and found to be excellent solvents and reaction medium for lignocellulose and its constituents [4, 13–22].

2 ILs as dissolving medium for lignocellulose

2.1 Dissolution of cellulose

Molten *N*-ethylpyridinium chloride was first suggested in 1934 to have a good capability for cellulose dissolution with the help of nitrogen containing bases [23]. Unfortunately, this finding did not arouse enough attention at the time, partly because the compound was somewhat esoteric and had a relatively high melting point. In 2002, Rogers and coworkers evaluated the solubility of cellulose in a series of alkyl-imidazolium ILs paired with different anions such as Cl^- , Br^- , SCN^- , BF_4^- and PF_6^- [11]. They found that halogen and halogen-imitating compounds exhibited good to excellent dissolving capabilities. For example, 10 wt% solubility was achieved in [bmim]Cl at 100 °C, and 25% of cellulose was dissolved under microwave heating. In contrast, ILs paired with larger and noncoordinating anions such as BF_4^- and PF_6^- did not dissolve any cellulose. The fact that anions with strong hydrogen acceptance ability can disrupt the intra and inter-molecular hydrogen bond in the covalent structure of cellulose is considered to contribute to the efficient dissolution. Further investigation demonstrated that the length of side-chain in the imidazolium cation of IL also affects its dissolution capability, as the chloride concentration can be adjusted by the length of the side chain. A sharp decrease was observed when the side chain was more than six carbons in length. It was also reported that the solubility of cellulose in 1-alkyl-3-methyl imidazolium chloride ILs is affected significantly by the odd-even effect. ILs with an even number of carbons on the side chain show much higher dissolved capability than the side chains with an odd number [24]. Inspired by these observations, a series of ILs with strong hydrogen bond acceptors (Scheme 1) were extensively explored for cellulose dissolution.



Scheme 1 ILs reported as cellulose solvents.

Zhang and co-authors [20, 21] reported that the allyl-functional IL, 1-allyl-3-methylimidazolium chloride ([Amim]Cl), is a powerful, nonderivatizing single-component solvent for cellulose. Raw cellulose material such as cotton can be dissolved in this IL rapidly with much higher solubility than in [bmim]Cl. Comparative studies of the pristine and regenerated cellulose using FT-IR, WAXD, and TGA measurements demonstrated that the crystalline form of cellulose film is completely transformed. Furthermore, this IL is thermostable, nonvolatile, and it can be easily prepared and recycled [20]. Intensive investigation demonstrated that the addition of another IL, *N*-methyl-*N*-allylmorpholine chloride ([AmMor]Cl) is able to improve the solubility of cellulose and accelerate the dissolution process significantly [25]. It is thought that the strong hydrogen bond-acceptor capability of the morpholine cation contributed to the observed effects. The hydroxide functionalized IL, 1-(2-hydroxyethyl)-3-methyl imidazolium chloride ([C₂H₄OHmim]Cl), was also proven to be a good solvent for cellulose, achieving 6.8% solubility even at 70 °C. However, this IL is thermo-unstable, and degrades when the temperature exceeds 80 °C, which largely limits its use [26]. In addition, dissolution of cellulose in carboxyl or other functionalized ILs 1-carboxymethyl-3-ethyl imidazolium chloride ([Cmeim]Cl), 1-methoxyethyl-3-ethyl imidazolium chloride ([C₂OC₁eim]Cl) and 1-[2-(2-chloroethoxy)ethyl]-3-ethylimidazolium chloride ([Cl-C₂OC₂eim]Cl) were also reported [17].

ILs based on 1-alkyl-3-methylimidazolium chloride are potential solvents for a variety of biomacromolecules. However, most of them are solids at room temperature. The requirement for higher melting temperature and the viscosity limits their use as solvents for biomass. Moreover, residual halogen in products synthesized or manufactured in chloride-containing ILs may cause problems. Recently, a series of 1,3-dialkyl imidazolium formates were produced and used for cellulose dissolution [18]. These formate ILs have significantly lower viscosity than previously reported chloride ILs. Because of the strong hydrogen bonding ability of these ILs, various polysaccharides including amylose

