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Perspective

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Bio-based ionic liquids: solvents for a green processing industry?

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ABSTRACT: Replacing conventional solvents by ionic liquids is often suggested as a possible route to greener industrial processes. However, ionic liquids are typically petroleum-derived. This critical review discusses the syntheses, applications and limitations of bio-based ionic liquids synthesized from amino acids, carbohydrates, lignin and other renewable sources. The practical aspects of applying such ionic liquids in lignocellulose processing, as a reaction solvent, organocatalyst or as metal extraction medium are highlighted.

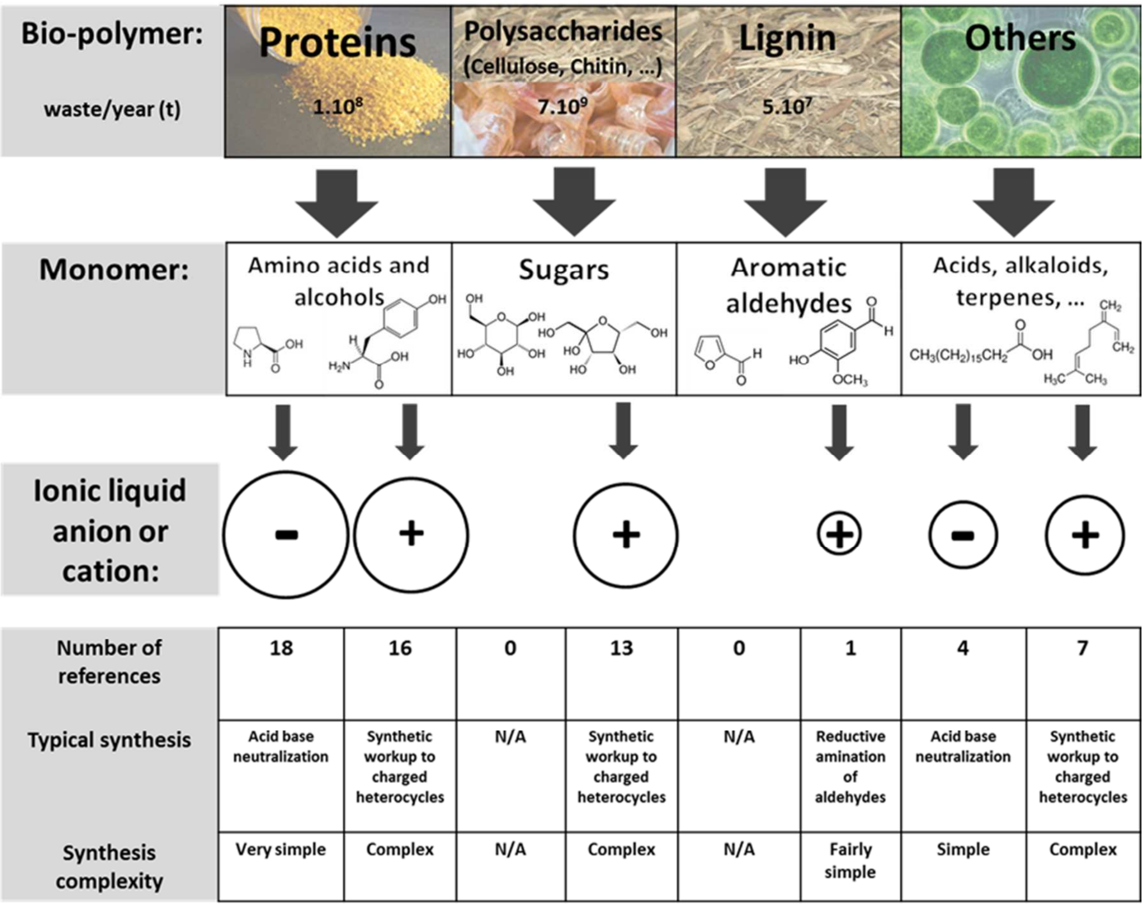
Introduction

Ionic liquids (ILs) are low-melting organic solvents that consist entirely of ions. Many ILs are thermally stable up to 250 °C and can dissolve a wide range of organic and inorganic compounds.[1] Interestingly, ILs are able to dissolve many polymers that are insoluble in conventional solvents, e.g. cellulose,[2] chitin,[3,4] chitosan[5] and polyvinylchloride,[6] and polystyrene.[7] ILs have a negligible vapor pressure, are fluid over a wide temperature range and many are non-flammable.[1] Additionally, both the chemical and physical properties of ILs can be fine-tuned through proper choice of the cation and anion, effectively making them designer solvents. For these reasons, ILs have been intensively researched for the last two decades as supposedly green alternatives to conventional organic solvents.[8,9,10]

However, there exist a number of issues related to the industrial use of ILs, resulting in a limited number of IL-based large-scale industrial processes.[8] Notably, even in the BASIL process, developed by BASF and often cited as being the most successful IL-based industrial process, the IL is not a solvent but rather a process aid formed *in situ* to improve acid removal.[8] Another industrial process making use of an IL was operated by the Eastman Chemical Company in the isomerization of 3,4-epoxybut-1-ene to 2,5-dihydrofuran, but this was discontinued in 2004 due to lack of demand. Other major industrial processes are in development, such as the Difasol process for the dimerization of alkenes.[8]

It has been observed that some ILs or their degradation products can be toxic.[11–13] In addition, the environmental impact of many ILs is higher than expected when their entire life cycle is taken into account, including synthesis from petroleum-derived building blocks.[14] One way to improve the green character of ILs is to base their synthesis on renewable compounds. Several building blocks derived from major renewable sources can be used as IL precursors: amino acids and amino alcohols from proteins; sugars from cellulose, chitin, starch and other polysaccharides; aromatic aldehydes from lignin, and a diverse group of other compounds such as fatty acids from vegetable or algae-derived oils, *etc*. As mentioned above, some large-volume, low-cost waste bio-polymers can only be dissolved and processed efficiently in ILs (e.g. cellulose).

Therefore, bio-based ILs would ideally be suitable to process their materials of origin, thus realizing a closed-loop bio-refinery that sustains its own need for process solvents in addition to the production of bio-derived chemicals.[15] To convert bio-based compounds to IL cations or anions, a number of synthesis steps are required. Care must be taken not to offset the renewable character of the building blocks in the preparation of bio-ILs. This review reports on the major synthetic routes towards bio-based ILs and critically examines the applicability of the resulting ILs for dissolving bio-polymers. In addition, the applications of bio-based ILs as reaction media and catalysts and for extracting metals are discussed. We anticipate that this overview will facilitate the identification of scalable IL synthesis protocols with specific applications in mind.



Number of references	18	16	0	13	0	1	4	7
Typical synthesis	Acid base neutralization	Synthetic workup to charged heterocycles	N/A	Synthetic workup to charged heterocycles	N/A	Reductive amination of aldehydes	Acid base neutralization	Synthetic workup to charged heterocycles
Synthesis complexity	Very simple	Complex	N/A	Complex	N/A	Fairly simple	Simple	Complex

Figure 1: Synthesis pathways towards bio-based ILs. For each renewable resource class, typical derived monomers are depicted. The intensity of research (i.e. number of published papers) on converting these monomers to IL anions or cations is represented by the radius of the circle around the '-' or '+' sign, respectively. Typical synthetic routes and their complexity are mentioned where available.

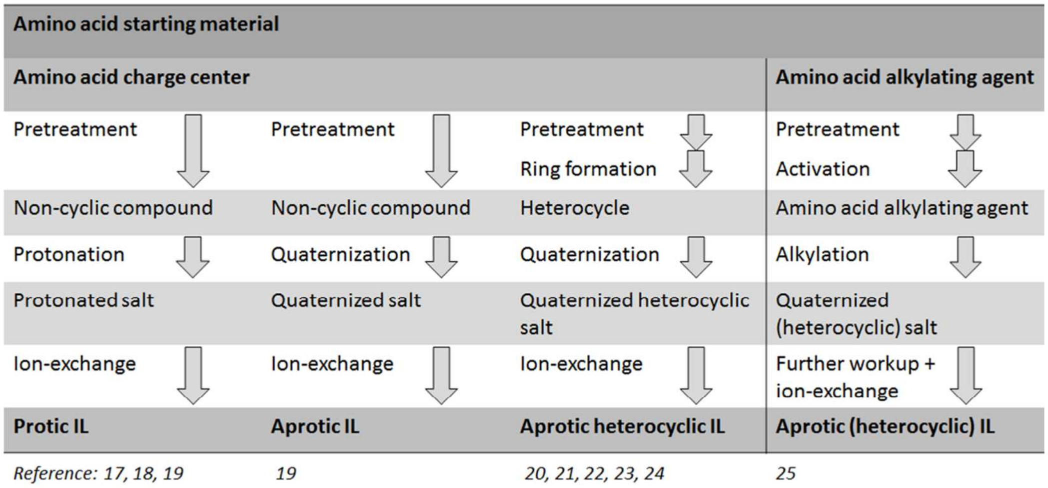
Bio-based IL synthesis

Figure 1 illustrates the major pathways to obtain bio-based ILs from different bio-polymer sources. By far, most reported bio-based ILs originate from proteins, with an approximate equal number of references describing the synthesis of IL anions and cations. In contrast, sugars resulting from the depolymerization of polysaccharides have only been converted to IL cations. Surprisingly, despite the wide availability of lignin waste, only a single report describes the synthesis of ILs from aromatic aldehydes obtained by lignin depolymerization.[15] While straightforward from a synthetic point of view, the latter example enabled proposing an integrated approach for processing lignocellulosic materials streams, thus illustrating the potential impact of a targeted IL synthesis effort with a well-understood application in mind. Therefore, in this review, we attempt to couple an overview of reported synthetic strategies with practical considerations for a series of suggested applications.

