Ionic liquids and deep eutectic solvents for lignocellulosic biomass fractionation

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Lignocellulosic biomass has gained extensive research due to its potential as renewable resource, which has the ability to overtake the oil-based resources. However, this is only possible if the fractionation of lignocellulosic biomass into its constituents, cellulose, lignin and hemicellulose, can be conducted more efficiently compared to the current processes. This article summarizes the currently most commonly used processes and reviews the fractionation with innovative solvents, such as ionic liquids and deep eutectic solvents. In addition, future challenges for the use of these innovative solvents will be addressed.

1. Introduction

Lignocellulosic biomass can be described as the primary building block of plant cell walls consisting of three main components, i.e. cellulose, hemicellulose and lignin. Next to these three main constituents lignocellulosic biomass is composed of small amounts of pectin, proteins, extractives and ash.[1] Per year approximately 2 x 10^{11} tonnes of lignocellulosic biomass is produced.[2] Plant biomass is produced via a photosynthesis reaction between carbon dioxide (CO_2), water (H_2O) and light, in which solar energy is mainly converted into chemical bonds and to a lesser extent into chemical energy (only 1%).[3] Lignocellulosic biomass is stated as Earth's biggest natural resource available.[4] This makes it interesting as renewable resource, decreasing the dependency of humanity on oil-based resources. Especially the fractionation of lignocellulosic biomass into its constituents - cellulose (40-80%), hemicellulose (15-30%) and lignin (10-25%) - is of major importance for the future use of lignocellulosic biomass as renewable resource.[5] Currently, the production of paper from wood is the most optimal operational commercial fractionation process, but it uses only 35% of its total biomass feed.[6] The other 65% is considered as waste and in most cases incinerated. Thus, the fractionation should be conducted more efficiently to compete with our oil-based resources. In this review, current fractionation processes are compared to treatments with novel solvent systems such as ionic liquids (ILs) and deep eutectic solvents (DESs). Furthermore, the solubility of lignocellulosic biomass and its constituents is evaluated in these novel solvent systems.

2. Lignocellulosic biomass constituents

2.1. Cellulose

Cellulose is the most abundant biopolymer on Earth.[7] It is a polysaccharide consisting of linear chains of 10.000 or more D-glucose monomers linked together via 1-4-β glycosidic bonds.[8] Between these linear chains there are many parallel and anti-parallel hydrogen bonding interactions, which are graphically depicted in Figure 1.[7] These bound linear chains are packed into microfibrils.[9] The exact nature of microfibrils varies between the different types of lignocellulosic biomass.[10] It can be concluded that the combination of the hydrogen bonding network and the microfibrils gives cellulose its rigid form and recalcitrance to dissolution.

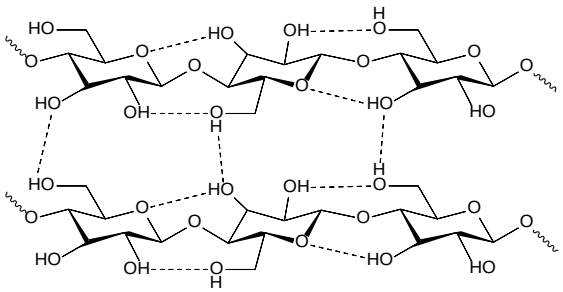


Figure 1: General form of the biopolymer cellulose with its intramolecular and intermolecular hydrogen bonds between the glucose monomers.

The crystalline structure of cellulose can be divided into seven different types, e.g. cellulose I (I_α and I_β), cellulose II, cellulose III (III_1 and III_{11}) and cellulose IV (IV_1 and IV_{11}).[10] The main differences between these distinct forms are their variations in the unit cell.

Cellulose has different applications. Probably the oldest and most common application is its use in the paper and pulp industry. Furthermore, it is often used as dissolving cellulose. Next to the use of cellulose itself, its hydrolysis is also of great interest. Multiple publications show the hydrolysis of cellulose into glucose,[11,12] and further decomposition or conversion into ethanol,[13,14] 5-hydroxymethylfurfural[15,16] and other constituents.

