



# Catalytic transformation of carbohydrates and lignin in ionic liquids

Z. Conrad Zhang\*

Ionic liquids with anions of strong hydrogen-bond basicity have been broadly reported in the literature as effective solvents for the dissolution of the components of lignocellulosic biomass. The key attributes of various ionic liquids are reviewed with a focus on their structural and functional properties related to biomass dissolution capacity. A number of the most studied ionic liquids with high solubility for cellulose and lignin have often been found not suited for catalytic conversions of these biomass components. Metal chlorides in chloride-based ionic liquids are robust catalyst systems for efficient cellulose and lignin conversions. Emerging leads in the literature related to the use of ionic liquids for catalytic conversions of cellulose, cellulosic carbohydrates, and lignin are discussed. © 2013 John Wiley & Sons, Ltd.

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## INTRODUCTION

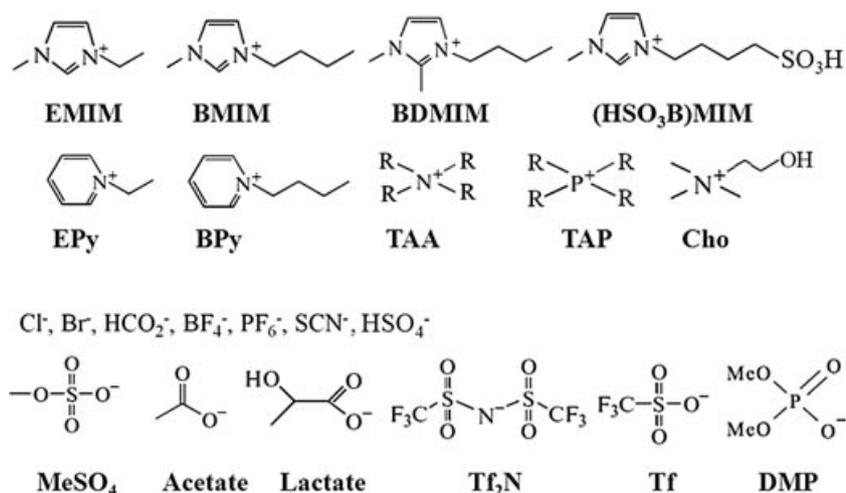
Lignocellulosic biomass such as agricultural residues, grasses, trees, and algae are highly abundant renewable feedstocks for the production of fuels and chemicals.<sup>1</sup> After decades of research and development in integrated biocatalytic fermentation processes in aqueous phase, conversion of lignocellulosic biomass based on such a technology platform still faces multiple challenges.<sup>2</sup> Thermocatalytic processes for cellulosic biomass conversion offer potential technology platforms as a wide set of operating conditions such as temperature and pH can be used along with flexibility in the choice of processing media. The main organic compositions of lignocellulosic biomass are dominated by cellulose, hemicellulose, and lignin. Because these polymeric components of lignocellulosic biomass are all solids that are nonmelting before decomposition and/or charring, a solvent is essential to provide a suitable medium for controlled depolymerization followed by conversion of these biomass components, and for stabilization of the products. Aqueous phase, known to have low

solubility for cellulose polymers, has been used for the conversion of cellulose to specific products; the process is typically accelerated to a limited extent by Brønsted acidity.<sup>3–10</sup> Recently, in recognition of certain types of ionic liquids having superior solvency in dissolution of cellulose and lignin polymers,<sup>11–14</sup> these ionic liquids have been extensively studied as solvents for dissolution of lignocellulosic biomass as well as reaction media for catalytic conversion of the dissolved polymers.<sup>15–18</sup> In this paper, recent progresses in the discovery and fundamental understanding of certain ionic liquids for lignocellulosic biomass dissolution and of catalytic conversion of dissolved biomass in the ionic liquids are reviewed and discussed.

## IONIC LIQUIDS

Ionic liquids are defined for those salts as having melting points near or below 100°C.<sup>19,20</sup> Typical attractive physicochemical properties of many ionic liquids for catalytic applications are their low vapor pressure, good thermal stability in moderate temperature range suited for typical catalysis, a wide selection of available cations and anions for desired solvency ranging from hydrophobic through hydrophilic properties, and the possibility to allow for recovery of products and reuse of the ionic liquids.<sup>21,22</sup>

\*Correspondence to: zczhang@yahoo.com  
KiOR Inc., Pasadena, TX, USA  
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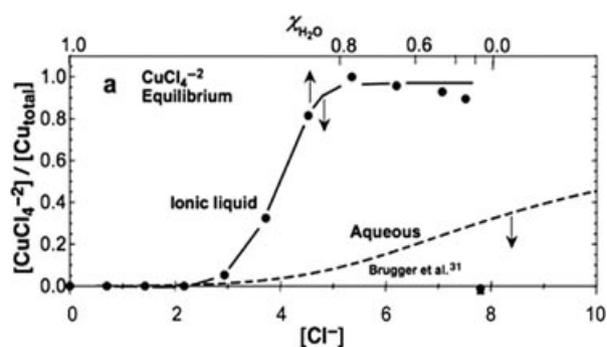
**FIGURE 1** | Structures of typical ionic liquids covered in this chapter.

A great number of ionic liquids have been evaluated for the dissolution of various biomass components under a wide range of conditions.<sup>14</sup> The cations and anions of most studied ionic liquids are shown in Figure 1. When a cation and an anion are paired in the selection of an ionic liquid suited for cellulose dissolution and/or conversion, the chosen ionic liquids should be able to first disrupt the hydrogen bonding of crystalline cellulose. Other solvents or modified solvents, such as N-methylmorpholine N-oxide,<sup>23</sup> NaOH/urea,<sup>24</sup> lithium chloride (LiCl)/dimethylacetamide,<sup>25</sup> have also been shown to be capable of dissolving cellulose. However, their direct application as solvents for cellulose conversion has been limited. Therefore, they are outside the scope of this paper.

Mixed solvents or ionic liquids, although appearing in only a limited number of publications, have also been studied for optimized biomass dissolution and conversion efficiency, for example, choline acetate, [Ch]Ac), tributylmethylammonium chloride, [TBMA]Cl,<sup>26</sup> and dimethylacetamide -lithium chloride (DMA -LiCl) -1-ethyl-3-methylimidazolium chloride ([EMIM]Cl).<sup>27</sup>

Following the original work in which metal chlorides, particularly Cr(II, III) chlorides, were reported to be efficient catalysts for carbohydrate conversions in ionic liquid solvents,<sup>28</sup> many researchers have broadly investigated metal chlorides in numerous functionalized ionic liquids under a wide range of reaction conditions for catalytic conversion of glucose and cellulose.<sup>29</sup>

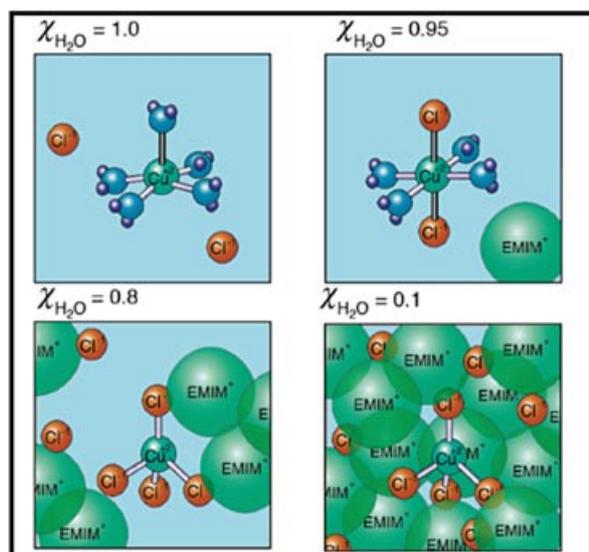
Some ionic liquids not only have unique solvent properties as pure liquids, but also remarkably change the properties of other solvents even as a minor component in the mixed solvent. Such modified



**FIGURE 2** | Mole fraction of the total Cu in the tetrahedral  $\text{CuCl}_4^{2-}$  form as a function of the  $[\text{Cl}^-]$  lower axis (M) or  $\chi_{\text{H}_2\text{O}}$  (upper axis, water mole fraction). (Reproduced with permission from Ref 30. Copyright 2010, American Chemical Society.)

solvent properties of mixed solvent consisting of ionic liquid and water ( $\text{H}_2\text{O}$ ), for example, appear to be responsible for some unique catalytic performance in cellulosic biomass conversion.