and cellulose can be dissolved at high concentrations under mild conditions [18]. For example, 10 wt% solubility of cellulose can be achieved at 60 °C in [Amim]COO, whereas the temperature must rise to 100 °C to obtain the same solubility in [Amim]Cl. These ILs can dissolve cellulose efficiently, but their thermostabilities are not optimal. Therefore, a series of highly thermostable alkylimidazolium salts containing dimethyl phosphate, methyl methylphosphonate, or methyl phosphonate were explored. These ILs have the potential to solubilize cellulose with good to excellent solubility under mild conditions. Especially, 1-ethyl-3-methyl imidazolium methylphosphonate enables the preparation of 10 wt% cellulose solution at 45 °C in 30 min [19].

In addition, 3-alkyl-1-methyl imidazolium salt ILs incorporating acetate, propionate, and diethylphosphate anions were also used to dissolve cellulose, and the effect of cations and anions was intensively investigated [27, 28]. Results showed that these ILs have a much better capability to dissolve cellulose than chloride salt ILs or conventional *N*-methyl-morpholine-*N*-oxide monohydrate solutions. However, one serious disadvantage of these ILs is their strong tendency to denature enzymes. This drawback prohibits transformation of the dissolved carbohydrates by enzymatic reactions. Recently, Zhao and collaborators [29] designed a series of ILs consisting of l-lysine-substituted cations paired with acetate anions that are able to dissolve carbohydrates but do not considerably inactivate the immobilized lipase B from *Candida antarctica*. The hydrogen-bond forming anions, oxygen-containing cations, and low cation bulkiness promote carbohydrate dissolution (more than 10 wt% of cellulose), while the low anion concentration appears to stabilize enzymes.

2-H on the imidazolium ring also has a remarkable effect on the dissolution of cellulose [28, 30]. For example, 1-butyl-2,3-dimethyl imidazolium chloride salt ([bDmim]Cl) and 1-allyl-2,3-dimethyl imidazolium bromine ([ADmim]Br) are less efficient than [bmim]Cl and [Amim]Br, respectively [30]. Compared with imidazolium salts, pyridinium-based ILs are much more efficient [31, 32]. For example, more than 39% of Avicel cellulose can be dissolved in 3-methyl-*N*-butylpyridinium chloride ([bmPy]Cl), whereas 18% solubility was achieved in [bmim]Cl at the same condition.

It has long been recognized that water is one of the most important barriers for cellulose dissolution in ILs. Cellulose solubility decreases sharply when the water content is more than 0.1872 g H₂O/g [bmim]Cl at 95 °C [33]. Unfortunately, cellulose hydrolysis is an essential step to obtain oligo- or mono-saccharides for energy generation. Natural biomass also contains a considerable amount of water. It is therefore difficult to satisfy these conflicting requirements. To overcome this problem, Ohno and his co-authors [34] reported that ILs containing hydroxide anions may be a promising alternative. They found that tetrabutylphosphonium hydroxides (TBPH) containing 30–50 wt% water dissolve

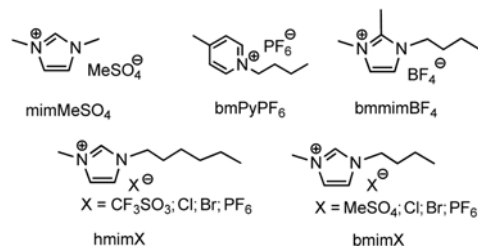
cellulose rapidly at ambient temperature. In particular, TBPH containing 40 wt% of water has great capability to dissolve cellulose, and a final concentration of 20 wt% of cellulose can be obtained within 5 min with mild stirring at 25 °C. Interestingly, with either higher (60%) or lower (10%) water content, cellulose was not soluble.

In brief, ILs are good solvents for cellulose. However, the high cost, relatively low efficacy, lower rate of dissolution, and the high viscosity of the solutions obtained cannot be neglected. Thus, advances towards improved processes for the dissolution of cellulose are still necessary. Recently, Rinaldi found that organic electrolyte solutions, which contain just a small molar fraction of IL, instantaneously dissolve large amounts of cellulose, yielding a much less viscous solution than when a single IL is used [35]. Furthermore, the author suggested that, in order to reduce the amount of IL required in the solvent system, both the molecular solvent and the IL should have high hydrogen bond basicity. In addition, to avoid the competition between the molecular solvent and cellulose for the hydrogen bond basicity of the IL, the molecular solvents should preferably show no hydrogen bond acidity.