It is generally speculated that a nearly limitless variety of chemicals can be produced via hydrolysis and subsequent conversion of cellulose.[9]

2.2. Hemicellulose

Hemicellulose, like cellulose, consists of groups of polysaccharides, but has a much lower degree of polymerization (100-200). Moreover, hemicellulose does not merely consist of glucose monomers, but it is a branched heteropolymer composed of three different monomer classes, i.e. pentoses, hexoses and sugar acids (Figure 2). The most common pentoses in hemicellulose are D-xylose and D-arabinose. Frequently occurring hexoses are D-mannose, D-glucose and D-galactose. Most known sugar acids are 4-O-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid. The more rare sugars are L-rhamnose, L-fucose, and various methylated neutral sugars.[17,18]

It should also be noted that the composition of hemicellulose differs per type of lignocellulosic biomass. [8] Similarly to cellulose, hemicellulose can be hydrolysed and further converted into different products, such as ethanol, xylitol, 1,2-butanediol and lactic acid, which makes further research into the applications of hemicellulose interesting.[18]

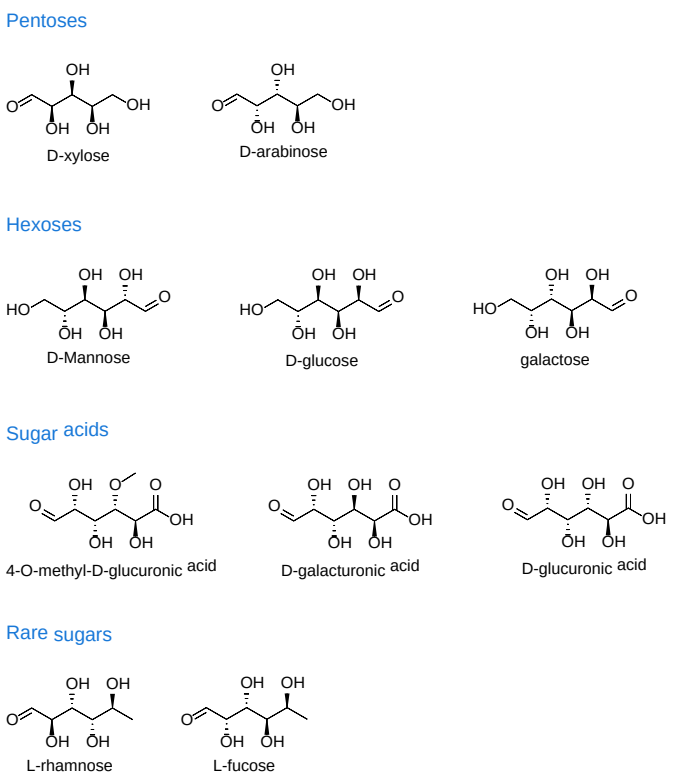


Figure 2: Monomers of hemicellulose.

2.3. Lignin

Lignin is a three-dimensional amorphous biopolymer insoluble in water in its native form.[19] It acts as a resin between the carbohydrate polymers cellulose and hemicellulose holding the lignocellulosic matrix together.[19,39] Crosslinks between lignin and the carbohydrate polymers increase mechanical strength and rigidity conferred on woody tissues, which allows trees to grow up to more than 100 meters in height. Moreover, lignin plays a part in the defence mechanism of lignocellulosic biomass. Due to the insolubility and complexity of the lignin polymer, it is resistant to degradation by most microorganisms.[8,20]

Despite investigations on the chemical structure of lignin for more than a century, the exact structure is still under debate.[21] This can be explained by the lack of precise qualitative analytical methods. Especially when the analytical method requires a soluble lignin derived preparation, serious problems occur due to the lack of a method for the isolation of lignin without changing its functional groups.[22] Recently, new methods were introduced showing great promise for the detection of lignin in plant and wood species. These methods are based on nuclear magnetic resonance (NMR) and Fourier transformation infrared (FTIR) spectroscopy.[23–25]

Although a proper analysis for the chemical structure of lignin is not available yet, it is widely accepted that lignin consists of the monolignols coniferyl alcohol, sinapyl alcohol, and p-coumaryl alcohol, also known as 4-hydroxycinnamyl alcohol, which subsequently after incorporation into the lignin polymer are renamed into guaiacyl, syringyl and p-hydroxyphenyl units (Figure 3).[8,26]

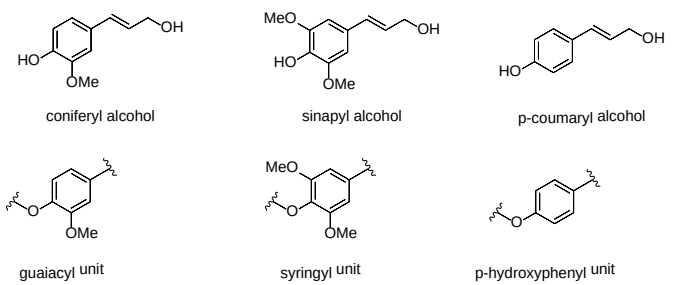


Figure 3: Alcohols present in lignin and their respective units within the lignin polymer.

From these aromatic compounds, multiple valuable products can be obtained.[19] Currently, the most successful commercial valorisation of a lignin derivative is the production of vanillin from the lignosulfonates produced with the Sulphite pulping process.[2] Lignosulfonates have also been commercially applied as dispersant (e.g. in the construction industry), emulsifier (e.g. in asphalt), and in resins on a smaller scale. Probably, numerous new or easier produced derivatives can be obtained after lignin is successfully removed from the supramolecular structure with cellulose and hemicellulose in lignocellulosic biomass. For example, aromatic compounds such as benzene, xylene, toluene and phenols could be potentially produced.