In the mixed solvents of [EMIM]Cl and  $\text{H}_2\text{O}$  with added LiCl in appropriate amount to adjust the total chloride concentration, the presence of [EMIM]Cl, even in minor proportion with respect to  $\text{H}_2\text{O}$ , drastically changed the coordination chemistry of metal chloride from what one would expect from pure  $\text{H}_2\text{O}$ .<sup>30</sup> In this study involving 0.035 M dissolved  $\text{CuCl}_2$  in mixtures of  $\text{H}_2\text{O}$  and [EMIM]Cl, the fraction of Cu ions present in  $\text{CuCl}_4^{2-}$  ion as a function of  $[\text{Cl}^-]$ , as followed by UV-VIS spectroscopy and X-ray absorption spectroscopy, showed considerable deviation from the curve in  $\text{H}_2\text{O}$ -only solvent (Figure 2). The fraction of total Cu that is  $\text{CuCl}_4^{2-}$  varies as a function of the  $[\text{Cl}^-]$  and the mole fraction of  $\text{H}_2\text{O}$  in the ionic liquid. Just above 5 M  $\text{Cl}^-$  concentration and near 80 wt%  $\text{H}_2\text{O}$ , the  $\text{Cu}^{2+}$  is



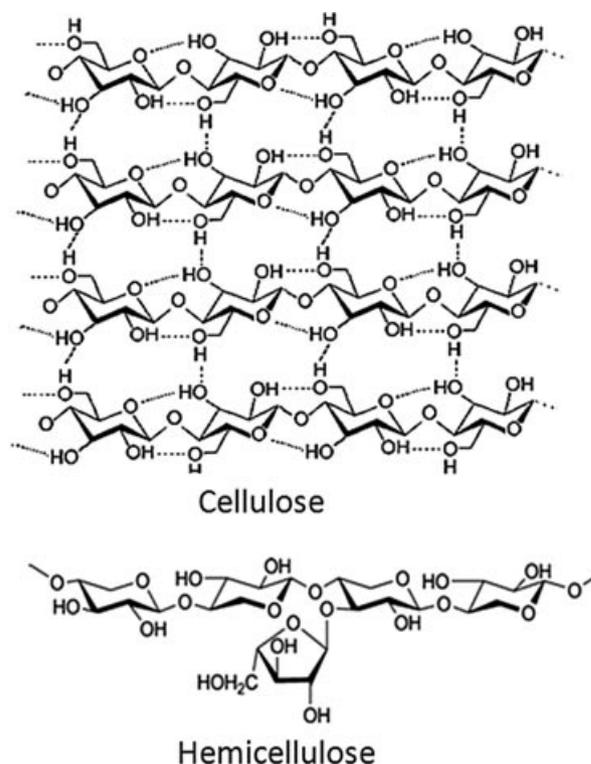
**FIGURE 3** | Schematic of various cation–anion structures in ionic liquid–water mixture for various mole fractions of water as indicated. (Reproduced with permission from Ref 30. Copyright 2010, American Chemical Society.)

completely in  $\text{CuCl}_4^{2-}$  coordination. In contrast, the mole fraction of  $\text{CuCl}_4^{2-}$  species that exist in aqueous solution containing the simple salt,  $\text{LiCl}$ , is considerably less.<sup>31</sup> In the mixed ionic liquid– $\text{H}_2\text{O}$  system, 50% of the  $\text{Cu}$  exists as  $\text{CuCl}_4^{2-}$  species for a total  $[\text{Cl}^-] = 4 \text{ M}$  (50 wt%  $\text{H}_2\text{O}$ ), whereas for the aqueous system only, about 3% of  $\text{Cu}$  is in this form. Therefore, it can be concluded that in the mixed  $[\text{EMIM}]\text{Cl}$  ionic liquid and  $\text{H}_2\text{O}$  solvents, metal ions are unproportionally favored in the polychlorinated forms because of the presence of  $[\text{EMIM}]\text{Cl}$ . The results on the effect of  $[\text{EMIM}]\text{Cl}$ , expressed as the fraction of  $\text{H}_2\text{O}$  in the mixed solvents, are illustrated in Figure 3. In the catalytic conversion of cellulose, hemicellulose, and lignin in ionic liquids, hydrolytic cleavage of these polymeric compositions of biomass is a critical step.  $\text{H}_2\text{O}$  is usually added together with catalysts to ionic liquid solvents to enable the hydrolysis reaction. The results in Figure 2 therefore indicate that hydration of metal ions as a result of metal chlorides hydrolysis, usual in aqueous media, is significantly restricted because the amount of  $\text{H}_2\text{O}$  added to promote biomass hydrolytic cleavage is usually in small concentrations relative to the amount of ionic liquids used.

## STRUCTURES AND PROPERTIES OF BIOMASS POLYMERS

### Cellulose

The chemical structure of cellulose is made of a polymer of anhydroglucose linearly linked by (1,4)- $\beta$ -D-



**FIGURE 4** | Two-dimensional schematic of cellulose and hemicellulose structures.

glucosidic bonds. The degree of polymerization (DP) is measured by the number of molecular glucose units in a polymer. An extensive network of such polymer chains in ordered alignment via hydrogen bonding<sup>32</sup> and van der Waals forces<sup>33</sup> results in a supramolecular cellulose structure, but with varied size, crystallinity, and complexity, depending on the type of biomass. A schematic two-dimensional structure of crystalline cellulose is shown in Figure 4. Decrystallization and hydrolytic depolymerization to glucose are mechanistically two separate steps prior to rendering crystalline cellulose into usable monosaccharide, whether for biocatalytic fermentations or for thermocatalytic processing. In most studied aqueous systems, because cellulose has little solubility, hydrolysis of bulk cellulose typically involves hydrolytic fragmentation to reduce the DP followed by continued hydrolysis to monosaccharide or glucose. Two heavily studied cellulose depolymerization processes in aqueous systems involve either multiple enzymes<sup>34</sup> or strong mineral acids<sup>35</sup> as catalysts. However, progress has been limited in part because of the lack of solubility of cellulose in  $\text{H}_2\text{O}$ .<sup>36</sup> Enzymatic hydrolysis of cellulose is typically slow and the rate is also inhibited by contaminants originating from other biomass components. A rather high temperature (180–230°C) is needed to obtain an acceptable rate of cellulose

hydrolysis using only a dilute mineral acid.<sup>37</sup> Degradation of the resulting glucose becomes an issue at this temperature.

Decrystallization is a process of disrupting the intermolecular hydrogen bonding (H-bonding) between cellulose polymers. It is a process of replacing saccharide-hydroxyl-based H-bonding with stronger H-bonding partners. Even though mineral acids are strong acids that are capable of forming stronger H-bonding with saccharides, the lack of cellulose solubility in H<sub>2</sub>O (even in strong acidic aqueous media) limits the rate of decrystallization of cellulose. When pure liquid trifluoroacetic acid was studied for cellulose decrystallization, it was found that the rate of cellulose decrystallization was accelerated with decreasing temperature.<sup>38</sup> At higher temperatures (above 25°C), trifluoroacetic acid is very reactive for esterification with hydroxyl groups on the surface of crystalline cellulose. As the temperature reaches below 0°C, dimers of trifluoroacetic acid become prevalent. These dimers are not reactive but are capable of penetrating the cellulose structure and forming H-bonds, resulting in complete decrystallization in 10 min. Certain ionic liquids discussed in this paper essentially play the same role of decrystallization. After decrystallization, dissolved cellulose polymers are exposed to catalysts in the liquid media for hydrolytic cleavage, leading to glucose. The function of catalysts then determines the end products. In a number of reported studies on catalytic cellulose conversions, the ionic liquids were functionalized to accelerate the hydrolysis of cellulose polymers.

## Hemicellulose

Hemicellulose is composed of branched-chain polysaccharides containing pentose and hexose monosaccharide building units such as xylose (C5), arabinose (C5), galactose (C6) and mannose (C6), plus glucuronic and galacturonic acids. A simplified structure of hemicellulose is shown in Figure 4. Hemicellulose has a random and amorphous structure. It is the weakest component of lignocellulosic biomass to degrade in acid or in alkaline solutions or even in hot H<sub>2</sub>O. Xylose is the dominant pentose monosaccharide of hemicellulose. Barks, twigs, and leaves of woody biomass have the highest content of hemicellulose, in amounts that are more than doubled that of cellulose content in these sources of biomass.<sup>39</sup>

## Lignin

Lignin is a natural polymer with an amorphous three-dimensional structure. Because the structure of lignin

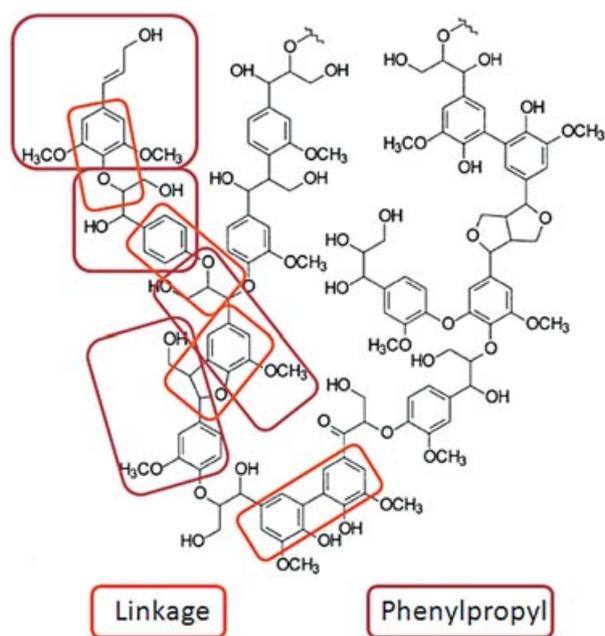


FIGURE 5 | Two-dimensional schematic of lignin structure.