2.2 Dissolution of lignin

Lignin, the amorphous, three-dimensional heteropolymer composed of phenylpropanoid units, is one of the main ingredients of lignocellulose, accounting for 15%–30% by weight and 40% by energy [36]. It is also produced on the scale of millions of metric tons per year as a byproduct of the pulp and paper industry, where about 98% is incinerated for energy recovery [37], resulting not only in resource waste but also in air pollution. However, it is much more recalcitrant to being dissolved and transformed due to its tight aromatic covalent structure. For example, the widely used cellulose solvent [bmim]Cl can dissolve more than 10 wt% of cellulose at 100 °C, while only 1.4% to 3.0% lignin solubility is achieved even at 130 °C [38].

Pu and his co-workers [16] used a series of anion functionalized ILs (Scheme 2) containing strong hydrogen bond acceptors as aprotic, green solvents for lignin isolated from pine pulp. Up to 20 wt% lignin could be dissolved in [hmim][CF₃SO₃], [mmim][MeSO₄], and [bmim][MeSO₄]. For the 1-butyl-3-methylimidazolium ILs, the order of lignin solubility for varying anions is as follows: MeSO₄[−] >



Scheme 2 ILs for lignin dissolution.

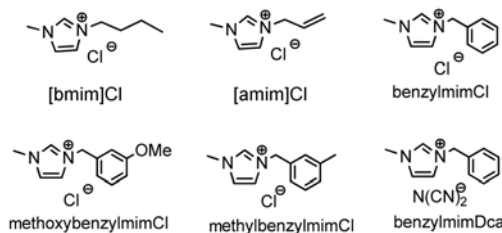
$\text{Cl}^- > \text{Br}^- \gg \text{PF}_6^-$, which indicates that the solubility of lignin is principally influenced by the nature of the anions. ILs containing the large, non-coordinating anions BF_4^- and PF_6^- were unsuitable as a solvent for lignin. It is in good agreement with the dissolution of cellulose in IL [11].

Based on the fact that sodium xylenesulfonate is an efficient reagent for hydrotropic pulping of lignocellulose, Tan and co-authors [39] reported an IL mixture containing a 1-ethyl-3-methylimidazolium cation and a mixture of alkylbenzenesulfonates with xylenesulfonate as the main anion as an efficient extraction solvent for bagasse lignin at atmospheric pressure and elevated temperature. Dissolved lignin can be recovered from the IL by precipitation, allowing the IL to be recycled. An extraction yield exceeding 93% was attained. Compared with conventional lignin extraction methods, this IL system has several advantages, including reaction at atmospheric pressure, no emission of toxic or odorous gases, capacity for recycling the IL, no requirement for prolonged drying of material, and the ability to produce lignin with particular functional groups. Recently, a class of food-additive derived ILs (with acesulfamate anions) with excellent dissolution abilities for natural lignin was reported [40]. Interestingly, these ILs can efficiently dissolve lignin, but not wood cellulose.

2.3 Dissolution of natural lignocellulose

The application of ILs for dissolution of lignocelluloses has also been examined intensively. Based on its excellent capability to dissolve cellulose, IL [bmim]Cl was used to dissolve natural lignocelluloses and to separate its constituents. Cellulose from hardwoods including poplar, eucalyptus, and oak can be extracted efficiently. Spectroscopic and thermogravimetric studies indicate that polysaccharides obtained in this manner are virtually free of lignin and have characteristics of pure cellulose samples that have been subjected to similar processing conditions [11]. Further investigation showed that both carbohydrate and lignin can be dissolved in the IL completely at 110 °C for 16 h [41]. This is the first reported study describing the dissolution of all components of lignocellulose in IL, making the comprehensive utilization of this renewable resource more feasible. Recently, Li *et al.* found that this complete dissolution of lignocellulose can be accelerated at temperatures above the glass transition of lignin (185 °C for 15 min) [42].