2.4. Other constituents

Next to the three main constituents, lignocellulosic biomass also contains other components of which the most prominent is water. Since wood and most other lignocellulosic biomasses are

hygroscopic, the water content varies with relative humidity of its surroundings. For instance, for raw loblolly pine the equilibrium moisture content typically varies between 10 and 25 wt% at common relative humidities and ambient temperature.[27] The dry material also contains monomeric sugars, organic acids, salts, amino acids, proteins, oils, resins and other hydrocarbons, including flavonoids, colorants, anti-oxidants and fragrances.

3. Conventional processes used for chemical pulping and cellulose dissolving

This paragraph focuses on the most often applied and/or investigated processes for the delignification of lignocellulosic biomass (Kraft, Sulphite and Organosolv pulping) and production of man-made cellulosic fibres (Viscose and Lyocell process).

3.1. Kraft pulping

The origin of Kraft pulping, also known as sulphate pulping, dates back to 1870 when a patent was filed for the delignification of lignocellulosic biomass with sodium hydroxide (NaOH) and sodium sulphide (Na_2S). In 1879 it was discovered that the addition of sodium sulphate (Na_2SO_4) during the recovery resulted in lower sulphide losses.[28] This discovery was the basis for the first industrial Kraft process for the removal of lignin and hemicellulose from lignocellulosic biomass, to remain with cellulose fibres.[29,30]

Nowadays, the Kraft pulping process is used in 80% of the world production of pulp. The wood chips are cooked using a mixture of white liquor and spent black liquor at the temperature of 150-180 °C. At this temperature the main part of the lignin is dissolved and also some of the hemicelluloses are removed. The residual lignin, although its content after the cooking is only 2-5 % of the dry pulp weight, is intensely coloured. The residual lignin is difficult to remove in the Kraft cook without severe carbohydrate degradation and it is therefore modified or removed in several bleaching stages.

The spent liquor from the cooking is concentrated and incinerated in a reductive recovery boiler, which has two main functions. One is to burn the dissolved organic material and produce a molten salt comprising sodium carbonate (Na_2CO_3) and Na_2S. The other purpose is to recover the heat in the hot flue gases as high-pressure steam for power generation in a turbogenerator system and to meet the steam needs of the mill.[31]

Disadvantages of the Kraft pulping process include the need for alkaline chemicals resulting in metal corrosion problems and malodorous smells, and the fact that the obtained lignin contains sulphur, which increases the difficulty for valorisation and requires a higher need for bleaching.[31]

3.2. Sulphite pulping

The sulphite process comprises four different methods for the removal of lignin and part of the hemicelluloses: the acid bisulphite (pH 1-2), bisulfite, i.e. magnefite (pH 3-5), neutral (pH 6-9) and alkaline (pH 10-13.5) sulphite process. Cooking temperatures vary from 120 °C to 180 °C, depending on the sulphite process. In comparison to the Kraft process, there are two different methods for the recovery of the chemicals. One method increases the concentration of the weak black liquor via evaporation. This concentrated liquid is incinerated in a recovery boiler to produce energy for steam and power generation where magnesium oxide (MgO) and sulphur dioxide (SO_2) are produced. MgO is separated from the flue gases via electrostatic precipitators or multicyclones, after which it is converted into magnesium hydroxide ($Mg(OH)_2$) upon addition of water. This slurry of $Mg(OH)_2$ in water is purified via sedimentation or filtration and reacted with sulphur dioxide or elemental sulphur to form the cooking acid magnesium bisulphite. The other method comprises stripping columns to remove excess SO_2 from the condensate to avoid disturbance of the bio-organisms in the anaerobic waste water treatment.

The process focuses on the separation and utilization of hemicellulose and lignin into its derivatives such as lignosulfonates, ethanol, fodder yeast, soda, vanillin, acetic acid and furfural.[31]

The main advantage of the Sulphite pulping process is the high flexibility of the cooking process. In fact, the entire pH range can be covered by varying the dosage and composition of the chemicals, which allows for the production of a broad range of types and qualities of pulp. The main disadvantage of the Sulphite pulping process is the lower strength of the pulp, which makes it a less desirable process in comparison to the Kraft pulping process.[31]

3.3. Organosolv pulping

Organosolv pulping has been investigated for more than 80 years.[32] Pulping studies with organic solvents, i.e. with alcohol and water, started already in the 1930s, and by the 1960s a rather wide array of solvents had been identified to be used with or without an acid catalyst.[33] The first patent involving an industrial process for organosolv pulping was filed in 1971.[34] In this patent a process was provided for the pulping of lignocellulosic biomass with a mixture of water and a water miscible volatile organic solvent. Many organosolv pulping papers have been published since. Numerous combinations of solvents, so-called organosolvs, and catalysts are known, and have been applied mainly at lab scale.