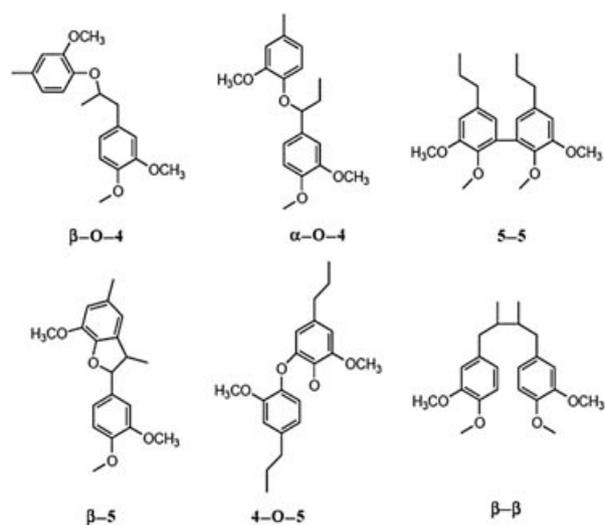


FIGURE 6 | Common linkages between phenylpropane units in lignin. (Reproduced with permission from Ref 41. Copyright 2004, Elsevier.)

has only been poorly characterized, it is typically described in models of random compositions of more reliable structural fragments. Figure 5 shows a structure of lignin, dominated by phenylpropane monomer unit primarily linked by C–O linkage of  $\alpha$ - and  $\beta$ -ether bonds.<sup>40</sup> The  $\beta$ -O-4 linkage is found to be dominant, representing approximately 50% among all the linkages in lignin, as shown in Figure 6.<sup>41,42</sup> Lignin is also highly branched and substituted polyaromatic polymers.

High-molecular-weight lignin is insoluble in sulfuric acid ( $\text{H}_2\text{SO}_4$ ), whereas low-molecular-weight lignin is considered as acid soluble.<sup>43</sup> Degradation of lignin takes place in heated alkaline solution.<sup>44</sup>

## CHARACTERISTIC ATTRIBUTES OF IONIC LIQUIDS FOR DISSOLUTION OF CELLULOSE, HEMICELLULOSE, AND LIGNIN

The mechanism of cellulose dissolution in certain ionic liquids has been established and is generally attributed to electronic properties of the anions of the ionic liquids with a strong H-bonding basicity. For example, the H-bonds are formed between the chloride anions of ionic liquids and the hydroxyl groups of the carbohydrates, in near stoichiometric ratios.<sup>45</sup>

Many reported works on this subject are particularly focused on the solubility of biomass components in specific ionic liquids and the process to reconstitute biomass components from the ionic liquids.<sup>14</sup> This is a potential strategy to fractionate biomass components so that cellulosic carbohydrates could be purified for biocatalytic processing. The results from such studies provide useful guidance in selecting ionic liquids. However, when ionic liquids are also used as catalytic reaction media after dissolution of the biomass components, additional requirements have to be met, including the stability of the ionic liquids in the presence of catalysts and under specific reaction conditions. In some cases, reactions between certain ionic liquids with biomass substrates can also take place.

### Dissolution of Cellulose in Ionic Liquids

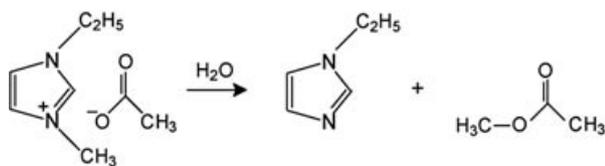
After dissolution of cellulose in ionic liquids, adding a solvent such as acetone, deionized  $\text{H}_2\text{O}$ , or alcohol causes precipitation leading to regeneration of the cellulose. The added solvent is called an antisolvent in this process.<sup>46,47</sup> Cellulose regenerated from ionic liquids is essentially amorphous and porous, and more prone to cellulose saccharification, although presence of a higher concentration of anions from ionic liquids can deactivate enzymes.<sup>48</sup>

For dissolution of cellulose in ionic liquids, the reported literature results can be summarized in the following list of key attributes:

1. With increasing alkyl chain length from C2 to C10 of 1-alkyl-3-methylimidazolium chloride, the solubility of cellulose decreases.<sup>49</sup> Cellulose is more soluble

in 1-alkyl-3-methylimidazolium-based ionic liquids with even-numbered alkyl chains compared with odd-numbered alkyl chains, below six-carbon units.<sup>12</sup>

2. The ability of halide-anion-based ionic liquids to dissolve cellulose decreases in the order of  $[\text{BMIM}]\text{Cl} > [\text{BMIM}]\text{I} > [\text{BMIM}]\text{Br}$  (partial solubility), consistent with the decrease in the strength of H-bonding basicity.<sup>48</sup>
3. Ionic liquids that contain large noncoordinating anions  $[\text{PF}_6]^-$  and  $[\text{BF}_4]^-$  are poor solvents for either cellulose or lignin.<sup>11,13</sup>
4. Phosphate- and phosphonate-anion-based ionic liquids such as  $[\text{EMIM}](\text{MeO})_2\text{PO}_2$ ,  $[\text{EMIM}](\text{MeO})\text{MePO}_2$ , and  $[\text{EMIM}](\text{MeO})\text{HPO}_2$  are able to dissolve cellulose at low temperature, that is, 45–65°C.<sup>50</sup>
5. With a given cation, the capabilities of anions to dissolve cellulose decrease in the order:  $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{HCOO}^- > \text{dicyanamide} \sim \text{NTf}_2$ .<sup>51</sup>
6. The effectiveness sequence of  $[\text{EMIM}]\text{Ac} > [\text{EMIM}](\text{C}_2\text{H}_5)_2\text{PO}_4 > [\text{MMIM}]\text{MeSO}_4$  was observed for lignin extraction following biomass pretreatment. Maximum cellulosic biomass yield was obtained at 120°C.<sup>52</sup>
7. Presence of a hydroxyl end group in the cation may cause the solubility of cellulose in the corresponding ionic liquids to decrease or to increase depending on the alkyl chain length. The  $[(\text{HO})\text{C}_2\text{MIM}]\text{Cl}$  is a good cellulose solvent at a temperature at which  $[\text{EMIM}]\text{Cl}$  remains a solid, whereas  $[\text{H}(\text{OEt})_3\text{MIM}]\text{Ac}$  has much lower solubility for cellulose than  $[\text{CH}_3(\text{OEt})_3\text{MIM}]\text{Ac}$ .<sup>51,53</sup> This phenomenon was rationalized on the basis of chain-length-dependent steric environment for the OH to form intermolecular hydrogen bonds with its anions (consuming cellulose dissolving anions) or to form H-bond to cellulose (in addition to the anion H-bonding formation potential).<sup>14</sup>
8. Presence of  $\text{H}_2\text{O}$  induces dealkylation of 1-alkyl-3-methyl imidazolium salts, following the mechanism as shown in Figure 7. Methyl chloride is formed as a product of decompositions from  $[\text{EMIM}]\text{Cl}$  and  $[\text{BMIM}]\text{Cl}$ .<sup>54,55</sup> It should be kept in mind that excess amount  $\text{H}_2\text{O}$  beyond reaction stoichiometry is needed for cellulose hydrolysis.



**FIGURE 7** | Thermal decomposition of [EMIM]Ac into methyl acetate and ethylimidazole.

9. Thermal stability of ionic liquids is impacted by the presence of cellulose, particularly for the chloride-based ionic liquids, as shown in Table 1.<sup>56</sup> H<sub>2</sub>O from dehydration of cellulose at higher temperatures combined with abundant chloride ions promotes dealkylation of alkylimidazolium cation. The presence of a methyl group on the C2 position ([EDMIM]Cl, [BDMIM]Cl) has only a moderate effect on the thermal stability. The thermal stability of the ionic liquids appears to follow an opposite order to that of cellulose solubility (attribute 5 above).
10. Viscosity of ionic liquids does not have a general correlation with the solubility of cellulose.<sup>57</sup>
11. Applying CO<sub>2</sub> in moderate pressure (50 psi) to [EMIM]Ac increases the solubility of cellulose and enhances the rate of cellulose dissolution in the ionic liquid, particularly at lower temperatures.<sup>58</sup>
12. At higher temperatures, for example, 150°C, [EMIM]Ac is not an inert solvent for cellulose. Acetylation of cellulose was observed.<sup>59</sup> When [EMIM](C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>PO<sub>4</sub> was used to dissolve cellulose, a large increase in inorganic residue was observed from the regenerated cellulose.<sup>60</sup> The loss of ionic liquids in both systems deserves attention to the reactivity of the ionic liquids.
13. [Ch]Ac has a lower solubility for cellulose. A mixed ionic liquid solvent prepared by replacing 10 wt% of [Ch]Ac with [TBMA]Cl or triethylmethylammonium chloride increases cellulose solubility by over 20 times that of the [Ch]Ac at identical dissolution conditions to a level even higher than the solubility of cellulose in [BMIM]Cl. [TBMA]Cl at 15 wt% is not fully soluble in [Ch]Ac.<sup>26</sup>
14. Even though H<sub>2</sub>O has been used as an antisolvent to precipitate dissolved cellulose, blending H<sub>2</sub>O in certain ionic liquids in optimum fraction can largely enhance the sol-

**TABLE 1** | Comparison of Onset Temperatures ( $T_{\text{on}}$ ) of Different Ionic Liquids Measured by Reaction Calorimetry (RC), Differential Scanning Calorimetry (DSC), and RC in the Presence of Cellulose

Ionic Liquid	$T_{\text{on}}$ (DSC) [°C]	$T_{\text{on}}$ (RC) [°C]	$T_{\text{on}}$ (Cellulose) [°C]
[EMIM]Ac	220	181	183
[BMIM]Ac	224	179	178
[EDMIM]Cl	274	222	213
[EMIM]Cl	268	235	202
[BMIM]Cl	270	229	204
[BMIM]BF <sub>4</sub>	360	315	
[BMIM]NTf <sub>2</sub>	401	365	