Argyropoulos and co-authors [43] reported that both hardwoods and softwoods such as Norway spruce, Southern pine, and their thermomechanical pulp fibers are readily soluble in various imidazolium-based chloride ILs functionalized by strong hydrogen bond acceptors such as aromatic rings and allyl groups (Scheme 3) between 80 and 130 °C in 8 to 13 hours. They found that the solubility of biomass is highly dependent on the particle size and moisture of the wood sample, with particle size as the dominant factor. These observations were further supported by analyzing



Scheme 3 Imidazolium-based chloride ILs for wood dissolution.

lignin phenolics and wood in the imidazolium chloride-based ILs [Amim]Cl and [bnmim]Cl by labeling hydroxyl groups as phosphite esters using quantitative ^{31}P NMR [44].

The biodegradable IL 1-ethyl-3-methylimidazolium glycinate was also capable of completely dissolving biomass [45]. The regenerated biomass from this system in a reconstitution solvent (acetone/water) was found to have a more homogenous macrostructure, which indicates that the crystalline form and structure of the cellulose changed from type I to type II during the dissolution and regeneration process.

As shown above, ILs can dissolve lignocellulose and/or its constituents efficiently. However, most of the current systems required relatively higher temperatures (> 100 °C), which demands greater energy input. From the viewpoint of energy conservation, the total energy used in the process of biomass treatment is significant and important. Ohno *et al.* found that some polar ILs with 1-methyl-3-alkyl incorporating methyl phosphonate can extract carbohydrate efficiently without any heating [46]. This offers a beneficial approach for the further investigation and use of ILs in biomass treatment.

Many ILs were identified early as potential solvents for the dissolution of (ligno-)cellulose. However, due to their multitude and high costs, a method for high-throughput screening on a small scale is essential to determine the most efficient IL. Zavrel [47] recently explored two high-throughput systems based on extinction or scattered light measurements. The quasi-continuous dissolution profiles allow a direct comparison of up to 96 ILs per experiment in terms of their dissolution kinetics. The screening results indicate that among the ILs tested, [emim]Ac is the most efficient for dissolving cellulose, while [Amim]Cl is the most effective IL for dissolving wood chips.

2.4 Dissolution mechanism

As shown above and in many other studies, renewable biomass can be dissolved in ILs efficiently, which facilitates its utilization. The mechanisms for this efficient dissolution have been examined intensively. For example, the reason for the high dissolution capability of 1-alkyl-3-methylimidazolium chloride salt can be attributed to the strong hydrogen-bond accepting ability of Cl^- , which is highly

efficient in breaking the extensive hydrogen bonding network of cellulose [11]. This mechanism is further confirmed by relaxation measurements of the IL ^{13}C and $^{35/37}\text{Cl}$ nuclei spectra [48] and molecular dynamics simulations [49]. The powerful capacity of other IL to act as solvents for biomass can also be attributed to the strong hydrogen basicity of functionalized cations and/or anions. However, the study of Lindman [50] recently showed that this hydrogen bonding is unable to entirely explain the phenomenon. The ability of significantly amphiphilic ILs with excellent cosolutes to weaken hydrophobic interactions between the solvent and cellulose also contributes. Van Spronsen [51] also found that the hydrolysis of lignocelluloses in ILs occurs prior to the dissolution of their ingredients (lignin, hemicelluloses, and cellulose), and this process can be accelerated significantly by the addition of an organic acid such as acetic acid.

3 ILs as medium for the transformation of biomass

Sustainable lignocellulosic biomass, the most abundant, carbon-neutral, and cost-effective resource for replacement of fossil fuels, is a promising material for production of industrial chemicals due to its fundamental composition of C, H, and O. These elements are dominant in the organic chemical and petro-chemical industry. Biorefineries of lignocellulose therefore have great significance. In particular, the findings that biomass and/or its constituents can be dissolved in ILs establish a path from biomass to biofuel/biochemical, overcoming a major barrier in the utilization of biomass. Biorefinery processes such as hydrolysis, enzymatic hydrolysis, and conversion to useful biochemical in ILs have been investigated extensively.