One of the most popular organosolv pulping methods uses 50-100% of methanol in water as solvent. It is mainly applied to the wood species spruce, pine, beech and aspen. The catalysts in this case vary between acids (HCl, H_2SO_4 and methyl sulphuric acid) and metal salts ($CaCl_2$, $Ca(NO_3)_2$, MgCl, $Mg(NO_3)_2$ and $MgSO_4$). The cooking temperatures used were 130-220 °C.[35]

Another often applied option is the use of 40-60% ethanol in water. This organosolv is tested on a broad variation of biomass including spruce, pine, beech, aspen, birch, eucalyptus, red oak, sweet gum, bagasse and rice straw. The catalysts used in this system are acids (HCl, H_2SO_4, and aromatic organic acids), bases (NH_3 and NaOH) and metal salts (Na_2CO_3, $CaCl_2$, $FeCl_3$

and $AlCl_3$). Moreover, $(NH_4)_3PO_4$, anthraquinone and methylanthraquinone can be used. These experiments were conducted at temperatures ranging from 120 to 140 °C.[35]

Many other solvents, including butanol, propanol and glycerol, are described elsewhere.[35,36]

The main advantage of the organosolv process is that sulphur-free lignin is produced that can be further valorised. However, considerate amounts of organic solvents are required for the dissolution of the lignin, resulting in high costs, high regeneration energy consumption, and hazardous and flammable emissions.[35,37]

3.4. Viscose process

The viscose process is used to manufacture regenerated fibres. Dissolving pulp, i.e. wood pulp having high cellulose content (>90%) is used as a raw material in this process. The viscose process involves the production of cellulose xanthate, commonly known as Viscose, by reaction of cellulose with carbon disulphide (CS_2).The cellulose xanthate is then dissolved in aqueous NaOH. The cellulose can be regenerated with sulphuric acid (H_2SO_4), by which CS_2 and hydrogen sulfide (H_2S) are liberated. The amount of highly pure cellulose that can be dissolved with the Viscose process varies from 8 to 12 wt%.[38] However, only 70-75% of the hazardous chemicals needed for the dissolution can be recycled.[7–9,38]

3.5. Lyocell process

The Lyocell process, also known as the NMMO process, is a more recent application for the dissolution of cellulose. Water-free N-methylmorpholine-N-oxide, NMMO, is used as solvent for the immediate dissolution of cellulose. About 10-15 wt% of cellulose can be dissolved in NMMO. The dissolved cellulose can be recovered by precipitation upon addition of water to the cellulose-NMMO solution. The fibres that are formed share the same name as the process, Lyocell, and are known for their excellent mechanical properties.[38,39]

The Lyocell process is a direct more advantageous dissolution process compared to the Viscose process, because NMMO is biodegradable and can be washed out with water with a recovery rate of about 99.3%.[38,39] However, unwanted by-products, such as N-methylmorpholine (NMM) and morpholine, can be produced and thermal runaways can occur.[7–9,38,39]

4. Innovative solvents: ionic liquids vs. deep eutectic solvents

Innovative solvents could enhance the biorefinery to a greener and more sustainable industry. For the replacement of conventional solvents and processes, research has been conducted into two categories of innovative solvents. These categories consist of ILs, which can be subdivided into aprotic ionic liquids (AILs) and protic ionic liquids (PILs) respectively, and DESs. ILs and DESs offer advantages over conventional solvents due to their properties, which can be tuned by adjusting the chemical structure and composition of its constituents.

ILs are salts composed of an organic cation and an organic/inorganic anion, with melting temperatures below 100 °C, often liquid at room temperature.[40] The key properties of ILs are negligible volatility, wide liquid range, high conductivity and high thermal stability. ILs are commonly regarded as designer solvents due to the large number of possible cation/anion combinations, which leads to a wide tunability of their physicochemical and toxicological properties.[40] Compared to conventional organic solvents, the unique properties of ILs favour their use in a variety of applications e.g. synthesis and catalysis, electronic devices, thermal fluids and separations.[41–45]

Generally, DESs are formed by mixing a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), being associated with each other by means of hydrogen bond interactions, upon which a eutectic mixture with a melting temperature much lower than its constituents is formed.[46,47]

DESs share the solvent characteristics of ILs, being able to tune their physicochemical properties by the proper selection of its components in terms of molecular structure, chemical nature, ratios and water content.[46–49] Despite being a still relatively young field, DESs already have been used in different applications such as metal electrodeposition,[48] catalysis,[50] drug solubilisation,[51,52] and separation processes.[53–55] Furthermore, a large number of DESs based on natural compounds such as organic acids, amino acids, and sugars were reported.[56,57] Later on, due to the generally high viscosity of these solvents, their properties have been tuned by the addition of water.[58]

It is often claimed that DESs offer advantages over ILs, such as a low price, chemical inertness with water and easy preparation by mixing its constituents at moderate temperature. Furthermore, it is expected that most DESs are biodegradable, biocompatible and non-toxic.[47] Nevertheless, to avoid a generalization it should be noted that all these characteristics are derived from the DESs' constituents.