ILs derived from proteins

From Figure 1, it is clear that the bulk of research on bio-based ILs has been performed on the synthesis of IL cations and anions from protein-derived amino acids. Amino acids are derived from proteins by hydrolysis in various ways, followed by amino acid separation.[16] In the following part, different synthetic pathways are illustrated for amino acid-derived cations and anions. Generally, cation synthesis involves a number of steps while anions are typically obtained through simple acid base neutralization.

Table 1: Major synthetic pathways towards amino acid-based IL cations

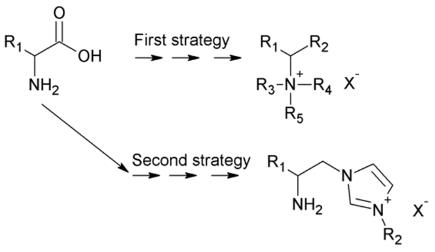


Amino acid starting material			
Amino acid charge center			**Amino acid alkylating agent**
Pretreatment	Pretreatment	Pretreatment Ring formation	Pretreatment Activation
Non-cyclic compound	Non-cyclic compound	Heterocycle	Amino acid alkylating agent
Protonation	Quaternization	Quaternization	Alkylation
Protonated salt	Quaternized salt	Quaternized heterocyclic salt	Quaternized (heterocyclic) salt
Ion-exchange	Ion-exchange	Ion-exchange	Further workup + ion-exchange
Protic IL	**Aprotic IL**	**Aprotic heterocyclic IL**	**Aprotic (heterocyclic) IL**
Reference: 17, 18, 19	*19*	*20, 21, 22, 23, 24*	*25*

Cations

In Table 1, the major synthetic pathways towards amino acid-derived IL cations are displayed. The first strategy entails the use of modified amino acids as positive charge carriers (amino acid charge center); the second employs amino acid-derived alkylating agents to quaternize on another *N*-containing molecule (amino acid alkylating agent) (exemplified in Scheme 1).

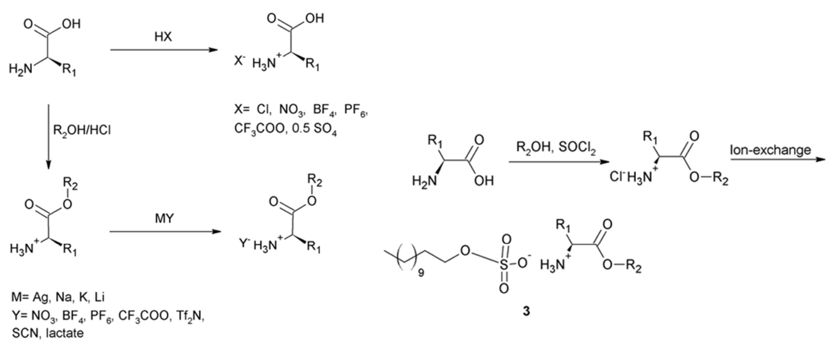
Scheme 1: Major strategies towards amino acid-based cation ILs



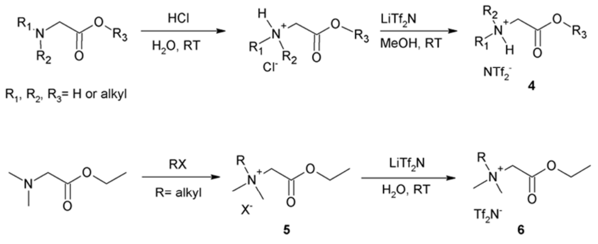
In both routes, a preliminary modification is typically performed, such as esterification of a carboxylic acid or the introduction of a protecting group. In the first route, following this pretreatment, a charge is introduced on the amino acid nitrogen atom, either by simple protonation or by quaternization through

N-alkylation. In many cases, a conjugated *N*-heterocycle is formed before *N*-alkylation to stabilize the introduced positive charge. In the second route, after pretreatment, the modified amino acid is activated and used to alkylate a tertiary amine, forming a quaternary ammonium compound with an amino acid-based side chain. The previous synthesis steps typically result in high-melting halide salts. To obtain ILs, the halide salts are subjected to ion-exchange, for example by using bistriflimide (Tf_2N^-) or tetrafluoroborate (BF_4^-) anions. Scheme 2 combines reaction schemes of the syntheses of ILs with protein-based cations.

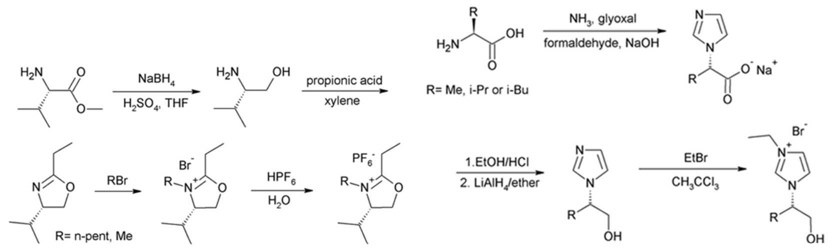
Scheme 2: Syntheses of protein based cation ILs



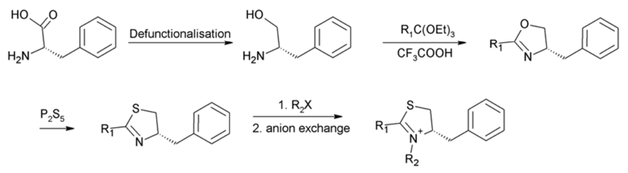
A: ILs derived from amino acids and amino acid esters. **B: Protic amino acid-based IL with lauryl sulfate anion.**



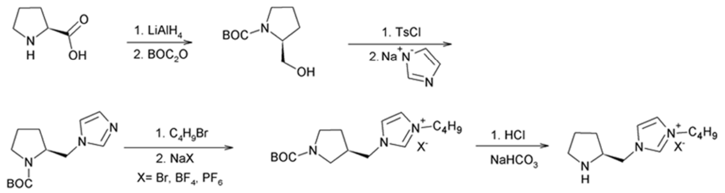
C: Glycine-based protic and aprotic ILs.



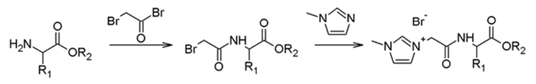
D: Amino acid-based dihydrooxazolium IL synthesis. **E: Synthesis of amino acid-based imidazolium ILs.**



F: Dihydrothiazolium IL derived from an amino alcohol.



G: Pyrrolidine based imidazolium ILs synthesis.



H: Synthesis of bio-IL with a neutral amino acid side chain.

Simple amino acid-based protic ILs were reported by Tao *et al.*, either by using the amino acids directly or after esterifying the carboxylic acid.**[17]** Amino acids and esters were acidified with an equimolar amount of strong acid (Scheme 2-A). By using different acids, more than 100 ILs were synthesized (**1**). Use of the amino acid esters greatly reduced the strength of the hydrogen bonding, resulting in lower melting temperatures (-18 to 75 °C) with almost half of them being room temperature ILs (**2**). However, most of the decomposition temperatures of these ILs, as determined by thermogravimetric analysis (TGA), were relatively low (150 -230 °C). The chirality of the amino acids was maintained in the ILs. In the report it is mentioned that some of the formed ILs can be considered the first completely biorenewable ILs, for example the ones with NO_3^- anions. However, it is questionable whether these protic ILs are stable under non-acidic conditions.

Another example of IL cations formed by amino acid protonation is described by Trivedi *et al.* They reported the synthesis of bio-based and biodegradable IL surfactants by combining amino acids and the renewable sodium lauryl sulfate.[18] The amino acids were first esterified using isopropyl or isobutyl alcohol. The obtained amino acid ester hydrochlorides were subsequently ion-exchanged with sodium lauryl sulfate resulting in clear, slightly viscous ILs (**3**) (Scheme 2-B). The melting point ranged from -22 °C to 56 °C and the termal decomposition temperatures from 221 °C to 280 °C. The use of a fatty acid-derived anion adds to the green character of these ILs and exemplifies fine-tuning the IL properties by using different fatty acid chain lengths.