3.1 Hydrolysis

Hydrolysis of cellulose to fermentable sugars is the crucial step in the production of high heating-value biofuel and/or useful biochemicals from biomass. Cellulose and biomass dissolved in ILs leaves the cellulose chains much more accessible to chemical transformations, which results in much gentler reaction conditions. In 2007, Zhao *et al.* [52] demonstrated, for the first time, that dissolved non-pretreated cellulose in [bmim]Cl can be hydrolyzed efficiently by H_2SO_4 and other mineral acids at a relatively lower temperature under atmospheric pressure. Of the total reducing sugar (TSR) yield, 62% to 77% was obtained at 100 °C for no more than 45 min. This result is equal to or higher than that of the traditional hydrolysis process at a higher temperature using concentrated H_2SO_4 . The catalytic hydrolysis of original biomass pre-dissolved in IL paired with different hydrogen bond accepting anions was further investigated [53]. TRS yields were up to 66%, 68%, 74%,

and 81% for hydrolysis of corn stalk, bagasse, rice straw, and pine wood, respectively. In addition, FT-IR spectra and elemental analysis of recovered residues indicated that modification of lignin occurred during sulfuric acid catalyzed hydrolysis. Moreover, chitosan, which has a similar molecular structure as cellulose, can also be hydrolyzed efficiently in the above IL-mineral acid catalytic system, with 63% conversion to TRS, facilitated by [bmim]Cl and 6 wt% HCl [54].

Proton acid is the most vigorous catalyst for the hydrolysis of lignocellulose and/or its constituents. However, its corrosiveness and the difficulties of production and recycling limit its large-scale application. Solid acid has therefore been considered. It has been reported that acidic resins with relatively large pores are highly suitable catalysts for the depolymerization of cellulose in IL [bmim]Cl. Compared with traditional mineral acid catalytic hydrolysis, this process is much more selective; cellulose is selectively converted to cello-oligomers, an ideal entry point into advanced value chains for biorefineries [55, 56]. Subsequent investigations found that the process is also strongly temperature-dependent though the amount of catalyst positively affects the depolymerization rate [57].

Task-specific IL catalysts, which are widely used in organic chemistry [5, 6], were also tested for hydrolysis of cellulose and lignocellulose. For example, Bao [58] found that up to 95% of the TRS yield can be obtained from the catalytic hydrolysis of cellulose when IL [bmim]Cl was used as the solvent and the acid IL 1-butyl sulfonic acid-3-methylimidazolium chloride ($[\text{C}_4\text{H}_8\text{SO}_3\text{Hmim}]\text{Cl}$) acted as the catalyst with dimethylformamide as a co-solvent. Recently, the catalytic capability of a series of acid ILs such as carboxylic and sulfonic IL for cellulose hydrolysis in [bmim]Cl under gentle conditions was also examined. All acid ILs examined showed good to excellent catalytic performance, and ^{13}C NMR characterization results confirmed that glucose is the majority product [59].

3.2 Enzymatic hydrolysis in ILs

Enzymatic hydrolysis is another efficient approach for lignocellulose utilization. Compared with chemical catalytic processes, enzymatic hydrolysis is efficient, gentle, and selective. However, most of the raw materials need to be pretreated. Due to its excellent dissolution capability for lignocellulose, ILs are recognized as one of the primary pretreatment solvents [60–62].

IL 1-ethyl-3-methyl imidazolium diethyl phosphate ([emim]DEP) was proven to be an excellent cellulose pretreatment reagent owing to its low viscosity, the potential for accelerating enzymatic hydrolysis, and recyclability [63]. Regenerated wheat straw from this IL was hydrolyzed more easily than that treated with water. A TRS yield of 54.8% was achieved when wheat straw was pretreated at 130 °C for 30 min followed by enzymatic hydrolysis for another 12

h. It was also reported that IL [emim]Ac was a good pretreatment solvent for the enzymatic hydrolysis of wood flour. In the pretreatment process, cellulose became far less crystalline without undergoing solubilization and lignin can be removed thoroughly, resulting in more than 90% of the cellulose hydrolyzed [60].