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ubility of cellulose and biomass. For example, tetrabutylphosphonium hydroxide with 10 wt% H<sub>2</sub>O does not dissolve cellulose, but with 40 wt% H<sub>2</sub>O, the mixture can dissolve 20 wt% cellulose. This phenomenon was attributed to the lowered viscosity by higher H<sub>2</sub>O dilution. The viscosity of the solution increases with a higher amount of cellulose dissolved.<sup>61</sup> In another example, the solubility of legume straw in a mixture of [BMIM]Cl with 20 wt% H<sub>2</sub>O was nearly tripled to 29 wt% from 9.8 wt% in pure [BMIM]Cl.<sup>62</sup>

### Dissolution of Hemicellulose in Ionic Liquids

Hemicellulose has the weakest structure in comparison with that of cellulose and lignin. Because of structural similarity to cellulose, ionic liquids that can dissolve cellulose are expected to dissolve hemicellulose as well, even though few reports show specific dissolution of hemicellulose. It is interesting, however, to note that a [BMIM]Cl–H<sub>2</sub>O mixture selectively removes hemicellulose from treated legume straw.<sup>62</sup> A maximum of 29.1 wt% legume straw is dissolved in the [BMIM]Cl–20 wt% H<sub>2</sub>O mixture at 150°C for 2 h. A hemicellulose-free lignin-rich material (64.0 wt% lignin and 35.3 wt% cellulose) was obtained by adding H<sub>2</sub>O.

### Dissolution of Lignin in Ionic Liquids

The mechanism for the dissolution of lignin in ionic liquids lacks sufficient study, likely because of the structural complexity of lignin. The reported literature appears to indicate that the dissolution of lignin also follows a similar mechanism involving anions of strong H-bonding basicity. Because of the heavily polyaromatic composition of lignin, cations

of ionic liquids with unsaturated bonds such as C=C in allyl group also enhance the overall solubility of lignin.<sup>63,64</sup>

For dissolution of lignin in ionic liquids, the following attributes have been established:

1. For [BMIM]-based ionic liquids, the order of lignin solubility was found to be  $\text{MeSO}_4^- > \text{Cl}^- \approx \text{Br}^- \gg \text{PF}_6^-$ .<sup>65</sup>
2. Polyoxometalate,  $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{5-}$ , is an effective catalyst for the dissolution and delignification of wood in [EMIM]Ac.<sup>66</sup>

### Dissolution of Lignocellulosic Biomass in Ionic Liquids

The literature on dissolution of woody biomass has been well reviewed.<sup>67</sup> In general, the attributes that are applicable to the dissolution of cellulose and lignin hold true for whole woody biomass. For full lignocellulosic biomass, however, fractionation through ionic liquid media is a practical pretreatment strategy to allow for catalytic conversions of purified biomass components. Additional attributes to woody biomass are summarized below.

1. 3-Allyl-1-butylimidazolium metal chlorides,  $[\text{ABIM}]\text{MCl}_{n+1}^-$ , is more effective for dissolution of wood than  $[\text{ABIM}]\text{Cl}$ .<sup>68</sup>
2. In ionic liquids of acetate such as [EMIM]Ac, presence of organic acid in woody biomass causes the formation of acetic acids as a result of acid exchange.<sup>69</sup>
3. Surprisingly, the dissolution of cellulose preceded that of hemicellulose in [EMIM]Cl.<sup>70</sup>
4. After dissolution in [EMIM]Cl ionic liquid, fractionation of cellulose from lignin is achieved by precipitating cellulose with  $\text{H}_2\text{O}$  antisolvent, followed by precipitation of lignin with acetone antisolvent.<sup>71</sup>
5. Oxygen accelerates the dissolution of wood in ionic liquids.<sup>72</sup>

### CATALYTIC CONVERSIONS IN IONIC LIQUIDS

Dissolution of lignocellulosic biomass in ionic liquids makes the cellulosic carbohydrate and lignin polymers accessible to catalysts, dissolved or dispersed in the same medium, for catalytic conversions. For cellulose, the dissolution process accomplishes decrystallization, which is one of the bottlenecks in the conversion of cellulose in aqueous media because of low

**TABLE 2** | Typical Compositions of Lignocellulosic Biomass Expressed in Relative Mass Content and in Energy Content

	Cellulose		Hemicellulose		Lignin	
	wt%	E%	wt%	E%	wt%	E%
Softwood	45	38	25	21	30	41
Hardwood	42	37	33	28	25	35
Straw stalks*	40	38	30	29	22	33

solubility of cellulose in  $\text{H}_2\text{O}$ . Soluble lignin in aqueous media after degradation by alkaline treatment, a typical practice in wood pulping process, has limited catalytic options because of the high pH needed to keep it in dissolved form. Neutralization of the alkalinity causes precipitation of the lignin from the aqueous phase. Dissolution of lignin in ionic liquids therefore allows new catalytic options to cleave the polymer into desired products.

Because the oxygen content in lignin is about half of that in cellulosic carbohydrates, the heating value of lignin on an equivalent weight basis is much higher than that of cellulose and hemicellulose. The typical relative mass contents and energy contents of cellulosic biomass sources are shown in Table 2. Straw stalks typically have 5–10 wt% minerals. Taking softwood such as pinewood as an example, its cellulose content is about 45 wt% and its lignin content is 30 wt%. The mass of cellulose in softwood is about 50% higher than that of lignin. However, the energy content (E% in Table 2) based on the heating value of lignin is even higher than that of cellulose. Therefore, converting lignin to liquid fuels has a great potential in utilizing ionic liquids as reaction media.

In reported studies, the purity of ionic liquids used is not always specified. The presence of impurities and their concentrations can have pronounced effects on the results. For [EMIM]Cl ionic liquid at different purity levels from three different sources, the results of cellulose conversion in these ionic liquids revealed some striking effects of the impurities.<sup>73</sup> For 10 wt% cellulose dissolved in all three ionic liquids, at 180°C for 5 min, cellulose was little converted in the high purity [EMIM]Cl. High glucose yield was obtained in the least pure [EMIM]Cl (93% purity), whereas in the [EMIM]Cl of 98% purity, 5-hydroxymethylfurfural (5-HMF) was the main product. This [EMIM]Cl of 98% purity was found to have copper and chromium impurities at low concentrations. Therefore, care must be taken to ensure that the effects of possible impurities are considered in catalytic conversions involving ionic liquids as solvents.

## Catalytic Hydrolysis of Cellulose in Ionic Liquids

### *Hydrolysis by Brønsted Acids*

For cellulose hydrolysis, strong Brønsted acids such as mineral acids are often used as catalysts in aqueous media. However, in an ionic liquid solvent with strong H-bonding basicity used to dissolve cellulose, some strong Brønsted acids based on mineral acids are not very efficient catalysts. This phenomenon is possibly due to H-bond formation between strong mineral acid protons with ionic liquid anions of strong hydrogen basicity, resulting in weakened acidity.

Although [EMIM]Ac is a superior solvent for cellulose dissolution, it was found to be a poor solvent to carry out cellulose hydrolysis by Brønsted acids. After dissolution of a cellulose in [EMIM]Ac at 135°C, hydrolysis by hydrochloric acid (HCl) at 103°C converted only 10% cellulose in [EMIM]Ac, only to cellobiose and 0% glucose. In comparison, cellulose conversions are near 100% in [BMIM]Cl and [EMIM]Cl solvents, with 83.7% and 87.1% to glucose, and 12.6% and 12.5% to cellobiose, in [BMIM]Cl and [EMIM]Cl, respectively, under identical conditions.<sup>74</sup> The drastically different catalytic results in the chloride-based ionic liquids from that in the acetate-based ionic liquids is rationalized by the ion exchange reaction:  $[\text{EMIM}]\text{Ac} + \text{HCl} \rightarrow [\text{EMIM}]\text{Cl} + \text{AcOH}$ . AcOH does not have sufficient acidity to hydrolyze cellulose. In general, among the anions chloride, acetate, nitrate, dimethylphosphate, triflate, and bromide with a common [BMIM]<sup>+</sup> cation or other cations, only the chloride-based ionic liquids provide the effective media for HCl-catalyzed cellulose hydrolysis.<sup>75</sup> Very little or no hydrolysis products were formed by HCl in ionic liquids of the other anions.

Amberlyst-15 is a sulfonic-acid-functionalized macroporous resin with a large external surface area, accessible to dissolved cellulose polymer in ionic liquid. It is stable in [BMIM]Cl, but is rapidly destroyed in [BMIM]Ac.<sup>76</sup> This is another example showing that a catalyst has to be compatible with the ionic liquid of choice, in addition to cellulose solubility criterion for the ionic liquid. In the first stage of cellulose depolymerization, cello-oligomers are formed, which are subsequently further broken down into sugars.<sup>76</sup> Among various solid acids including Nafion<sup>®</sup> (DuPont, Wilmington, DE) and zeolites, Amberlyst-15 and Amberlyst-35 (Dow Chemical, Midland, MI) are the most efficient catalysts in [BMIM]Cl for cellulose depolymerization.