He *et al.* reported the synthesis of glycine-based ILs.**[19]** *N*-unsubstituted and *N*-dialkylglycine ILs were synthesized by acidification of the corresponding glycine or glycine ester precursor with HCl (Scheme 2-C). These chloride compounds were subsequently anion-exchanged with $LiTf_2N$ in water to yield various low-melting protic ILs (**4**). Beside these protic amino acid-based ILs, also trialkyl-substituted ILs based on glycine were synthesized by alkylation of glycine ethyl ester using bromo- or iodoalkanes. This route resulted in aprotic halide ILs (**5**). Ion-exchange was performed on these halide ILs using $LiTf_2N$, resulting in lowered melting points (**6**). The protic ILs (**4**) have melting points between -48 °C and 50 °C and thermal decomposition temperatures ranging from 195 °C to 256 °C. The aprotic halide ILs (**5**) had melting points or glass transition points between 71 °C and 86 °C and decomposition temperatures between 196 °C and 238 °C. The bistriflimide-based aprotic ILs (**6**) had significantly lowered melting points (glass transition) between -64 °C and -59 °C and thermal decomposition temperatures between 199 °C and 240 °C. Incorporating the bistriflimide anion resulted in significantly lowered melting points but practically unchanged decomposition temperatures. Arguably, aprotic trialkyl substituted glycine-based ILs are more chemically stable than their protic counterparts and this research is an important step forward to the even more stable heterocyclic, quaternary *N*-based ILs, which resemble conventional imidazolium ILs.

One of the first *N*-heterocyclic amino acid-derived ILs was reported by Wasserscheid *et al.*[20] They describe the synthesis of dihydrooxazolium ILs based on valine methyl esters (Scheme 2-D). The amino acid ester was first reduced to valinol. Next, the intermediate was cyclized using propionic acid, yielding a 4,5-dihydrooxazole that was subsequently alkylated using bromopentane or bromomethane. Finally, the bromide salt was anion-exchanged using hexafluorophosphoric acid resulting in the 4,5-dihydrooxazolium hexafluorophosphate IL. This study was also the first example of a heterocyclic amino acid-based IL in which the precursor chirality was maintained. However, the overall yield was relatively low (40%), the stability in acid environment was limited and the melting points of the *n*-pentyl and methyl quaternized compounds were rather high at 63 °C and 79 °C, respectively.

Bao *et al.* reported the synthesis of chiral imidazolium ILs based on the amino acids valine, leucine and alanine.[21] In a first step, a condensation reaction was carried out between the amino acids and glyoxal under basic conditions and in the presence of formaldehyde to form an imidazole ring (Scheme 2-E). The resulting imidazole carboxylate salt was esterified with ethanol and subsequently reduced to an alcohol by using $LiAlH_4$, yielding for instance 2-(1-imidazolyl)-propyl alcohols when starting from alanine. Finally, the imidazolium ring was alkylated using bromoethane to yield the imidazolium bromide IL. The overall yield of this synthesis was 33%. The melting points of the obtained ILs were less than 80 °C and the ILs were found to be thermally stable to at least 180 °C.

Similar approaches were reported by Clavier *et al.*[22] and González *et al*.[23] In both cases, amino acids were transformed to imidazolium ILs, by using 2-*t*Bu-aniline or ammonium acetate as nitrogen source, respectively. The rest of the synthesis procedures was similar to the one proposed by Bao.[21] Several of the synthesized ILs were liquid at room temperature.

A number of 4,5-dihydrothiazolium ILs derived from the bio-based amino alcohol phenylalaninol were prepared by Plaquevent *et al*.[24] Phenylalanine is first reduced to phenylalaninol (Scheme 2-F). This route illustrates the different strategy in using bio-based building blocks compared to routes starting from petrochemicals. While the latter typically require functionalization, the former makes use of existing functionalities. The IL was subsequently prepared in four steps, by first reacting phenylalaninol with an orthoester, followed by sulfurization using P_2S_5 to yield 4,5-dihydrothiazole. Finally, this compound was alkylated using haloalkanes yielding 4,5-dihydrothiazolium halide salts which were then ion-exchanged. A number of the resulting ILs were liquid at room temperature.

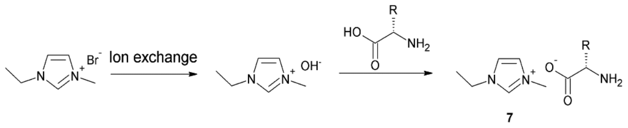
Luo *et al.* synthesized a series of chiral pyrrolidine-based ILs by coupling proline to an imidazolium ring.[25] Also in this case, the amino acid is first reduced to an amino alcohol by $LiAlH_4$, followed by Boc-protection (Scheme 2-G). This compound was subsequently reacted with *p*-toluenesulfonyl chloride and used to *N*-alkylate an imidazolate, followed by a second *N*-alkylation of the imidazole moiety using *n*-bromobutane. After Boc deprotection, the bio-based ILs were obtained as viscous oils with an overall yield of approximately 45%. Many different cations can be synthesized this way, by using other N-alkylating reagents.

Bio-IL cations with a neutral amino acid side chain were synthesized by Coleman *et al.*[26] Starting from amino acid esters, the amino-group was first acylated using bromoacetyl bromide, the resulting compound was used to alkylate 1-methylimidazole (Scheme 2-H). In another case, first two amino acid esters were coupled and subsequently treated with bromoacetyl bromide, followed by alkylation. Yields of 67-99% were reached. In one case, an antibiotic effect was detected towards *Methicillin resistant Staphylococcus aureus.*

Anions

The synthesis of IL anions from amino acids typically consists of neutralization of the amino acid. Because of its simplicity, this route is very atom efficient.[27] Ohno *et al.* reported the synthesis of 20 amino-acid-based ILs.[28] Their procedure started with passing an aqueous solution of 1-ethyl-3-methylimidazolium bromide over an Amberlite anion exchange resin (Scheme 3) to obtain the hydroxide form. This intermediate was subsequently neutralized using different protonated amino acids resulting in IL (**7**), with overall yields of 66-89%. Glass transition temperatures of the resulting ILs were between -65 °C and 6 °C, with a strong dependency on the amino acid side chain. The thermal decomposition temperatures of these ILs were not determined.

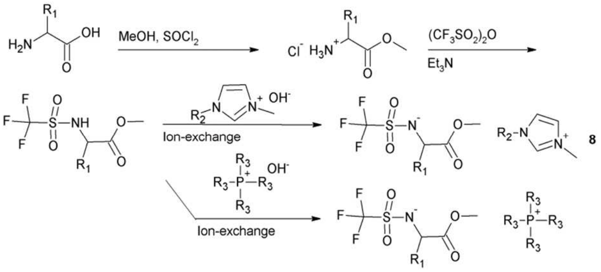
Scheme 3: Synthesis of an IL with an amino acid based anion



Kagimoto *et al.* reported on the synthesis of other cations than 1-ethyl-3-methylimidazolium to synthesize amino-acid-anion-based ILs.[29] First, alanine-based ILs were synthesized using tetrabutylammonium, triethylhexylammonium, N-butyl-N-methylpyrrolidinium, butylpyrrolidinium and tetrabutylphosphonium. The method employed was the same as in Scheme 3. In the case of butylpyrrolidinium, no IL was formed due to decomposition of the butylpyrrolidinium cation. The melting- or glass transition temperatures of the ILs were in the -70 to 76 °C range. The decomposition temperatures were rather low (150-176 °C) except for tetrabutylphosphonium alaninate. Due to the advantageous characteristics of the tetrabutylphosphonium alaninate IL, tetrabutylphosphonium ILs were synthesized based on 19 other amino acids, including lysine, threonine, tryptophan, etc. Glass transition temperatures of these amino acids were in the range of -70 °C to -4 °C. The thermal decomposition temperatures were quite high, from 220 °C to 319 °C.

Fukumoto and Ohno also reported on the synthesis of bio-ILs with a modified amino acid as the anion.[30] The amino acids alanine, valine and leucine were esterified with methanol and derivatized with a trifluoromethylsulfonyl group (Scheme 4). The resulting intermediate was neutralized with tetrabutylphosphonium hydroxide or 1-ethyl-3-methylimidazolium hydroxide. In contrast to the previously discussed amino acid-based anions, these IL anions carry the negative charge on the nitrogen atom rather than on the carboxylate. The resulting ILs can be significantly more hydrophobic. For instance, (**8**) is not water miscible in contrast to the 1-ethyl-3-methylimidazolium variants that have a carboxylate anion (**7**). The glass transition temperatures were in the -70 to -35 °C range while the thermal decomposition temperatures were around 250 °C.

Scheme 4: Trifluoromethylsulfonyl-derivatized amino acids as IL anions



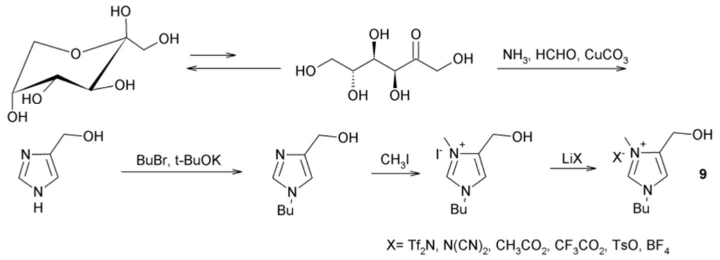
ILs derived from polysaccharides

Besides protein- or amino acid-derived ILs, another major scientific effort has been made to develop ILs based on sugars that are obtained by depolymerization of polysaccharides or by direct refining. The largest available source of polysaccharides is biomass cellulose, from which glucose can be extracted through depolymerization. Fructose can be extracted from plants, also making it an abundant feedstock. Since many potential processes for the breakdown of hard-to-dissolve polysaccharides depend at least partly on the use of ILs, it would be beneficial to develop sugar-based ILs that can be used in ‘closed-loop processing’ of the parent polysaccharides. So far, all research on sugar-based bio-ILs has focused on cation synthesis.