Enzymatic hydrolysis of renewable lignocellulose to sugar is also highly efficient. However, its high cost would be one of the dominant barriers towards the development of economically competitive biorefineries. A high-throughput screening method for IL solvent may be one of the answers for this problem. Conventional biomass enzyme assays are typically labor-intensive and time-consuming, requiring relatively large amounts of enzymes, substrates, and other reagents. Recently, Bharadwaj *et al.* [64] found that a microplate-based high-throughput enzyme-screening platform for IL-pretreated lignocellulose is efficient and cost-effective, allowing the integration of biomass regeneration, washing, saccharification, and imaging steps in a single microtiter plate.

3.3 Transformation for platform chemicals in ILs

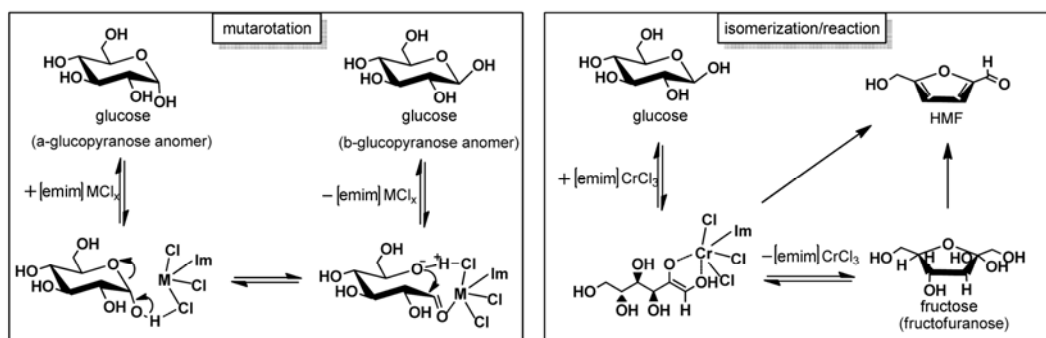
In addition to the catalytic hydrolysis to TRS and glucose, catalytic transformation of sustainable lignocellulose dissolved in ILs to typical value-added platform chemicals such as furfural and its derivatives, 5-hydroxymethylfurfural (HMF) and levulinic acid, was examined extensively. HMF, which is generally obtained from the dehydration of fructose, is considered as a key biorenewable platform molecule and an important intermediate for synthesis of fine chemicals. However, the selective transformation of glucose, the dominant sugar in cellulosic biomass, remains a challenge. In 2007, Zhao *et al.* [65] first reported a 70% yield of HMF from glucose in [emim]Cl with CrCl_2 as catalyst. They considered that a novel catalytically active compound [emim] CrCl_3 was formed during the dehydration. The CrCl_3^- anion plays a role in proton transfer, facilitating the mutarotation of glucose in IL which leads to the isomerization of glucose to fructose is responsible for the high selective yield (Scheme 4). This mechanism was further confirmed by Pidko through the combination of kinetic experiments, *in*

situ X-ray absorption spectroscopy (XAS), and density functional theory (DFT) calculations [66].

Yong [67] also showed that *N*-heterocyclic carbene/ CrCl_x was an efficient catalyst for the conversion of both fructose and glucose to HMF in [bmim]Cl, with 81% to 96% yields. Binder and Raines [68] reported that cellulose and lignocelluloses such as corn stover were converted preferentially to HMF in IL [bmim]Cl while *N,N*-dimethylacetamide and LiCl were applied as co-solvents in the presence of a mineral acid catalyst. Production of the platform chemicals HMF and furfural from other lignocellulosic biomass such as corn stalk, rice straw, and pine wood in IL solvent was also studied in the presence of CrCl_3 under microwave irradiation [69]. Recently, the catalytic activity of a series of metal chlorides in [emim]Cl for the transformation of cellulose and reed straw was tested in a high-throughput screening method. The combination of CrCl_2 and RuCl_3 was found to be the most efficient, with a 60% yield of HMF obtained [70].

The above transformation processes for lignocelluloses in the presence of ILs are powerful and selective. However, IL solvents in most of the current work have been over-used for the initial complete dissolution of feedstock, resulting in low reactor efficiency due to the limited solubility of biomass in ILs. The use of a heterogeneous catalyst is propitious for the subsequent separation process, but a lower reaction activity caused by restricted contact between the catalyst and the biomass is an important barrier for transformation processes with heterogeneous catalysts. Other disadvantages include the use of inorganic salts and water. Inorganic salts may present difficulties for post separation and purification, while water is a major problem for the dissolution of lignocellulose in IL, which is necessary in current biomass conversion systems and cannot be neglected.