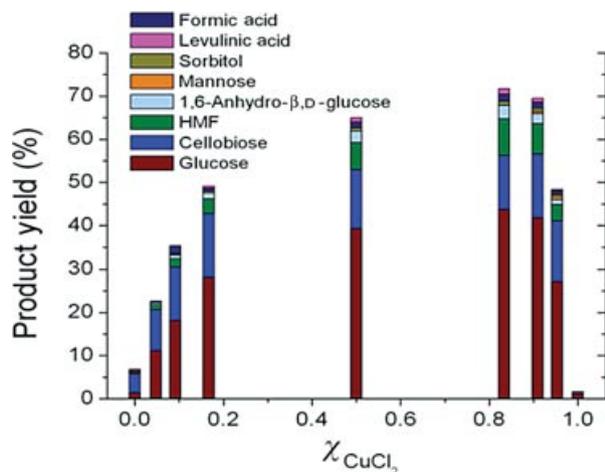
When a solid acidic resin was used as the catalyst, the glucose yield was the highest when the

amount of [BMIM]Cl added equaled the number of protons available in the resin catalyst, but further addition of [BMIM]Cl did not lead to substantial changes in the glucose yield.<sup>77</sup> It was therefore proposed that the protons of the sulfonate groups in the resin was ion exchanged with imidazolium ions and these released protons, in the case of halide anions, are the catalyst for the hydrolysis reaction. The released protons associated with acetate are weak and have low hydrolysis activity.

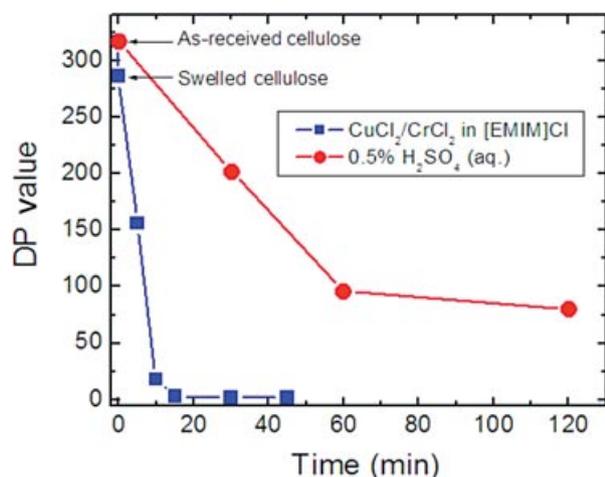
H-type zeolites are efficient catalysts for hydrolysis of cellulose in [BMIM]Cl to glucose at 130°C without pretreatment.<sup>78</sup> H<sub>2</sub>O was gradually added as the reaction progressed. With acidic faujasite zeolite HY at equivalent proton concentration of 11.1 mol%, the glucose yield reached 50.0% at the highest, and the total yield of three main products (glucose, cellobiose, and 5-HMF) reached up to 97.2%. Among all the controlling factors, the amount of H<sub>2</sub>O and the timing of H<sub>2</sub>O addition are critical for high hydrolysis efficiency. Even though [BMIM]Cl was found to enter the channels of HY, cellulose hydrolysis are unlikely to take place inside the zeolite channel simply because of the larger size of cellulosic polymers than the zeolite channel opening. The released Brønsted acid via ion-exchange mechanism, similar to that observed for solid acidic resin,<sup>77</sup> was suggested to be the hydrolysis catalyst.

### *Hydrolysis by Metal Chlorides*

Metal chlorides are particularly efficient catalysts for hydrolysis of cellulose in [EMIM]Cl and [BMIM]Cl ionic liquids.<sup>15,16</sup> Paired metal chlorides containing CuCl<sub>2</sub> and a trace amount of a second metal chloride such as CrCl<sub>2</sub>, CrCl<sub>3</sub>, FeCl<sub>3</sub>, or PdCl<sub>2</sub> showed largely enhanced activity over that of individual metal chloride of the pair. In the case of paired CuCl<sub>2</sub> and PdCl<sub>2</sub> at a constant total metal chloride loading of 37 mmol/g [EMIM]Cl, the cellulose hydrolysis product yield is a function of the fraction of CuCl<sub>2</sub> in the pair. As shown in Figure 8, neither pure CuCl<sub>2</sub> nor pure PdCl<sub>2</sub> is an active catalyst at 120°C. However, replacing CuCl<sub>2</sub> with a small amount of PdCl<sub>2</sub> leads to a largely enhanced catalyst performance. The optimum product yield occurs at 10–20% PdCl<sub>2</sub> in the pair. For paired CuCl<sub>2</sub> and CrCl<sub>2</sub> catalysts, a similar pattern of the effect of paired metal chlorides was observed, but the amount of CrCl<sub>2</sub> as little as 3 wt% in the total of the pair was sufficient to activate the paired metal chloride catalyst to a maximum yield of 65% at 120°C from less than 1% product yield.<sup>15</sup> By varying the ratio of CrCl<sub>2</sub> to CuCl<sub>2</sub>, the product selectivity shifts from saccharides in CuCl<sub>2</sub>-rich



**FIGURE 8** | Hydrolysis product yield from cellulose using single and paired  $\text{CuCl}_2/\text{PdCl}_2$  catalysts having  $\chi_{\text{CuCl}_2}$  ranging from 0 to 1 at  $120^\circ\text{C}$  for 1 h. The cellulose was dissolved in [EMIM]Cl at  $100^\circ\text{C}$  for 1 h before initiating the reaction by adding water. Total metal chloride loading is 37 mmol/g [EMIM]Cl (6 mol% with respect to the glucose monomer concentration present in the cellulose feed). (Reproduced with permission from Ref 16. Copyright 2011, Elsevier.)



**FIGURE 9** | Changes in the degree of polymerization (DP) values of cellulose/hydrolyzed cellulose in aqueous 6 mol%  $\text{H}_2\text{SO}_4$  (●) and in [EMIM]Cl containing 6 mol% (i.e., 37 mmol/g [EMIM]Cl) total  $\text{CuCl}_2$  and  $\text{CrCl}_2$  ( $\chi_{\text{CuCl}_2} = 0.91$ ) (■) at  $120^\circ\text{C}$ . (Reproduced with permission from Ref 15. Copyright 2009, Elsevier.)

pairs to 5-HMF in  $\text{CrCl}_2$ -rich pairs in pure [EMIM]Cl solvent.

The relative rate of cellulose hydrolysis catalyzed by paired  $\text{CuCl}_2$  and  $\text{CrCl}_2$  in [EMIM]Cl solvent was compared with that catalyzed by mineral acid in an aqueous solvent (i.e., a conventional hydrolysis medium) using the measured values of the DP (a measure of the average number of glucose units in the polymer chains) during hydrolysis (Figure 9).<sup>15</sup> Dissolution of the crystalline cellulose

(DP = 317) in [EMIM]Cl solvent containing a  $\text{CuCl}_2/\text{CrCl}_2$  ( $\chi_{\text{CuCl}_2} = 0.91$ ) catalyst at  $120^\circ\text{C}$  did not appreciably change the DP value (DP = 286). However, upon addition of  $\text{H}_2\text{O}$  at the same temperature, hydrolysis occurred rapidly in this paired metal chlorides–[EMIM]Cl system. The DP value dropped to 18 after 10 min and to 1.9 after 30 min. The initial rate of depolymerization, defined as the rate of decrease of the DP value, was about  $30 \text{ min}^{-1}$ . In comparison, in the dilute aqueous  $\text{H}_2\text{SO}_4$  system, the depolymerization of cellulose was much slower, requiring 60 min to reach a DP value of 96. The initial rate of depolymerization of cellulose in the dilute aqueous  $\text{H}_2\text{SO}_4$  solution was about an order of magnitude slower. Most strikingly, the hydrolysis products in the  $\text{H}_2\text{SO}_4$  aqueous system consisted only of fragmented cellulose oligomers. Little glucose was detected after mineral acid hydrolysis for 2 h.

At a higher temperature ( $140^\circ\text{C}$ ), 5-HMF in 62% yield was produced in a short time (10 min) using a combined equal amount of  $\text{CrCl}_3$  and  $\text{LiCl}$  as catalyst. This 5-HMF yield is higher than that (52%) of  $\text{CrCl}_3$  catalyst alone under same reaction conditions.<sup>79</sup>

Paired  $\text{ZrOCl}_2$  and  $\text{CrCl}_3$  in  $\text{ZrOCl}_2$  to  $\text{CrCl}_3$  ratio of 3 was reported effective for 5-HMF production (57% yield) from both cellulose and sugarcane bagasse in DMA–LiCl solvent at  $120^\circ\text{C}$ , but the addition of a large amount of [BMIM]Cl (up to 44 wt%) was critical for the higher 5-HMF in reference to 5-HMF yield in DMA–LiCl alone.<sup>80</sup> Similarly, 5-HMF yields of up to 54% was obtained in mixed solvents consisting of DMA–LiCl and [EMIM]Cl, with  $\text{CrCl}_2$  or  $\text{CrCl}_3$  as the catalysts.<sup>27</sup> Adding a small amount of LiCl or LiBr to the  $\text{CrCl}_3$  + [EMIM]Cl system showed a small improvement in the 5-HMF yield, even though at reduced  $\text{CrCl}_3$  concentration.<sup>79</sup>

An acidic ionic liquid,  $[\text{HSO}_3\text{BMIM}]\text{HSO}_4$ , was reported to have superior catalytic activity over other acidic [BMIM] $\text{HSO}_4$  and [BMIM] $\text{H}_2\text{PO}_4$  ionic liquids for cellulose hydrolysis in mixtures of the ionic liquids with  $\text{H}_2\text{O}$ . Cellulose conversion was near 70% in the  $[\text{HSO}_3\text{BMIM}]\text{HSO}_4$ – $\text{H}_2\text{O}$  mixture at  $150^\circ\text{C}$  in the presence of a methylisobutylketone (MIBK) organic phase.<sup>81</sup> There is a lack of reference to the performance of  $\text{H}_2\text{SO}_4$  under identical conditions in this study, however. The presence of metal chlorides,  $\text{CrCl}_3$ ,  $\text{MnCl}_2$ ,  $\text{FeCl}_3$ ,  $\text{FeCl}_2$ , and  $\text{CoCl}_2$ , in the  $[\text{HSO}_3\text{BMIM}]\text{HSO}_4$ – $\text{H}_2\text{O}$  mixture showed considerably enhanced cellulose conversions, up to 87.8% and 88.6% with  $\text{CrCl}_3$  and  $\text{MnCl}_2$ , respectively. Yield to 5-HMF was the main product in all these metal-chloride-containing media. However, levulinic acid, a product of hydrolytic cleavage

of 5-HMF, is significant in the products even in the presence of a MIBK extraction phase, suggesting the presence of rather strong Brønsted acidity. Similar effect was observed for the sulfate salts of these metal ions.