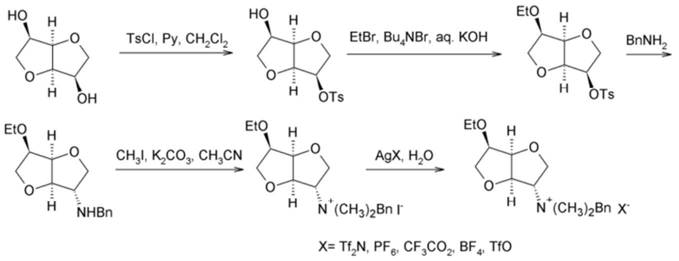
Cations

Table 2 summarizes the major synthetic pathways towards polysaccharide-derived IL cations. Similarly to the amino acid based ILs, there are two major routes in the synthesis of saccharide-based ILs. In a first approach, the saccharide is modified to form a heterocyclic compound and subsequently quaternized. Alternatively, the saccharide is activated and used as alkylating agent for a tertiary amine. As is the case for amino acid-based ILs, quaternization usually results in halide salts. These halide anions can be exchanged with other anions to lower the melting point, increase thermal stability or achieve other desirable characteristics. Scheme 5 combines reaction schemes of the syntheses of ILs with polysaccharide-based cations.

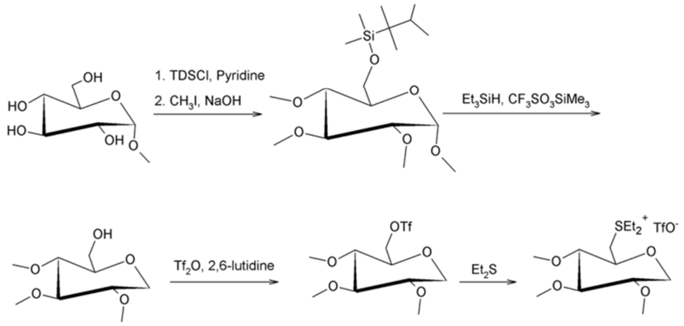
Scheme 5: Syntheses of polysaccharide based cation ILs



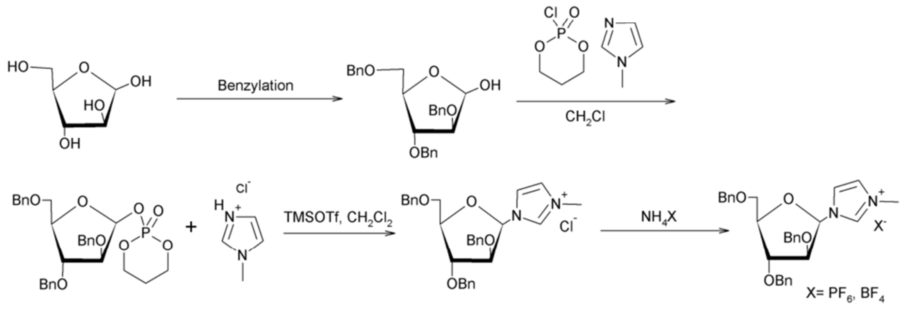
A: Fructose-based IL synthesis.



B: Synthesis of isomannide-based ILs.

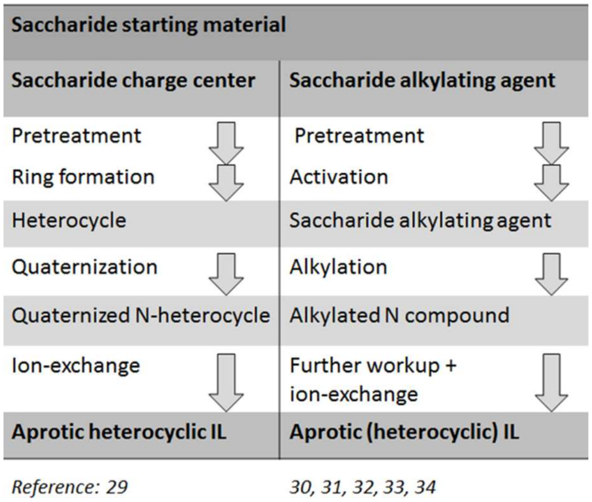


C: Synthesis of a glucopyranoside-based IL.



D: Synthesis of arabinose-based ILs

Table 2: Major synthetic pathways towards ILs with saccharide-based cations



Saccharide starting material	
Saccharide charge center	**Saccharide alkylating agent**
Pretreatment ⇩	Pretreatment ⇩
Ring formation ⇩	Activation ⇩
Heterocycle	Saccharide alkylating agent
Quaternization ⇩	Alkylation ⇩
Quaternized N-heterocycle	Alkylated N compound
Ion-exchange ⇩	Further workup + ion-exchange ⇩
Aprotic heterocyclic IL	**Aprotic (heterocyclic) IL**
Reference: 29	*30, 31, 32, 33, 34*

Handy *et al.* reported in 2003 on the development of bio-ILs based on fructose.[31] Fructose in the open-chain form was ring-closed by using ammonia and formaldehyde in the presence of 2 equivalents of copper catalyst, with a yield of 60% based on fructose (Scheme 5-A). The ring closed compound was *N*-alkylated using 1-bromobutane. Iodomethane was then used to *N*-methylate the second heterocyclic N, yielding an imidazolium cation. Finally, anion exchange was performed with a number of different anions to yield a series of ILs (**9**). The overall yield was around 40%. The resulting ILs were liquid at room temperature. No thermal decomposition experiments were performed.

Jain *et al.* reported the synthesis of glucose-tagged triazolium ILs (**10**)(Figure 2).[32] First, glucosylated alkyne and azide precursors were synthesized. These two precursors are then reacted with diisopropylethylamine by copper(I)-catalyzed cycloaddition of the alkyne with the azide. This stage was followed by a number of further synthesis steps including quaternization of the formed heterocycle by using iodomethane. The final products of this relatively complex procedure are three different glucose-tagged triazolium bio-based ILs.

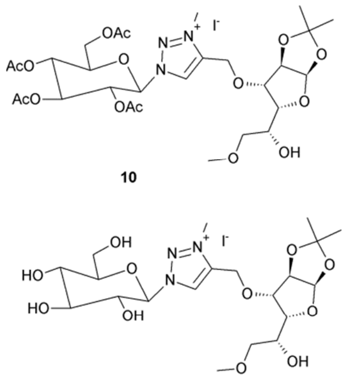


Figure 2: Glucose-based triazolium ILs

Isomannide was used by Kumar *et al.* to synthesize a number of tetraalkylammonium ILs in a similar approach as in the synthesis by Van Buu (see further).[33, 34] Isomannide can be derived from fructose via hydrogenation followed by double dehydration. The synthesis itself uses an activation step of one of the hydroxyl groups, followed by etherification of the other hydroxyl group (Scheme 5-B). Subsequently, the activated hydroxyl group is reacted with benzylamine followed by quaternization of the nitrogen atom by reaction with iodomethane. Finally, the iodide is anion-exchanged using a number of different anions. Unfortunately, only ILs with Tf_2N^- or PF_6^- anions were room temperature ILs, with the others having melting points between 80 °C and 170 °C.

Poletti *et al.* described the development of a glucopyranoside-derived IL.[35] Starting from O-methyl glucopyranoside, the primary hydroxyl group was protected using thexyl dimethylsilyl chloride (TDSCl) (Scheme 5-C). This step was followed by methylation of the remaining hydroxyl groups. The resulting compound was deoxygenated at C1 and the TDS protecting group was cleaved. The freed hydroxyl group was converted to the triflate and subsequently subjected to nucleophilic substitution reactions using diethylsulfide, resulting in an IL with a sulfonium cation and triflate anion. The final compound had glass transition and thermal decomposition temperatures of -53 °C and 200 °C, respectively.

Van Buu *et al.* reported on the synthesis of a chiral IL based on isosorbide.[34] Isosorbide is a commercially available glucose derivative that is produced on an industrial scale by the hydrogenation of glucose, followed by double dehydration. The synthesis procedure of the isosorbide-derived IL is relatively lenghty and entails the following six steps: (1) selective protection of one of the hydroxyl groups using benzylchloride, (2) activation of the other hydroxyl group as a benzenesulfonate, (3) reaction of the benzenesulfonate group with three different primary amines, (4) reaction of the formed secondary amines with formaldehyde to yield tertiary amines, (5) methylation of the tertiary amines using iodomethane and finally (6) cleavage of the benzyl protecting group on the first hydroxyl group using triflic acid. This last step also exchanged the I^- anion with triflate. The compounds formed after the last step were already ILs, but triflate was also exchanged in an additional step with bistriflimide anions to yield three other ILs. Five out of six of the formed salts were viscous oils at room temperature. The synthetic complexity of these ILs and the use of protection-deprotection chemistry diminishes the green character of these ILs, even though bio-based isosorbide is used as the starting material.