4.1. Preparation of ionic liquids and deep eutectic solvents

The increasing interest in ILs as possible alternatives for the current hazardous organic solvents led to an advancement in their synthetic methods and purification.[40,44] Several methods exist for the preparation of ILs, where the ability to obtain a product of high purity is an important selection criterion.[44] Depending on if it is an AIL or a PIL, the synthesis is conducted by a different procedure, which have been reviewed in the literature.[59,40,44,60,61]

The most common synthesis of AILs is the quaternization of an amine, phosphine or sulfide with haloalkanes upon the formation of a halide salt. The second step is the anion metathesis reaction by addition of metal salt, whereby the halide anion is exchanged for the salt anion. In Figure 5 the most widely used cations and anions of AILs are shown.

A more detailed description of the several synthetic methods to synthesize ILs can be found in literature.[40,44,62,63]

Despite the first IL prepared in 1914 was a PIL, AILs have largely dominated the literature. However, research into PILs has recently gained popularity mainly due to their potential for applications in fuel cell technologies and biomass fractionation.[8,64] PILs are easily prepared by proton transfer from a Brønsted acid to a Brønsted base, in equimolar proportions. The preparation of a PIL is most commonly an exothermic reaction, so cooling is necessary.

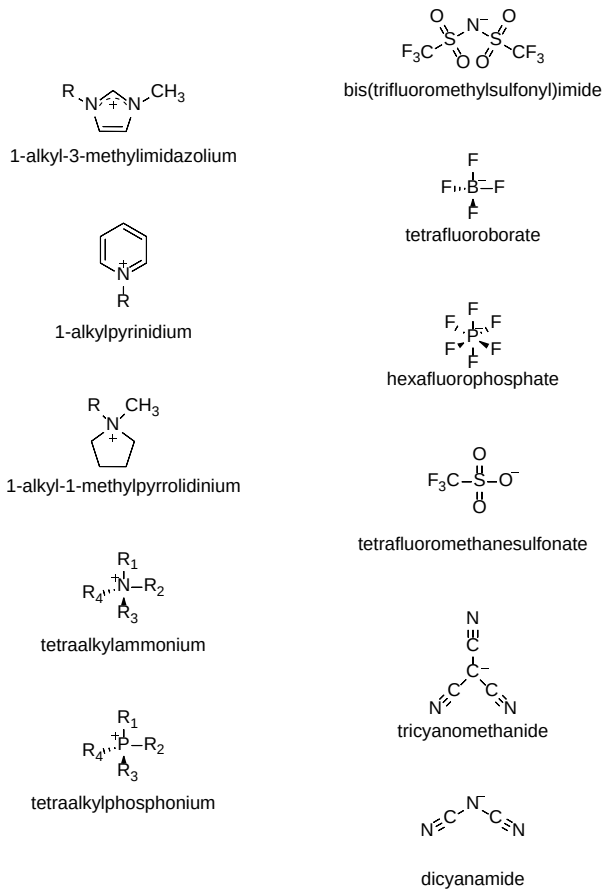


Figure 5: Commonly used cations and anions for aprotic ionic liquids.

In Figure 6 some representative cations and anions for PILs are presented.

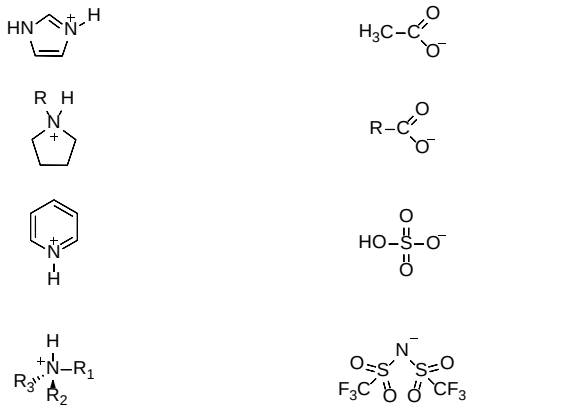


Figure 6: Commonly used cations and anions for protic ionic liquids.