Ionic liquids consisting of a  $\text{SO}_3\text{H}$ -functionalized alkyl (A) group in the  $[\text{AMIM}]^+$  cation and an acidic anion, for example,  $[\text{C}_4\text{SO}_3\text{Hmim}][\text{CH}_3\text{SO}_3]$ , when used together with  $\text{CuCl}_2$  in an  $[\text{EMIM}]\text{Ac}$  solvent, were found to be highly efficient catalyst for the formation of 5-HMF (64.9% yield) from microcrystalline cellulose at  $160^\circ\text{C}$ . The presence of a metal chloride,  $\text{CuCl}_2$  in particular, provided a pronounced enhancement for the 5-HMF yield.<sup>82</sup>

Sorbitol is a useful product from glucose hydrogenation. By combining a catalyst with hydrogenation activity and a catalyst capable of hydrolyzing dissolved cellulose in an ionic liquid to glucose, a one-pot production of sorbitol can be realized. A combination of a Pt or Rh hydrogenation catalyst and a ruthenium complex in  $[\text{BMIM}]\text{Cl}$  was shown to be effective, at sorbitol yield of 51–74%, for the formation of sorbitol from cellulose in one pot.<sup>83</sup> The main possible role of the ruthenium compound was suggested to enhance the transfer of hydrogen to the heterogeneous metal catalyst.

## Catalytic Conversion of Cellulosic Carbohydrates in Ionic Liquids

Conversion of cellulosic carbohydrates is a consecutive step following hydrolysis of cellulose, although one-pot conversion of cellulose to desired products mechanistically via glucose is possible.<sup>15</sup> For reasons that ionic liquids composed of anions other than halides do not work for acid-catalyzed cellulose hydrolysis, they are generally found poor solvents for carbohydrate conversions. Therefore, chloride-based ionic liquids are mostly used for catalytic conversion of cellulosic carbohydrates including cellulose.

Converting glucose to 5-HMF is particularly attractive in the utilization of cellulosic biomass because 5-HMF is a potential platform chemical for the production of fuels and a broad range of chemicals. The most critical step in converting glucose to 5-HMF is catalytic isomerization of glucose to fructose because the conversion of fructose to 5-HMF is a straightforward Brønsted-acid-catalyzed dehydration reaction. In ionic liquid media such as  $[\text{EMIM}]\text{Cl}$ ,  $[\text{BMIM}]\text{Cl}$ , and tetraethylammonium chloride (TEAC), the most effective catalysts reported in the literature remain Cr(II, III) salts.<sup>28,29,84</sup> In  $[\text{EMIM}]\text{Cl}$  solvent, little levulinic acid, a typical degradation product of 5-HMF

catalyzed by Brønsted acid, was formed. Other forms of chromium-ion-based catalysts, for example, N-heterocyclic carbene (NHC)Cr(II)Cl<sub>2</sub> complexes were also found to be effective in glucose conversion to 5-HMF at  $100^\circ\text{C}$ .<sup>85</sup>

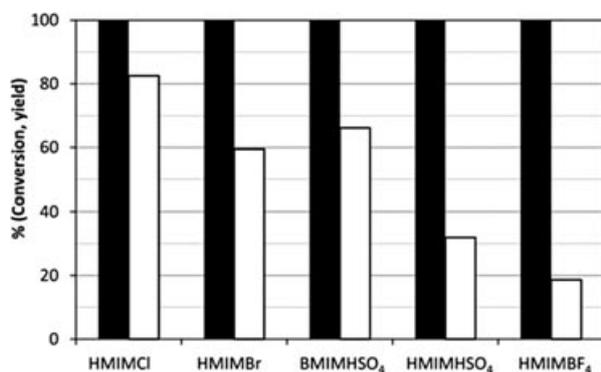
The role of Cr(II) ions in the isomerization of glucose was studied in-situ EXAFS measurement during the reaction and supported by density function theory free energy calculations.<sup>86</sup> The presence of O- or Cl-bridged Cr dimers was identified during the catalytic cycle. When all the glucose had been nearly converted, this Cr–Cr dimer coordination was no longer observed.

Glucose was converted to 5-HMF by  $\text{SnCl}_4$ , but this catalyst was found effective mainly in  $[\text{EMIM}]\text{BF}_4$  ionic liquid.<sup>87</sup> The yield of 5-HMF reached 61% when the concentration of glucose in  $[\text{EMIM}]\text{BF}_4$  was as high as 23 wt% at  $100^\circ\text{C}$  for 3 h. High 5-HMF yield was also obtained from sucrose in a similar system under the same conditions. Surprisingly,  $\text{SnCl}_4$  in a number of other ionic liquids [e.g.,  $[\text{BMIM}]\text{Cl}$ , 1-butyl-3-methylimidazolium tetrafluoroborate ( $[\text{BMIM}]\text{BF}_4$ ), 1-butyl-3-methylimidazolium hexafluorophosphate ( $[\text{BMIM}]\text{PF}_6$ ), 1-butyl-3-methylimidazolium bistriflateimide ( $[\text{BMIM}]\text{Tf}_2\text{N}$ ), 1-butyl-3-methylimidazolium trifluoroacetate ( $[\text{BMIM}]\text{TFA}$ ), 1-butyl-3-methylimidazolium trifluoromethylsulfonate ( $[\text{BMIM}]\text{Trif}$ ), 1-butyl-3-methylimidazolium saccharin ( $[\text{BMIM}]\text{Sacc}$ ), N-butylpyridinium tetrafluoroborate ( $[\text{BPy}]\text{BF}_4$ )] was considerably less selective for 5-HMF in glucose conversion under the same conditions.

Some non-imidazolium-based ionic liquid solvents are also suited for chromium (II, III) chloride catalysts in glucose isomerization to fructose and in subsequent fructose dehydration to 5-HMF. For example,  $\text{CrCl}_3$  in TEAC ionic liquid was shown to convert 10 wt% glucose to 5-HMF in 71% yield at  $130^\circ\text{C}$  for only 10 min.<sup>84</sup> The 5-HMF yields were 76% and 61% from sucrose and cellobiose, respectively, under the same conditions. The 5-HMF yield was 66% at 30% glucose concentration. The TEAC– $\text{CrCl}_3$  system was found to be tolerant to high  $\text{H}_2\text{O}$  content and high glucose concentration and could be recycled.

## Catalytic Conversion of Lignin in Ionic Liquids

The challenges encountered in the full characterization of complex structure and composition of lignin, together with the complicated lignin composition, also limit the progress in the understanding of catalytic lignin conversions. Therefore,



**FIGURE 10** | Conversion (■) and guaiacol yield (□) after 20 min under 150°C using GG as model compound. (Reproduced with permission from Ref 88. Copyright 2011, Elsevier.)

reported research works have been mainly focused on the study of lignin model compounds. Several new approaches have appeared in literature involving catalysis in ionic liquids. These approaches include Brønsted-acid-catalyzed hydrolytic cracking, organic-base-catalyzed hydrolytic ether bond cleavage, metal-chloride-catalyzed ether bond cleavage, and oxidative cleavage.

### Catalysis by Acidic Ionic Liquids

Ionic liquids based on the 1-methylimidazolium cation with chloride ([HMIM]Cl), bromide ([HMIM]Br), hydrogen sulfate ([HMIM]HSO<sub>4</sub>), and tetrafluoroborate ([HMIM]BF<sub>4</sub>) counterions along with 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO<sub>4</sub>) were studied in the degradation of two lignin model compounds, guaiacylglycerol- $\beta$ -guaiacyl ether (GG) and veratrylglycerol- $\beta$ -guaiacyl ether (VG).<sup>88</sup> All the ionic liquids are strongly acidic with their Hammett acidity between 1.48 and 2.08, with their relative acidity strength in the order of [HMIM]Cl > [HMIM]BF<sub>4</sub> > [MIM]HSO<sub>4</sub>  $\approx$  [HMIM]Br  $\approx$  [BMIM]HSO<sub>4</sub>. At 150°C, the relative maximum guaiacol yield produced by each ionic liquid is in the order of [HMIM]Cl > [BMIM]HSO<sub>4</sub> > [HMIM]Br > [HMIM]HSO<sub>4</sub> > [HMIM]BF<sub>4</sub>, as shown in Figure 10. Most ionic liquids are effective in converting GG and VG model compounds. However, the selectivities to guaiacol are largely different depending on the anions. Therefore, the acidity of the ionic liquid is not the only influence factor for the hydrolysis of the lignin model compounds.