In 2008, the synthesis of imidazolium-like ILs from arabinose was reported.[34] Arabinose can be synthesized from glucose, but is also a part of hemicellulose and pectin. IL synthesis starts by benzylating all but one of the hydroxyl groups of arabinose, forming 2,3,5-tri-O-benzyl-d-arabinofuranose (Scheme 5-D). The last hydroxyl group of this compound is then reacted with propane-1,3-diyldioxyphosphoryl chloride. This step was followed by reaction with 1-methylimidazolium chloride to yield an IL with chloride as the anion. Finally, this chloride IL was subjected to anion exchange. The glass transition temperatures of the resulting compounds ranged from -36 °C to 18 °C.

An interesting synthesis of a chitin-based IL was reported by Huang *et al.* [36] According to the authors, it was the first reported synthesis of an polysaccharide-containing IL. In the synthesis, biologically sourced chitin is first partially deacetylated to chitosan which is subsequently reacted with chloroacetic acid to yield carboxymethylated chitosan in the sodium salt form. After purification, protonated carboxymethylated chitosan is obtained. This compound is then mixed with 1-ethyl-3-methylimidazolium hydroxide in equimolar amounts according to the number of carboxylic groups on the chitosan. The resulting carboxymethylated chitosan IL (Figure 3) had glass transition and thermal decomposition temperatures of -80 °C and > 300 °C, respectively.

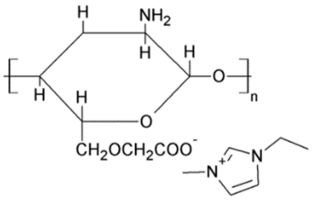


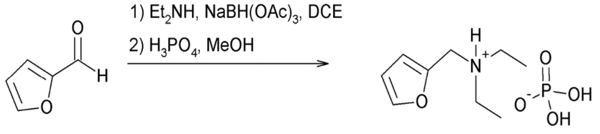
Figure 3: Chitosan-based IL.

ILs derived from lignin

Lignin is abundantly available, as it is a major constituent of woody plant residuals. To establish a bio-based, closed-loop economy, it would be beneficial to have the ability to process lignin with ILs derived from lignin itself. It is well-researched that lignin can be refined and processed using certain ILs.[8] However, little work has been done on the development of lignin-based ILs.

Thus far, the only example of a lignin-based IL was reported by Socha *et al.* in 2014.[15] Lignin-derived furfural was first reacted in a reductive amination with diethylamine, followed by protonation of the tertiary amine using phosphoric acid (Scheme 6). This simple method yielded a furfural-based protic IL (**11**) that is liquid at room temperature. Note that this method is similar to the one used by Tao and others in the synthesis of protic IL cations from amino acids.

Scheme 6: Lignin based IL synthesis



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ILs derived from other bio-based sources

Beside proteins, sugars, polysaccharides and lignin, there are a number of other bio-sourced molecules that can be used to synthesize ILs. Examples are fatty acids, alkaloids, *etc*. In the following section, a short description will be given of some syntheses involving these building blocks.

Cations

The group of Kwan *et al.* reported the synthesis of lipid-based ILs.[37] In a first case, the double bond in oleic acid methyl ester was first transformed into a cyclopropyl moiety by using diiodomethane and diethylzinc in a second case, methyl oleate or methyl stearate were used as such. Starting from these three fatty acid chain types, the carboxylic acid methyl ester group was reduced to a hydroxyl group which was subsequently activated by conversion to a mesylate group and reacted with sodium iodide. The obtained alkyliodide was reacted with 1-methyl imidazole or 1,2-dimethyl imidazole and the iodide was exchanged with bistriflimide resulting in imidazolium bistriflimide ILs. Melting points for the six resulting ILs were found to be dependent on both the type of fatty acid chain and the imidazolium substituents. The lowest melting temperature of -21 °C was achieved using the 1-methyl imidazolium cation and oleic acid, while the highest melting temperature of 70 °C was achieved by using 1,2-dimethyl imidazolium and saturated stearic acid. Similar to the preparation of some amino acid- and saccharide-based ILs, this synthesis is another example of using a modified bio-based compound to alkylate a tertiary amine.

Anions

Parmentier *et al.* described how oleate and linoleate can serve as anions for tetraalkylammonium cations.[38] Four ILs were synthesized; tetraoctylammonium linoleate, methyltrioctylammonium oleate, methyltrioctylammonium linoleate and tetraoctylammonium oleate. The synthesis consisted simply of neutralizing the fatty acid first with NaOH, followed by ion exchange with tetraalkylammonium chlorides. The resulting ILs all had melting points below -25 °C, but the thermal decomposition temperatures were relatively low (around 170 °C). These ILs have been used for solvent extraction of metal ions.

The group of Gausepohl *et al.* reported the use of malic acid as an IL anion building block.[39] Malic acid is present in large quantities in some plants but is currently mainly produced synthetically. The synthesis consisted of two steps, starting with malic acid dimerization in the presence of $B(OH)_3$ and NaOH. The Na^+ ions were subsequently exchanged using methyltrioctylammonium chloride to yield an IL with a melting point of -32 °C.

Lastly, many other biobased compounds like alkaloids have been used to make ILs. Examples include nicotine based ILs by Wilhelm *et al.*[40], ephedrine based ones by Truong *et al.*[41] and ampicillin based ILs by Ferraz et al.[42] Although many of these compounds can be used as flexible building blocks for bio-ILs, their limited supply makes their widespread industrial use questionable.

Applications

To get a better understanding of the possible practical implementation of the bio-based ILs described above, a selected number of applications are discussed: bio-polymer processing in ILs, ILs as reaction media and metal ion separation using ILs. While many conventional ILs have been described for use in these domains, there exists considerably less research on the application of bio-based ILs. Based on their structure, thermal stability and other characteristics, bio-based ILs will be compared with the conventional ILs confirmed to be useable in the selected processes.

General practical considerations

When implementing any IL in an industrial process, a number of practical considerations must be taken into account. First, the ILs need to be thermally stable under the process conditions for a long period of time. For most of the bio-ILs described earlier, the thermal decomposition temperatures have been reported. However, these are usually measured using dynamic thermogravimetry with relatively fast heating rates, often under inert gas atmosphere. When assessing bio-ILs for process implementation, more thorough thermal stability tests are required, for example by using relevant temperatures for a relevant duration and by working under the same atmosphere and pressure as the actual process. Generally, accelerated aging protocols need to be developed and preferably standardized. The chemical stability of ILs needs to be evaluated in detail as well. For example, it is questionable whether the simple protic amino acid cation ILs are useable in many chemical environments because of the expected limited stability of the protonated tertiary nitrogen. Also, in certain cases, anion exchange could occur, followed by volatilization of the protonated acid (e.g. acetic acid for ILs with acetate anions) and/or degradation of the original IL anion.[6] In certain processes, anion exchange issues force the use of a limited set of anions, potentially resulting in ILs with less favorable characteristics (e.g. higher viscosity or melting point). This compromise is for instance observed in PVC dehydrochlorination, which imposes the use of ILs with chloride anions.[6]

Regarding the green character of bio-based ILs, it should be noted that some of the syntheses described above are less efficient than others. For example, quite a few syntheses use protecting agents and large quantities of catalysts. These all lower the atom efficiency and green character of the resulting ILs. However, since the produced bio-ILs are meant to be reused a considerable number of times, these problems can be somewhat alleviated. Furthermore, when using biomaterials to synthesize ILs, defunctionalization instead of functionalization of the starting material is often key. In contrast to conventional petroleum-based Ils, this characteristic benefits the atom efficiency and overall green character of bio-based ILs since less auxiliary chemicals are needed. To further increase the green character of these ILs, one possible strategy is to combine bio-based cations and anions or using bio-based alkylating agents to quaternize bio-based tertiary amines.

In the following sections, the possible application of bio-based ILs in several applications will be discussed with special attention to practical aspects. Because of the limited research on the application of bio-ILs, literature data on the use of conventional ILs will be used to examine the potential of bio-based ILs in the selected processes.

Bio-polymer processing in bio-ILs

Certain bio-polymers, such as starch and proteins, are effienctly processed industrially in aqueous media because of their easy depolymerization. In contrast, the depolymerization of lignocellulose, necessary to enable conversion into value-added chemicals, typically requires high temperatures, harsh chemical conditions or enzymes. The primary cause for the difficulties in depolymerization is the near-insolubility of this feedstock in conventional solvents. In lignocellulose, efficient hydrogen bonding between the polysaccharide chains results in a high degree of crystallinity and insolubility. To facilitate chemical or enzymatic depolymerization, the cellulose component is therefore pretreated to reduce the crystallinity. Usually the pretreatment steps consist of mechanical treatment (e.g ball-milling), steam explosion or high-temperature treatment in dilute acids or bases.[15]

A different pretreatment option is to dissolve the crystalline biopolymer in an IL, to make the cellulose chains more accessible to depolymerization agents. The IL anion type is the main determining factor in cellulose dissolution capacity, with chloride ions typically being the most beneficial choice for breaking interchain bonds, due to their hydrogen bond-accepting characteristics.[43] Therefore, most ILs with bio-based anions are likely not suitable as cellulose dissolution media. Shorter alkyl chains on the IL cation are beneficial but the effect is less pronounced than the anion choice. Among the best reported ILs for cellulose dissolution are [BMIM][Cl], [EMIM][CH_3COO], [EMIM][Cl] and [BMPy][Cl].[2, 44, 45] Notably, some ILs have also been used to dissolve lignin, for example [BMIM][Cl], [EMIM][CH_3COO] and [BMIM][$MeSO_4$].[46, 47] Also in this case, the anion played the most important role in the dissolution capacity of the ILs. Large, uncoordinating anions like PF_6^- do not work well.