For PILs it has to be considered that there is a possibility that they are not only composed of ions, but slightly neutral (< 1%) due to the dependence on the acid-base equilibrium.[61]

Unlike (A)ILs, DESs are generally easy to prepare. In the most easy and commonly used preparation method, the heating method (mixing under heating), no solvent is needed and no reaction occurs. Consequently, no purification steps are needed, making them promising and economically viable alternatives for conventional organic solvents.[48,65,66]

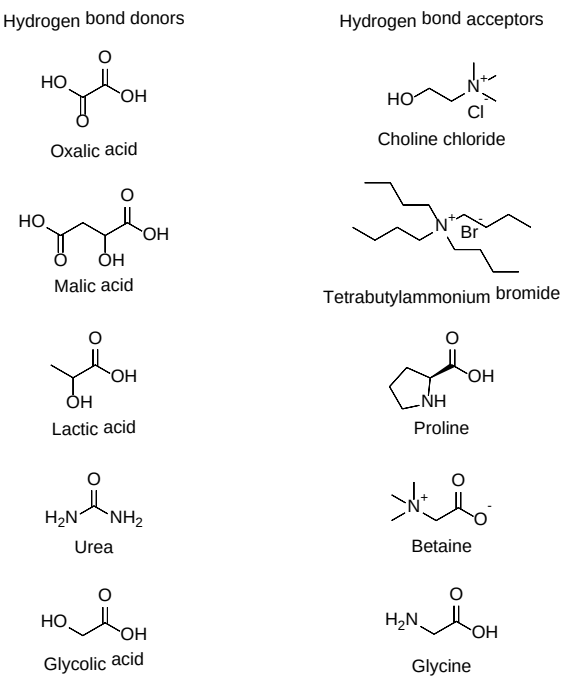


Figure 7: Structures of some hydrogen bond donors and hydrogen bond acceptors used to form deep eutectic solvents.

Other methods reported for the preparation of DESs are the vacuum evaporating, grinding and freeze-drying methods.[49,65,48,67,47,68] In the evaporating method, the components are dissolved in water, after which the majority of water is evaporated at 50 °C under vacuum. The final mixture is

kept inside a desiccator with silica gel until it reaches a constant weight.[68] In the grinding method the two solid components are added to a mortar, after which they are grinded until a clear, homogenous liquid is formed in the nitrogen atmosphere of a glovebox.[69] For the freeze-drying method both the HBD and the HBA were dissolved in approximately 5 wt% of water. These two solutions were mixed, frozen and subsequently freeze-dried to form the clear, homogenous mixtures.[70] Figure 7 illustrates some of the HBDs and HBAs that have been studied to date.

4.2. Physicochemical properties of ionic liquids and deep eutectic solvents

The main advantage of these innovative solvents is the possibility to tune their physicochemical properties by varying the nature (and also ratio in case of DESs) of the constituents. The most important macroscopic properties to assess the possible use of a given liquid solvent in a particular application are melting temperature, thermal stability, viscosity, density, vapour pressure, toxicity, environmental impact and costs.[71,72,61] These properties for ILs and DESs have been reviewed several times in the literature and are not described here in detail.[40,44,61,72,59,71,49,58,47,73,74,75] Therefore, only a brief description of thermal phase behaviour, density, viscosity and toxicity are presented.

4.2.1. Thermal phase behaviour

Both AILs and PILs exhibit a wide liquid range, which depends on the lower temperature limit (glass formation or crystallization) and upper temperature limit (usually the thermal decomposition temperature). For many ILs, the cooling of the liquid phase goes through a metastable state (supercooling), and later to a glass transition, which is detected typically in the region of -60 to -100 °C. In these cases, the kinetics of the transition play an important role. Thermal phase behaviour investigations have also revealed multiple solid-solid transitions (crystal-crystal polymorphism) and in other cases the ILs even exhibit plastic-crystal transitions.[76,77,78]

The upper temperature limit for ILs is usually related with the thermal decomposition temperature, mainly due to their low volatility. Most of the ILs can be kept in the liquid phase up to 400 °C, showing thermal decomposition around 300 to 430 °C, depending most strongly on the choice of the anion[73]

DESs are usually composed of asymmetric components contributing to a decrease of the lattice energy and consequently lower melting temperatures.[48] The melting temperature of DESs is related to the magnitude of the interactions between the HBD and HBA. DESs are characterized by having a lower melting temperature than the individual components. DESs that are liquid at room temperature are the focus of intense research.[48,47,49,79]

Like ILs, some room temperature DESs do not crystallize, but undergo a supercooled state or glass transition.[68,55,69] In other cases, the thermal behaviour is quite complex and can exhibit multiple solid-solid transitions or plastic crystal behaviour.[80,81]