Analysis of the reaction intermediates (enol ether and vinyl ether) and the products revealed that the reaction pathways of GG and VG (Figure 11) are determined by whether the anions of the ionic liquids

are coordinating. Both Cl<sup>-</sup> and Br<sup>-</sup> are coordinating and the others are noncoordinating. Therefore, the ability to form H-bond with the model compound is a major contributor to the ability of an acidic ionic liquid to effectively catalyze hydrolysis of the  $\beta$ -O-4 ether linkage, with stronger coordination leading to a chemical environment more conducive to ether bond hydrolysis.<sup>88</sup>

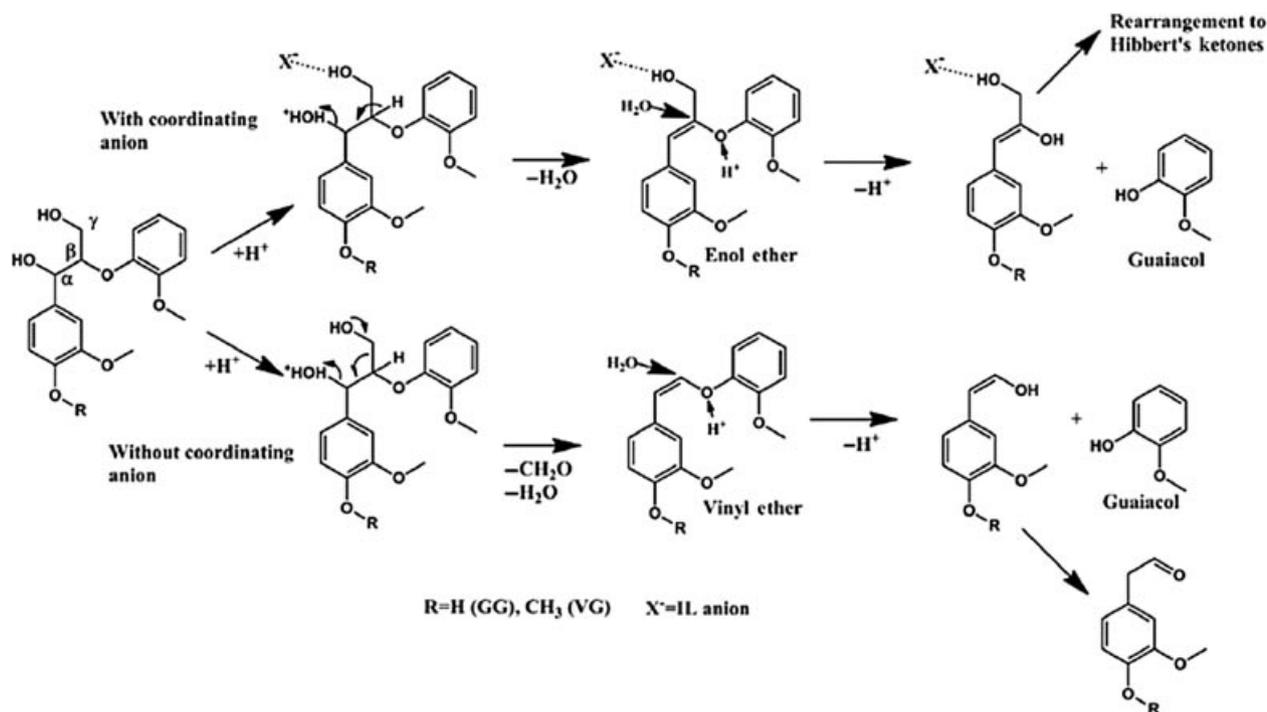
### Catalysis by Strong Organic Bases in Ionic Liquid

Strong organic bases were studied for their catalytic activity in catalyzing the hydrolysis of the  $\beta$ -O-4 ether linkage in GG and VG.<sup>89</sup> [BDMIM]Cl was used as a solvent for this work because of the reported instability of most common dialkyl-substituted imidazolium-based ionic liquids under basic conditions. The tested bases, with structures shown in Figure 12, and their pK<sub>a</sub> values reported in acetonitrile are listed in Table 3.

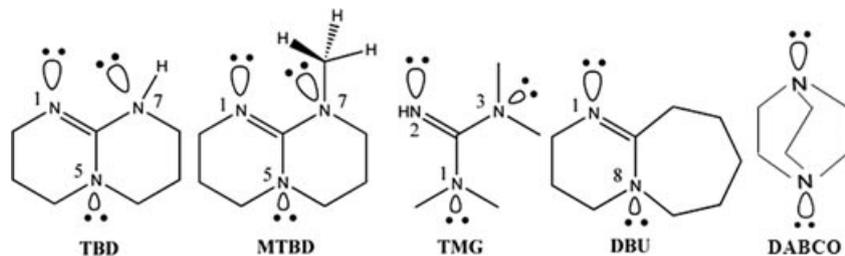
The GG conversions at 130°C for 2 h in the ionic liquid catalyzed by 1,5,7-triazabicyclo[4.4.0]dev-5-ene (TBD); 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene; 1,8-diazabicyclo[5.4.0]undec-7-ene; 1,1,3,3-tetramethylguanidine; and 1,4-diazabicyclo[2,2,2]octane are 66.9%, 36.6%, 31.2%, 11.1% and 2.4%, respectively. Evidently, the GG conversion correlates well with strength of the basicity. The yield of guaiacol and the concentration of enol ether also follow the same trend. TBD, as the strongest base of the organic bases studied in this work, was suggested to function both as a base and as a nucleophile.<sup>89</sup>

### Catalysis by Metal Chlorides in Ionic Liquid

As discussed above, some metal chlorides are active catalysts for the hydrolytic cleavage of cellulose in a number of ionic liquids. Even though the ether bonds in lignin are very different in the chemical nature from those in cellulose, metal chlorides were also found effective in catalyzing the hydrolysis of  $\beta$ -O-4 ether linkage of lignin model compounds.<sup>90</sup> FeCl<sub>3</sub>, CuCl<sub>2</sub>, and AlCl<sub>3</sub> were catalytically effective in cleaving the  $\beta$ -O-4 bond of GG in [BMIM]Cl to form guaiacol. A number of other metal chlorides are considerably less active. VG is less reactive than GG in hydrolytic cleavage of  $\beta$ -O-4 bond. AlCl<sub>3</sub> functioned more effectively in cleaving the  $\beta$ -O-4 bond of VG than did FeCl<sub>3</sub> and CuCl<sub>2</sub>. The results are shown in Table 4. The catalytic activity of the metal chlorides was suggested to be associated with the HCl, working as the acid catalyst, formed in situ by the hydrolysis of the metal chlorides. A phenolic hydroxide group may interact with metal chlorides to form HCl. A lower



**FIGURE 11** | Pathways of GG and VG degradation in acidic ionic liquids. Analogous chemistry occurs with GG and VG dimers. (Reproduced with permission from Ref 88. Copyright 2011, Elsevier.)



**FIGURE 12** | Structures of TBD, MTBD, TMG, DBU and DABCO.

reactivity of VG as compared with GG was attributed to the absence of phenolic protons in VG. A dehydration product and dimer products from GG were detected and proposed as the possible intermediate products in the GG reaction.

**TABLE 3** | The  $pK_a$  of Different N-Bases in Acetonitrile

N-base	Abbreviation	$pK_a$
1,5,7-Triazabicyclo[4.4.0]dec-5-ene	TBD	25.9
7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene	MTBD	25.43
1,8-Diazabicyclo[5.4.0]undec-7-ene	DBU	24.32
1,1,3,3-Tetramethylguanidine	TMG	23.3
1,4-Diazabicyclo[2,2,2]octane	DABCO	18.29

### Oxidative Cleavage of Lignin in Ionic Liquid

In research to mimic natural manganese peroxidases in white-rot fungus, oxidative depolymerization of lignin by  $Mn(NO_3)_2$  as a catalyst in  $[EMIM]CF_3SO_4$ ,  $[MMIM]MeSO_4$ ,  $[EMIM]EtSO_4$ , and  $[EMIM]MeSO_4$  at  $100^\circ C$  and  $80 \times 10^5$  Pa air pressure produces 52.6% total extracted products from  $[EMIM]CF_3SO_4$  ionic liquid, followed by 28.8% in  $[EMIM]EtSO_4$ .<sup>91</sup> The total extractables are combined amounts from extractions by toluene, dichloromethane, and ethylacetate. Vanillin, syringol, syringaldehyde, and 2,6-dimethoxy-*p*-benzoquinone are the main products.