After cellulose dissolution, lignocellulose constituents that remain insoluble (e.g. lignin and hemicellulose) can be simply removed. Subsequently, water can be added as a non-solvent to reprecipitate cellulose as an amorphous material that is more easily depolymerized. Lignin removal is beneficial since it can interfere with the cellulose depolymerization, for example by enzyme poisoning.[48] After cellulose reprecipitation by adding water, the IL must be regenerated for the following process cycle in a thermally intensive evaporation step to remove the water. It is therefore paramount that ILs selected for lignocellulose pretreatment are stable for prolonged times at the regeneration temperature, even though the dissolution process itself can take place at lower temperatures. In the following parts, thermal stability is hence taken as the most important IL paramater to estimate the practical use potential, beside dissolving ability.

While the dissolution of cellulose, lignin[44] and other bio-polymers[49] in conventional ILs has been intensely studied, few reports exist on the use of bio-based ILs for this purpose, which is nevertheless a requirement for a closed-loop process. Socha *et al.* reported in 2014 the first pretreatment of lignocellulose material by ILs derived from the same lignocellulosic feedstock.[15] After pretreatment, the biomass is enzymatically saccharified to yield sugars and residual lignin and hemicellulose. The latter constituents are further depolymerized by pyrolysis, biological treatment or catalyzed oxidation.[15] The resulting aromatic aldehydes are used to synthesize the bio-based ILs (**9**) used in the initial process stage. These ILs were shown to be excellent pretreatment solvents, comparable to the conventional IL [EMIM][Cl], efficiently dissolving cellulose and removing lignin under moderate conditions (3h at 160 °C). Furthermore, the estimated costs of $12/kg for the lignin-derived bio-IL is approximately half of that of the conventional IL. However, no stability or reuse tests were reported.

In addition to this system, especially amino acid- and saccharide-derived dihydrooxazolium, imidazolium and triazolium ILs seem promising to test for lignocellulose pretreatment, especially when combined with chloride or acetate anions, due to their resemblance to conventional ILs well-characterized for this application. Most of these suggested bio-ILs have reported thermal decomposition temperatures of at least 150 °C. However, as stated above, these data are typically extracted from fast thermogravimetric analysis, often not under process-relevant conditions.

Energy-intensive water evaporation, which is necessary when biopolymers are reprecipitated from the IL solution, is a constraint on IL thermal stability. This step can be skipped if the dissolved biopolymer is depolymerized directly in the IL medium. For example, Ignatyev *et al.* reported that cellulose could be converted to alkylglycosides using [BMIM][Cl] in combination with a solid acid Amberlyst catalyst at 110 °C.[50] Other catalyst-IL systems have been used to depolymerize cellulose, such as [EMIM][Cl] in combination with sulfuric and methanesulfonic acid at 90 °C.[51] Similarly, various imidazolium ILs have been applied for lignin depolymerization. For example, Stärk *et al* used [EMIM][CF_3SO_3] in combination with $Mn(NO_3)_2$ at 100 °C to achieve 63% lignin conversion to various industrially interesting aromatic aldehydes.[52] The same IL was used in combination with a Brønsted acid instead of $Mn(NO_3)_2$, but reaction temperatures were higher (200 °C) and conversions lower.[53] Cox *et al.* reported on the use of the protic acidic IL [HMIM][Cl] to depolymerize lignin at 110 °C.[46] From these reports, it is clear that the conventional ILs capable of dissolving lignin and/or cellulose are similar to the ones that can be used as media for catalytic bio-polymer depolymerization.

Nanoparticle catalyst stabilization is another way in which bio-IL reaction media could facilitate biopolymer breakdown. Interestingly, nanoparticles in conventional ILs have been used in processing lignocellulose and derived products. For example, Ignatyev *et al.* reported that besides its use as a cellulose solvent, [BMIM][Cl] could also assist the depolymerization of this biopolymer by using a heterogeneous Pt or Rh catalyst and a homogeneous Ru catalyst in the presence of H_2 at 150 °C. This approach resulted in full cellulose conversion and a 51% combined sorbitol and glucose yield, besides other small molecules.[54] Zhu and coworkers reported the use of a boric acid functionalized IL (**12**) (Figure 4) to stabilize Ru(0) nanoparticle catalysts in combination with [BMIM][Cl] for the one-step conversion of cellulose (94% at 80 °C) to sorbitol. Both IL constituents of this reaction medium could potentially be replaced with bio-based alternatives, resulting in a greener system. IL-nanoparticle systems have been used for lignin processing as well. The use of Pd nanoparticles, generated *in situ* from H_2PdCl_4 in [BMIM][$MeSO_4$], in combination with *N*-pentyl-4-methylpyridinium iron bis(dicarbollide) as a co-catalyst resulted in 72% lignin conversion (18h, 120 °C) to aromatic aldehydes. The catalyst system could be reused at least 3 times without significant loss of activity.[55] Also in this case, the [BMIM] cation could potentially be replaced with a bio-based one.

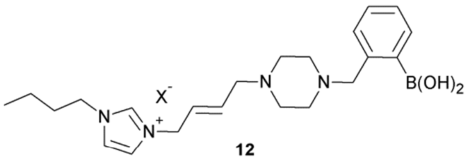


Figure 4: Boric acid functionalized IL.

As is clear from the above, direct processing of dissolved biopolymers in ILs is in some cases possible under relatively mild conditions. Nevertheless, IL thermal stability will in most cases still be the limiting factor when optimizing reaction conditions. It should also be noted that at maximum biopolymer dissolution capacity, the viscosity of the IL system rises to such an extent that depolymerization at these high substrate concentrations becomes unfeasable.[54] Interestingly, however, the use of the protic IL [HMIM][Cl] in lignin depolymerization indicates the potential use of protic bio-based ILs (e.g. **1-4**) in this process. The latter class of bio-ILs might even have an advantage over the conventional ILs currently tested because they lack the imidazolium moiety that has been linked to difficulties in separating aromatic lignin depolymerization products from the IL due to π-π interactions.[56]

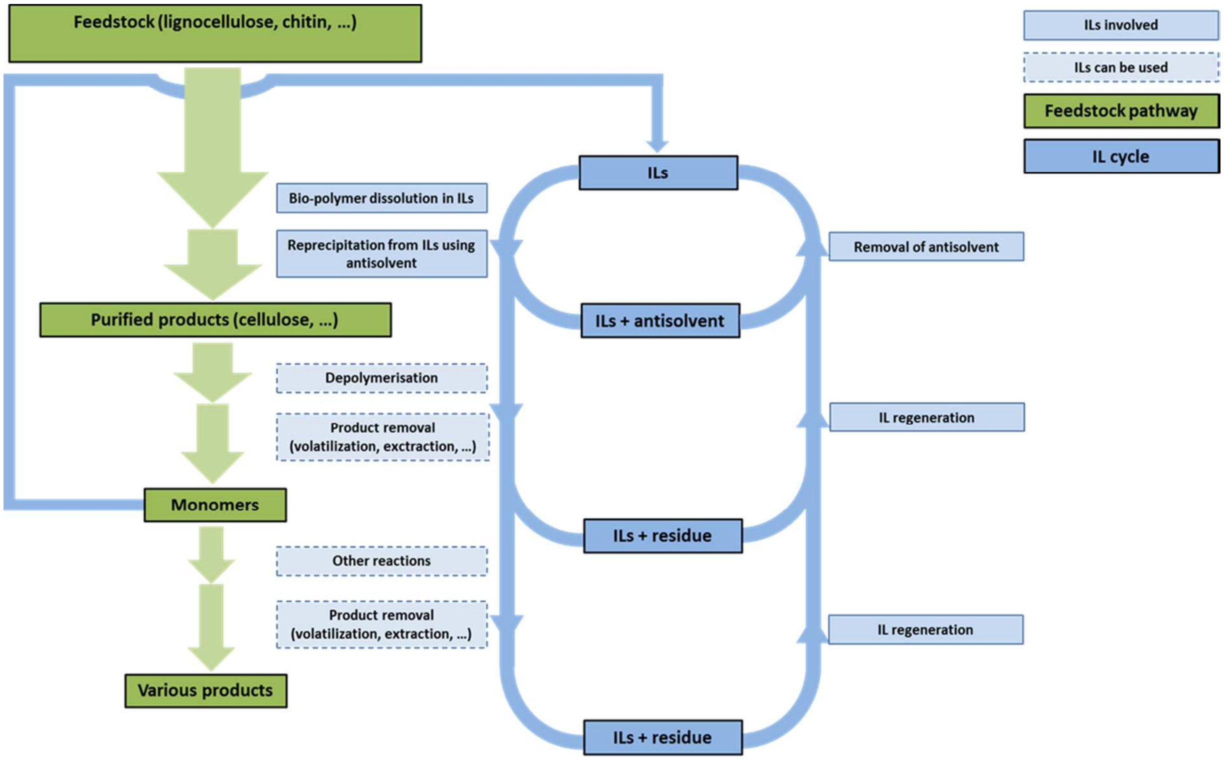


Figure 5: Flow scheme of closed-loop bio-polymer processing using ILs.