The glass transition of DESs is typically detected in the region of -60 to -100 °C, as observed for ILs.[69,49,65,82,55,47,48] Regarding the thermal stability, most of the reported DESs present a decomposition temperature around 200 °C or below, being relatively less stable than ILs.[55,47,49,48,68]

4.2.2. Density

The density of a material depends on how the molecules can pack together, which in turn is related to the size and shape of their molecules and intermolecular interactions. Densities of most of the ILs (AILs and PILs) range between (800 to 1600) $kg \cdot m^{-3}$.[83,84,85,86] Literature reviews of thermophysical properties were published, describing the main aspects of the effect of the cation or anion, impurities and methodologies.[87,40,84,88,85,86,89,90,91]

DESs present densities within the same range of the ILs, being higher than water. Recently, hydrophobic DESs consisting of decanoic acid and quaternary ammonium salts have been reported in the literature, with densities within the range of 889 to 942 $kg \cdot m^{-3}$.[80] These values are considerable lower than found for most of the reported hydrophilic DESs and water. Following the trend that was observed for ILs, densities of DESs decrease with an increase of the alkyl chains of its components.[55,47,92,93,69,80,94,95] It was also observed that the densities decrease as the relative ratio of the salt to HBD is increased.[96,97]

4.2.3. Viscosity

Viscosity is an important property, it describes the internal resistance of a fluid to a shear stress. At ambient temperatures, ILs present a higher viscosity (around 10 mPa·s to 726 mPa·s) than typical molecular liquids (around 0.2 mPa·s to 10 mPa·s).[40,84,98] The viscosity of an IL widely depends on the combination of cation and anion or impurities present, their effects are well studied in literature.[71,40,84,99,100] For example, the presence of very low concentrations of chloride drastically increases the viscosity, whereas the presence of water significantly reduces the viscosity.[101,102,103,104,105,106]

DESs exhibit relatively high viscosities (> 100 mPa·s at ambient temperature). Depending on the combination of the HBD and HBA viscosities above 10000 mPa·s can even be reached.[107] The viscosity of a DES is mainly affected by the chemical nature and ratio of its components, the temperature and the water content. Recently, the addition of water has been presented as a method to tailor the viscosity of DESs.[58,70,108] However, it should be noted that individual DES components are fully solvated at water contents between 25 and 50 wt%.[58,108] Hence, if the DES' interactions are to be preserved, there are limits to the addition of water to tailor the viscosity. In general, in a viscous liquid, as an IL or a DES, the decrease of viscosity with increasing temperature is more pronounced than in a molecular liquid.[87,84,109,110,55,47,69,80,94] The higher viscosities are directly related with their intermolecular interactions. The increase of the temperature will considerably decrease their intensity and consequently decrease the viscosity.

4.2.4. Toxicity

ILs and DESs are usually regarded as 'green' solvents, especially due to their low volatility. However, the high solubility in aqueous media represents a risk to the aquatic environment. The stability of ILs makes them poorly decomposable by microorganisms,[111,112–114] persisting in the environment for some time.[115] The antimicrobial activity towards microorganisms in a wide range of ILs was investigated,[116] using an adaptation of the Agar diffusion test.[56] Most importantly, an increase of toxicity with the increase of the cation alkyl chain length was observed. One of the main advantages of DESs is the promising low toxicity compared to ILs. DESs have usually been considered as non-toxic solvents, due to use of natural components for their preparation. The toxicity of phosphonium-based DESs was evaluated and it was found that the toxicity depends on the composition, viscosity and ratio of each component.[117] Additionally, the toxicity of the DESs were compared with the individual constituents, concluding that the studied DESs presented either higher[117] or lower[ref] toxicity. More information on toxicity of DESs can be found in the literature.[115,79,115,118]

5. Lignocellulosic fractionation by using ionic liquids and deep eutectic solvents

Currently, cellulose and lignin are two of the most investigated components of lignocellulosic biomass. For example, many papers have been published on the conversion of lignin and cellulose into its building blocks, such as glucose for cellulose and aromatic groups for lignin. However, these investigations can only be conducted after fractionation and processing of the lignocellulosic biomass, which will be discussed in this chapter. The focus will be on the dissolution of cellulose and lignin and the extraction of these constituents from lignocellulosic biomass with ILs and DESs. Specifically, the IL/DES properties that are beneficial for biomass dissolution will be evaluated.