In another study,  $CoCl_2 \cdot 6H_2O$  in  $[EMIM]Et_2PO_4$  was shown to be an effective catalytic system for oxidative lignin depolymerization by molecular oxygen.<sup>92</sup> The ionic liquid is a

**TABLE 4** | GG and VG Conversion and Guaiacol Yield in the Presence of FeCl<sub>3</sub>, CuCl<sub>2</sub>, an AlCl<sub>3</sub> at 150°C for Different Times<sup>a</sup>

Reaction Time (min)	FeCl <sub>3</sub>		CuCl <sub>2</sub>		AlCl <sub>3</sub>		AlCl <sub>3</sub>	
	GG Conversion (%)	Guaiacol Yield (%)	GG Conversion (%)	Guaiacol Yield (%)	GG Conversion (%)	Guaiacol Yield (%)	VG Conversion (%)	Guaiacol Yield (%)
15	61	33	63	37	91	63	nt	nt
60	95	61	95	67	100	76	57	31
120	100	69	100	70	100	80	67	42
180	100	69	100	68	100	80	75	50
240	nt	nt	nt	nt	nt	nt	79/96 <sup>b</sup> /99 <sup>c</sup>	52/74 <sup>b</sup> /73 <sup>c</sup>

nt, not tested.

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<sup>a</sup>10 mg of GG (or 10.4 mg of VG) was heated in 100 mg of [BMIM]Cl with catalyst (5 mol% to GG or VG) and 18 μL of H<sub>2</sub>O (32:1 to GG or VG by mol%) at 150°C.

<sup>b</sup>10 mol% (to VG) AlCl<sub>3</sub> was added.

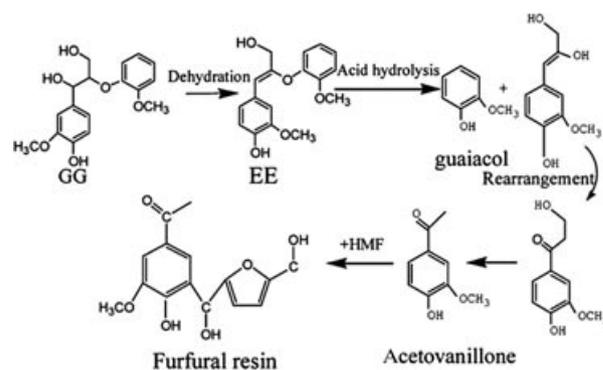
<sup>c</sup>15 mol% (to VG) AlCl<sub>3</sub> was added.

suitable media for the dissolution of lignin. The catalytic oxidation is limited to oxidizing benzyl and other alkyl alcohol functionalities in lignin, but 5–5, β–O–4, phenylcoumaran linkages (Figure 6), and the phenolic functionality in guaiacol, syringol, and vanillyl alcohol are not oxidized. The catalyst system oxidizes the alcohol functionality in cinnamyl alcohol to cinnamaldehyde or cinnamic acid or the double bond to benzoic acid or epoxide. The benzyl functionality in veratryl alcohol is selectively oxidized to veratraldehyde at a maximum turnover frequency of 1440 h<sup>-1</sup>. Cobalt ions strongly bound by tetradentate ligands such as tetradentate porphyrin or salen yielded reduced activity relative to those of simple Co(II) salts in the ionic liquid.

### Catalytic Conversion of Lignocellulosic Biomass in Ionic Liquids

HCl (7 wt%) in [BMIM]Cl is efficient for the hydrolysis of corn stalk, rice straw, pinewood, and bagasse at 100°C, producing total reducing sugar yields of up to 66%, 74%, 81%, and 68%, respectively, in 1 h.<sup>17</sup> Acidic ionic liquid [HSO<sub>3</sub>BMIM]HSO<sub>4</sub> and [BMIM]HSO<sub>4</sub> in [BMIM]Cl also efficiently catalyzed the hydrolysis of corn stalk; its effect is similar to that of HCl. However, the acidic ionic liquids, [HSO<sub>3</sub>BMIM]HSO<sub>4</sub> and [BMIM]HSO<sub>4</sub>, when used alone produced low yield to identifiable hydrolysis products. In a similar study, highest yields of reducing sugars from hydrolysis of cellulose were observed by [HSO<sub>3</sub>BMIM]Cl in [HSO<sub>3</sub>BMIM]HSO<sub>4</sub> and [BMIM]Cl, but not by [BMIM]HSO<sub>4</sub> in the [BMIM]Cl.<sup>93</sup>

Fractionation of lignocellulosic biomass to obtain lignin and cellulose or their fragments is an important subject of research to enable consecutive thermocatalytic and biocatalytic processing of fractionated components. After dissolution of biomass in



**FIGURE 13** | Proposed decomposition pathway of GG in [BMIM]Cl and the synthesis of furfural–lignin resin. (Reproduced with permission from Ref 94. Copyright 2012, American Chemical Society.)

certain ionic liquids, preferential precipitation of either lignin or cellulose by proper choice of antisolvent has been investigated. Conversion of fractionated biomass components could alleviate some of the problems, particularly by biocatalysis, faced in the conversion of full biomass.

Built upon CrCl<sub>3</sub>-catalyzed conversion of glucose to 5-HMF in [BMIM]Cl ionic liquid, the presence of lignin allows for copolymerization of lignin with 5-HMF formed in situ, producing HMF–lignin resin in the form of a solid product that separates from the ionic liquid.<sup>94</sup> The sequence of the reaction involving lignin depolymerization and copolymerization with 5-HMF is shown in Figure 13, in which a lignin model compound, GG, was used as feed. The 5-HMF was formed in the same medium from glucose in [BMIM]Cl in the presence of CrCl<sub>3</sub>·6H<sub>2</sub>O as catalyst. It was reported that at a high temperature, 5-HMF and sugars prefer to condense with lignin than condense themselves. Lignin and sugars are quantitatively converted to resin by CrCl<sub>3</sub>·6H<sub>2</sub>O as catalyst in the ionic liquid between 170 and 190°C.

About 7% lignin was left unconverted at 170°C when CrCl<sub>3</sub> was used as the catalyst.

## SUMMARY AND PROSPECTIVE

Ionic liquids are unique solvents for the dissolution and fractionation of lignocellulosic biomass components. Ionic liquids with anions of strong H-bond basicity have high solubility to cellulose, hemicellulose, and lignin. However, ionic liquids of acetate and dialkylphosphate anions were found not inert at higher temperatures, although these ionic liquids have been found to have superior solubility for cellulosic biomass. Chloride-based ionic liquids are relatively inert to biomass and to most catalysts, and are therefore broadly suited for catalytic conversions of the biomass components. Ionic liquids with Brønsted acidic anions and/or Brønsted acid cations have not been shown to have superior catalytic performances for cellulosic carbohydrate conversions as compared with catalytic systems with introduced Brønsted acids, such as mineral acids or solid-ion-exchange resins, in chloride-based ionic liquids.

Hydrolytic cleavage of the ether bonds in lignin is a more demanding reaction than that in cellulose. Some Brønsted acidic ionic liquids were found effective for catalytic lignin hydrolysis. Catalytic conversion of lignin remains a challenging subject because of the complexity of the lignin structure and a lack of sufficient fundamental understanding of lignin structures. In the course of lignin conversions, reoligomerization of lignin fragments in many solvents complicates the situation even further. Strong-organic-base-catalyzed lignin  $\beta$ -O-4 ether bond cleavage in ionic liquids is feasible; the presence of a nucleophile is essential. Strong Brønsted acids in ionic liquid have been shown to be effective for the hydrolytic cleavage of ether bonds in lignin model compounds. Some metal chlorides, such as AlCl<sub>3</sub>, CuCl<sub>2</sub>, and FeCl<sub>3</sub>, are highly effective in chloride-based ionic liquids for hydrolytic lignin fragmentation with highest selectivity to guaiacol. However, some metal chlorides perform poorly. Early experimental results suggest that HCl from the reaction of metal chlorides with phenolic protons may play a role, but other unidentified factors also appear

to exist in the metal-chloride-catalyzed reactions in ionic liquids. Oxidative cleavage of lignin is another interesting approach for research in lignin catalysis in ionic liquids. However, the most effectively oxidized functionalities in lignin are not the most abundant linkages in lignin. In addition, adding oxygen to lignin effectively lowers the heating value of the products for liquid fuel applications.

Partition and fractionation of biomass components in multiple-phase systems involving ionic liquids could be applicable for catalytic conversions of the components.<sup>95</sup> Ideally, the solvents are compatible with catalysts employed and the process conditions so that end products could be directly recovered from fractionation.

Although the primary function of ionic liquids is the dissolution of cellulose and lignin components of cellulosic biomass, structural design of ionic liquids to allow selective catalytic transformations of cellulose and lignin remains a challenge. The potential of tailoring the functionalities of ionic liquids to maximize desired product yields while facilitating product separation and reuse of the ionic liquids should be further investigated. Such functionalities include optimized balance of hydrophobicity/hydrophilicity. The higher cost of ionic liquids relative to some conventional solvents requires the full reuse of the ionic liquids.

Chromium chlorides are highly effective catalysts in ionic liquids for the conversion of cellulosic carbohydrates to 5-HMF and furfural. Paired metal chlorides in ionic liquids provide a potential route to cellulosic biomass conversions under mild conditions. These catalytic systems, along with other emerging leads discussed in this paper, need continued research to achieve fundamental understanding.

The key attributes of various ionic liquids are reviewed with a focus on their structural and functional properties related to biomass dissolution capacity. Metal chlorides in chloride-based ionic liquids are robust catalyst systems for efficient cellulose and lignin conversions. Emerging leads in the literature related to the use of ionic liquids for catalytic conversions of cellulose, cellulosic carbohydrates, and lignin are discussed.

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