Further downstream processing, beyond biopolymer depolymerization, can be performed in IL media as well. For example, Chen *et al.* demonstrated the use of *in situ* generated Cr(0) nanoparticles stabilized in [EMIM][Cl] as a dehydration catalyst to convert glucose into 5-hydroxymethylfurfural (HMF) with a 49% yield at 120 °C.[55] Interestingly, cellulose depolymerization to glucose (e.g. in [BMIM][Cl]) and further conversion into HMF can be performed in similar ILs, hinting at the possibility to develop an integrated approach, potentially based on bio-ILs. The IL synthesized by Handy *et al.* (**9**) could be an interesting starting point to investigate this concept, for example by varying the alkyl chains on the imidazolium core or changing the anions [57]. A major advantage of bio-based ILs in the downstream processing of biomonomers, for instance to pharmaceuticals, is the chirality intrinsic in many compounds. This aspect will be elaborated on in the next section. Figure 5 summarizes the process flows of bio-polymer pretreatment, possible subsequent depolymerization and conversion to value-added chemicals, regeneration of the ILs, possibly in a closed-loop system.

Bio-ILs as reaction media and organocatalysts

A number of bio-based ILs have been described as solvents and/or organocatalysts for various reactions. Many of these processes target asymmetric synthesis by taking advantage of the retention of chiral moieties present in the starting materials (e.g. amino acids). In contrast to bio-polymer processing, much more research has been done on the use of bio-based ILs as solvents and organocatalysts. As is the case in lignocellulose treatment, these processes require the removal of products and process aids (e.g. conventional solvents) or another form of IL regeneration, for instance by distillation or extraction. As these operations frequently rely on thermal treatments, often harsher than during the reaction itself, the thermal stability of selected ILs remains a key issue. Scheme 7 combines reaction schemes performed with bio based ILs.

Miao *et al*. reported the use of ILs containing a chiral proline group for the direct asymmetric aldol reaction of 4-cyanobenzaldehyde with acetone.[58] The IL was synthesized by esterification of an imidazolium bearing a hydroxypropyl group with hydroxyproline. Reactions were performed at room temperature in DMSO or the pure ketone with 30 mol% IL catalyst, resulting in a conversion and enantiomeric excess (ee) of 59% and 72%, respectively. Various other aldehyde and ketone substrates were tested using the same chiral bio-IL (Scheme 7-A), with yields between 50% and 90% and ee's of 70-90%. The IL catalyst could be reused up to 4 times without loss of activity. Due to the low reaction temperatures used in this reaction and the ease of product separation, many other bio-based ILs with a chiral moiety could be tested for similar aldol reactions.

Luo *et al.* reported on the use of proline-based bio-ILs as efficient catalysts for the asymmetric Michael addition of cyclohexanone to nitroolefins (Scheme 7-B).[25] Reactions were performed at room temperature with 15 mol% of IL and 5 mol% of trifluoroacetic acid (TFA) co-catalyst without additional solvents. Near-quantitative yields were reached with some ILs, while enantiomeric excess was in the 95–99% range. The IL could be reused up to three times without loss of activity.

Jain *et al.* reported the synthesis of glucose-tagged triazolium ILs (**10**) and the application of these compounds as organocatalysts in the amination of iodo-, bromo- and chlorobenzenes with aqueous ammonia, using CuI and THF as catalyst and cosolvent, respectively (Scheme 7-C). In the absence of ILs, amination did not occur, while the use of 20 mol% IL resulted in conversions of up to 82% at 90 °C.

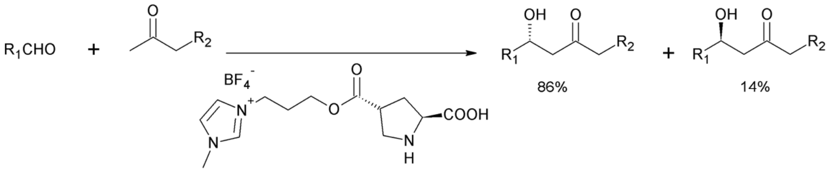
The methyltrioctylammonium (MtOA) malic acid-based IL synthesized by Gausepohl *et al.* (**13**) was used as chiral reaction solvent in the aza-Baylis-Hillman reaction of activated alkenes with imines (Scheme 7-D),[39] resulting in 35% conversion and 84% ee. No other solvent was used beside the IL. This study was the first example of an asymmetric reaction in which the chirality was induced completely by the IL solvent. The absence of other solvents in the reaction simplifies product removal and IL regeneration and diminishes thermal degradation of the IL since solvent-solvent separation by distillation is avoided.

The fructose-derived ILs synthesized by Handy *et al.* (9) were used as protic solvents for the Heck reaction between methyl acrylate and various aryliodides, catalyzed by palladium acetate (Scheme 7-E).[31] Conversions of around 95% were reached at 100 °C after only 1h. The IL-catalyst systems can be reused at least 5 times and regenerated simply by washing with water and drying at 80 °C in vacuum.

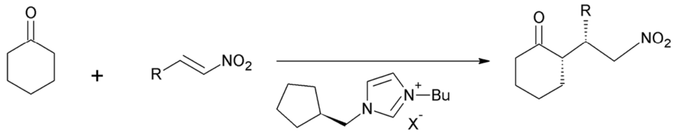
Wu *et al.* used the completely natural IL [choline][proline] (30 mol%) as a catalyst in aqueous solution to couple various ketones and aldehydes with a yield of up to 99% at room temperature.[59] The IL was reuseable for up to 4 times without significant loss of activity. This example illustrates the feasibility of using purely bio-based ILs and the opportunities that lie in the many possible combinations of bio-based cations and anions described earlier. Care should be taken that the functional groups present in most bio-ILs do not interfere with the catalyzed process, for instance by participating in side reactions. If required, defunctionalized bio-based ILs could be developed. However, in such cases a suitable IL could potentially be synthesized more efficiently from less functionalized petroleum-derived starting materials.

Gathergood and Bouquillon *et al.* used a range of tetrabutylammonium based ILs with bio-based anions like lactic acid and pyruvic acid as ligands for the $PdCl_2$ catalyzed selective hydrogenation of 1,5-cyclooctadiene to cyclooctene, with water as a co-solvent (Scheme 7-F).[60] It was found that these IL-catalyst systems gave better conversions towards cyclooctene than systems without ILs or systems using BMIM ILs. In the latter cases, more side-products like cyclooctane, 1,4-cyclooctadiene or 1,3-cyclooctadiene were formed. Full conversion of 1,5-cyclooctadiene with around 90% selectivity for cyclooctene was reached using tetrabutylammonium succinate. The same authors also reported on the use of a tetrabutylammonium prolinate IL for the Pd-catalyzed enantioselective hydrogenation of α,β-unsaturated ketones.[61]

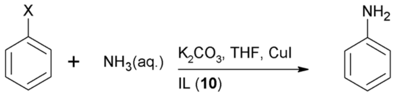
Scheme 7: Reactions performed using bio based ILs



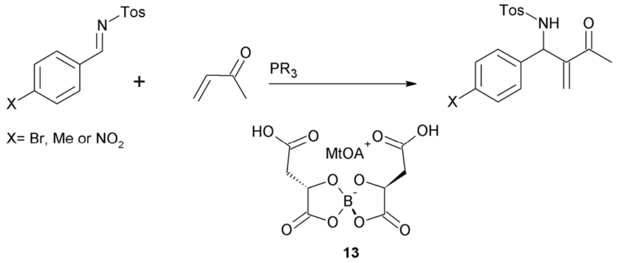
A: Aldol reaction catalyzed by proline-tagged ILs.



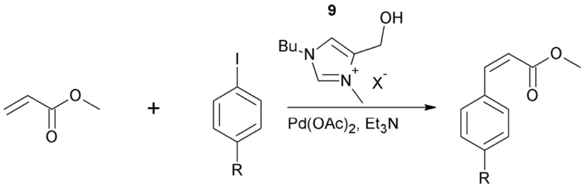
B: Asymmetric Michael addition using chiral proline-tagged ILs.



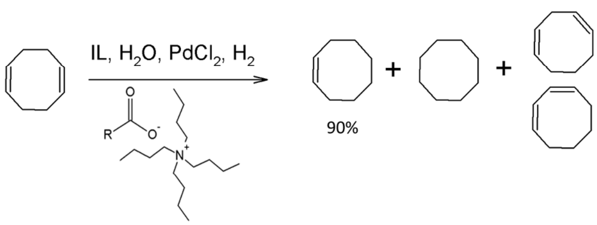
C: Amination assisted by glucose-tagged triazolium ILs.



D: Aza-Baylis-Hillman reaction assisted by a malic acid-based chiral IL.