Previously, an efficient and greener catalytic system for the liquefaction of bagasse, one of the abundant and widely available agricultural residues containing lignocellulose, using IL as catalyst and subcritical water as solvent had been developed [71]. This liquefaction system was powerful and highly selective, but the reaction temperature is relatively high. Recently, a novel and efficient system using



Scheme 4 Proposed mechanism for catalytic conversion of glucose to HMF.

cooperative IL pairs was successfully constructed [72, 73]. This system is composed of an IL solvent for the dissolution of biomass or its constituents and another acid IL catalyst. It is very interesting that commercial microcrystalline cellulose can be selectively degraded with high efficiency to value-added biochemical under mild conditions. Cellulose in ILs was selectively converted into 2-(diethoxymethyl) furan and other useful biochemical due to the dissolution and *in situ* catalysis mechanism [72]. The decomposition temperature of cellulose dissolved in IL was far lower than the temperature for untreated cellulose, as determined by TG analysis [73]. Our recent investigation of the performance of the system with natural lignocelluloses confirmed that this environmental benign procedure is highly efficient not only for transformation of lignocellulose but also for its delignification [74].

In additional, efficient catalytic conversion of cellulose into biodegradable surfactants, synthesis of cellulose furoates, and hydroxyalkylation of cellulose facilitated by IL were also reported, and excellent results were achieved [75–77].

3.4 Separation and recycling of IL

The dissolution of lignocellulose and/or its constituents in IL is a novel and efficient approach for the utilization of this renewable carbon resource. However, biomass-dissolving ILs and products such as sugar monomers and smaller carbohydrate oligomers are all soluble in water. This complicates the recovery and recycling of the IL and products. Recently, a solvent extraction technique, based on the chemical affinity of boronates such as phenylboronic acid and naphthalene-2-boronic acid for sugars, was applied to the extraction of glucose, xylose, and cellobiose from aqueous mixtures of [emim]Ac. Up to 90% of mono- and disaccharides were extracted [78]. Shill *et al.* [79] also reported that IL can be recycled efficiently through the addition of kosmotropic phosphates such as K_3PO_4 and K_2HPO_4 . These studies speed remarkably the industrial application of IL and the transformation of renewable biomass.

4 Summary and outlook

ILs with strong hydrogen bond acceptors have proven to be excellent solvents for lignocellulose and/or its components. These findings successfully bridge the big gap between biomass and biofuel/biochemicals and overcome a major barrier in utilization of sustainable carbon resources. Some powerful biorefinery approaches such as catalytic hydrolysis, enzymatic hydrolysis, modification and transformation for platform chemicals under mild reaction conditions have become more feasible. However, some challenges remain.

(1) The solubility of lignocellulose, particularly of lignin, is still low. This is also the reason that little research focuses

on the transformation of lignin in IL. Nonetheless, as one of main ingredients of biomass, lignin is considered to be the perfect renewable starting material for aromatic chemicals. Exploration of much more powerful IL solvents for lignin and natural biomass without pretreatment is therefore of great significance.

(2) The current efficiency of reactors is relatively low, which is partly due to the limited capability of IL solvents to dissolve cellulosic biomass. Presently, most of the biorefinery systems need to dissolve biomass and/or its constituents preceded may also contribute to the low reactor efficiency. Technologies for simultaneous dissolution and *in situ* catalytic transformation are therefore highly desirable.

(3) The accurate mechanism for both dissolution and catalytic conversion must be investigated further.

Additionally, the current high cost of ILs requires development of novel, simple, and efficient approaches for the recovery and recycling of ILs for commercial use in biomass pretreatment and refining.

The authors gratefully acknowledge the financial support of the National Natural Science Foundation of China (20876055, 21076085), the Natural Science Foundation of Guangdong Province (S2011020001472), and the Fundamental Research Funds for the Central Universities, SCUT.

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