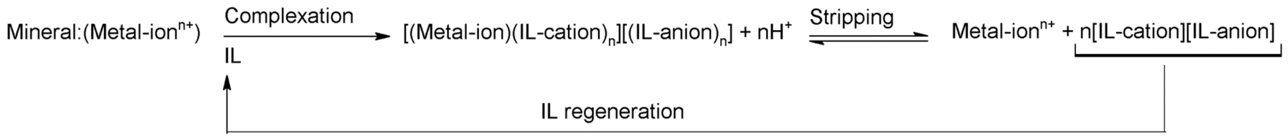


E: Heck reaction using fructose-derived IL.



F: Selective hydrogenation of 1,5-cyclooctene using bio-ILs

Scheme 8: Separations of metal ions using ILs



Metal ion separations in bio-ILs

As suggested by their ability to stabilize metal nanopoarticles, the presence of functional groups in bio-based ILs can be leveraged to chelate and extract metal ion species. Metal ion extraction from aqueous phases requires less harsh thermal and chemical conditions than typical reaction media, therefore providing opportunities to apply a wider range of bio-based ILs. It is worth mentioning that some organic molecules can also be extracted with ILs.[62] This however falls beyond the scope of this review and will not be discussed further.

To perform the extraction process efficiently, hydrophobic ILs that spontaneously phase separate from water are required. As many bio-based ions are relatively hydrophillic, hydrophobicity should be introduced. In conventional ILs, hydrophobicity is often achieved using fluorinated anions such as Tf_2N^-, that could be used in conjunction with bio-based cations as well. However, bio-based anions based on fatty acids could possibly replace these expensive and sometimes toxic fluorinated anions.[14] Alternatively, bio-based long-chain alkylating agents could be used in the synthesis of hydrophobic cations.

Different mechanisms for IL-based metal extractions have been reported, including the formation of neutral complexes that subsequently migrate to the IL phase and the formation of anionic complexes that exchange with the IL anions.[63] However, the most common mechanism for bio-ILs is through complexation of the metal ions by the functional groups on the IL cation and/or anion.[63] In this case, extractions are performed by mixing under strong agitation the aqueous metal ion solution with the hydrophobic IL, if needed under heating. After phase separation, the metal ions are stripped from the IL phase by an acid (Scheme 8).

Binnemans *et al.* described metal extractions using an IL derived from betaine, a sideproduct of sugar production from beetroots.[64] Betainium bistriflimide ([Hbet][Tf_2N]) was synthesized by dissolving HbetCl and $LiTf_2N$ in water, followed by spontaneous phase separation.

Extractions were performed by mixing this IL for 10 min with an aqueous Sc(III) chloride solution at 70 °C. After the mixture was allowed to cool and phase separate, the residual metal concentration in the aqueous phase was determined. In most cases, around 95% of Sc(III) could be removed, depending on the pH of the aqueous phase among other parameters. Other rare earth metals were also tested but it was found that the [Hbet][Tf_2N] only has a high affinity for Sc(III), which is beneficial in rare earth separation. After extraction, Sc(III) was stripped using an acid (analogous to Scheme 8):

$$[Sc(bet)_3][(Tf_2N)_3] + 3H^+ \rightleftharpoons 3[Hbet][Tf_2N] + Sc^{3+}$$

After washing with water to remove residual acid, the IL could be reused with only minor drops in extraction efficiency, to 90%. Since the extraction mechanism relies on deprotonation-protonation of the betaine carboxylic group, other protic ILs, such as the bio-based ones synthesized by Tao *et al.*, Trivedi *et al.* and He *et al.* (**1**-**4**), could be interesting for metal ion extraction, as long as the right anion is used to make the IL hydrophobic.

The same authors also combined the bio-based choline ($Chol^+$) cation with Tf_2N^- and hexafluoroacetylacetone ($hfac^-$) anions, to obtain the ILs [Chol][Tf_2N] and [Chol][hfac].[65] These ILs were used to extract Nd(III) salts from an aqueous feed in a homogeneous liquid-liquid extraction system by shaking for 3 min at 80 °C. Extraction and recovery efficiencies close to 100% were reached. Unfortunately, the $hfac^-$ anion proved to be relatively unstable upon heating and storage.

Fatty acid-based anions combined with tetraalkylammonium and tetraalkylphosphonium cations were used in metal separations.[38,66] The synthesis of these oleate and linoleate ILs is described in Section 1.4.

It was found that phosphonium cations are preferred over ammoniums due to their improved thermal stability. The fatty acid-based ILs were used to extract a great number of metal ions, including transition metals, alkali, alkaline earth metals and rare earth metals. Most of these metals could be extracted efficiently from aqueous solutions. In the case of tetraalkylammonium oleate or linoleate ILs, alkali metal salts were hardly extracted, while a high affinity for period IV metal salts was found.[38] In the case of tetraalkylphosphonium oleate ILs, the extraction selectivity could be fine-tuned to a great extent by varying the pH of the watery solution. For example, rare earth metals are not extracted at pH values lower than 5 whereas Zn, Cu, Fe and In do get extracted at those pH levels.[66]

These and other examples of ILs with different metal ion affinities suggest an integrated IL-based approach for hard-to-separate metal ion mixtures.[67] Because of their high degree of functionalization, bio-based ILs could play an interesting role in a sustainable approach to such processes. Undoubtedly, there remains plenty of opportunities in this field. For instance, since [BMIM][Tf_2N] ILs have been studied extensively for metal ion separations, it would be interesting to test bio-ILs based on imidazolium and related cations as well, as long as the anion choice results in a sufficiently hydrophobic IL.[68]

Conclusion

Bio-based ILs offer an interesting alternative to conventional ILs and solvents. Whereas conventional ILs are synthesized from petroleum-derived starting materials, bio-ILs are based on renewable and widely available feedstocks. Nevertheless, as discussed in Section 1, some bio-based ILs syntheses consume large amounts of environmentally unfriendly and non-renewable reagents. Work needs to be done to reduce the use of such chemicals in the synthesis of bio-based as well as conventional ILs. Most bio-based ILs reported so far are based on either amino acids or sugars. Although highly interesting, few examples of bio-based ILs synthesized from lignin degradation products have been reported, leaving many opportunities in this area. The application of bio-based ILs has been described in a number of fields. Still, many possible uses of bio-based ILs have not yet been explored in depth, including some currently relying on conventional ILs. Examples include lignocellulose processing, organic transformations and metal ion separations. In addition to a well-designed chemical functionality, it is crucial that ILs suggested for a given application possess long-term stability under relevant process conditions. While the chemical and thermal stability of bio-based ILs varies, so do the requirements in the wide range of processes that could benefit from such solvents. Moreover, exciting opportunities exist in fine-tuning the properties of fully bio-sourced ILs by the surprisingly uncommon approach of combining cations and anions that are both bio-based.

ASSOCIATED CONTENT

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Author Contributions

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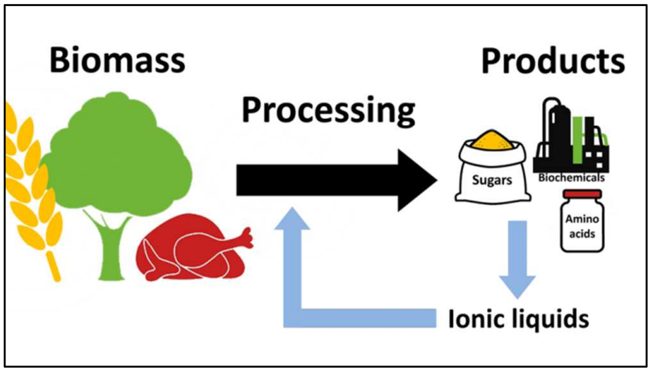

Synopsis:

This perspective describes bio-based ionic liquids, their synthesis and how they can be applied in a modern, green chemical industry.

Manuscript title:

‘Bio-based ionic liquids: solvents for a green processing industry?’

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Biographies and photos:

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Koen Binnemans obtained his M.Sc. (1992) and Ph.D. (1996) degrees in Chemistry at the University of Leuven (KU Leuven). In the period 1999–2005, he was a postdoctoral fellow of the Research Foundation Flanders. He did postdoctoral work with Prof. Dr. Jacques Lucas (Rennes, France) and Prof. Dr. Duncan W. Bruce (Exeter, United Kingdom). In 2000, he received the first ERES Junior Award (ERES: European Rare-Earth and Actinide Society). From 2002 until 2005 he was (part-time) associate professor, from 2005 until 2010 professor, and presently he is full professor of chemistry at the University of Leuven. He has published over 360 papers in international scientific journals. He made significant contributions to the field of ionic liquids. His current research interests are the use of ionic liquids for solvent extraction, battery applications and processing of polymers, the separation of rare earths, and the recycling of critical raw materials.

Rob Ameloot was born in Hasselt (Belgium) in 1985. He obtained his PhD in Bioscience Engineering/Catalytic Technology at KU Leuven with Dirk De Vos in 2011 and was awarded by the Royal Academy of Belgium for this work. In 2012-2013, he worked with Jeffrey Long as a postdoctoral fellow at UC Berkeley. Currently, he is a tenure-track research professor at the KU Leuven Centre for Surface Chemistry and Catalysis. He is passionate about pushing the envelope in porous materials and process technology, with a healthy disregard for traditional subject boundaries.