5.1. Cellulose dissolution with ILs

5.1.1. Which ILs can dissolve cellulose?

The first publication on the dissolution of cellulose in an IL originates from 2002 when up to 25 wt% of cellulose was dissolved in the IL 1-butyl-3-methylimidazolium chloride [C_4mim][Cl] under microwave heating and up to 10 wt% upon heating to 100°C.[119] Until now, 2276 papers related to this topic have been published (Scopus March 2015 with the search entries 'ionic liquids' followed by 'cellulose dissolution'). One of the major problems related to the comparison of results in literature is the many different types of pure cellulose available on the market, e.g. Avicel, micro crystalline cellulose (MCC), pre-hydrolysis sulfate pulp, α-cellulose. They all have different characteristics, such as molecular weight and morphology, which are not always completely analysed. Especially an increase in molecular weight will lead to a decrease in dissolution ability and subsequently to the difficulties in comparing results. In addition, comparison is complicated due to the wide variety of dissolution conditions. For instance, temperatures varying between 25 °C and 110 °C have been reported. For a broad overview of ILs able to dissolve cellulose it is referred to elsewhere.[7–9]

5.1.2. What is the role of the anion?

The influence of the anion was already noticed in the first publication about the dissolution of cellulose with ILs. With the use of $[C_4mim]^+$ as cation, five different anions were used for the dissolution of cellulose via microwave heating, i.e. $[Cl]^-$, $[Br]^-$, $[SCN]^-$, $[BF_4]^-$ and $[PF_6]^-$. The use of the anions $[BF_4]^-$ and $[PF_6]^-$ led to no dissolution, while the anions $[Br]^-$ and $[SCN]^-$ gave a cellulose dissolution of 5-7 wt%. The use of $[Cl]^-$ as anion introduced a cellulose dissolution as much as 25 wt%. These results clearly state the high importance of the anion.[119] In 2008 an investigation was conducted to investigate the influence of phosphonium containing anions, namely 1-buyl-3-methylimidazolium methylphosphonate [C_4mim][(MeO)(H)PO_2], 1-butyl-3-methylimidazolium methyl methylphosphonate [C_4mim][(MeO)(Me)PO_2] and 1-butyl-3-methylimidazolium dimethylphosphate [C_4mim][(MeO)MeO)PO_2]. It was expected that [C_4mim][(MeO)(Me)PO_2] had the largest cellulose (MCC) dissolution capability since this IL has the highest Kamlet-Taft β parameter. However, it was observed that the IL [C_4mim][(MeO)MeO)PO_2] had a higher ability to dissolve cellulose at low temperatures, which was contributed to its lower viscosity.[120] The first observation of the screening of dissolving cellulose in 2008 was the fact that hydrophobic ILs were not able to dissolve cellulose. Furthermore, it was observed that dicyanamide as anion could only dissolute up to 1% of cellulose, so it can be considered useless for this application. On the other hand, ILs with chloride are able to dissolve cellulose, although they are not considered as preferable solvents due to their high melting points, their hygroscopic behaviour and their toxic behaviour. ILs composed of formate anions generally show high solvability for cellulose, but they also show low thermal stability caused by decarboxylation at high temperatures. Finally, it was concluded that ILs containing acetate could dissolve substantial amounts of cellulose and were thermally stable.[121] NMR studies into chloride anions showed large $^{35/37}Cl$ relaxation parameters, indicating hydrogen bonding interactions between the chloride anion and the hydroxyl groups of cellulose. Changes in the ^{13}C relaxation parameters for the IL [C_2mim][CH_3COO] were also observed, although less pronounced.[122] Next to the more general accepted anions for the dissolution of cellulose, it was shown in 2009 that the ILs composed of phosphonium anions, 1-ethyl-3-methylimidazolium diethyl phosphate ([C_2mim][Et_2PO_4]) and 1,3-dimethylimidazolium dimethyl phosphate ([C_1mim]-Me_2PO_4), were able to dissolve 14 wt% and 10 wt% of cellulose. An increase of the alkyl chain in the anion of these ILs led to a decrease in cellulose dissolution capacity. Molecular dynamics between the [C_2mim][CH_3COO] and glucose as model compound for cellulose showed that the acetate anion has hydrogen bonding interactions with the three

hydroxyl groups of glucose. In a comparison between water and the before mentioned IL it was observed that the hydrogen bonding energy between water and glucose was considerably lower than that between the IL and glucose (5 kcal·mole^{-1} vs 14 kcal·mole^{-1}).[123] In 2010 a publication focused specifically on the effect of the anion on the dissolution of MCC. A decrease in cellulose solubility was detected over the following range of anions: $[CH_3COO]^-$ > $[HSCH_2COO]^-$ > $[HCOO]^-$ > $[(C_6H_5)COO]^-$ > $[H_2NCH_2COO]^-$ > $[HOCH_2COO]^-$ > $[CH_3CHOHCOO]^-$ > $[N(CN)_2]^-$. It was observed that the introduction of an electron withdrawing group, such as OH, SH, NH_2 or CH_3OH, decreased the solubility of cellulose.[124] Furthermore, they concluded that hydrogen bond accepting played an important role and a linear correlation was proposed between the solubility of cellulose in wt% and the Kamlet-Taft β parameter as visualized in Figure 8.

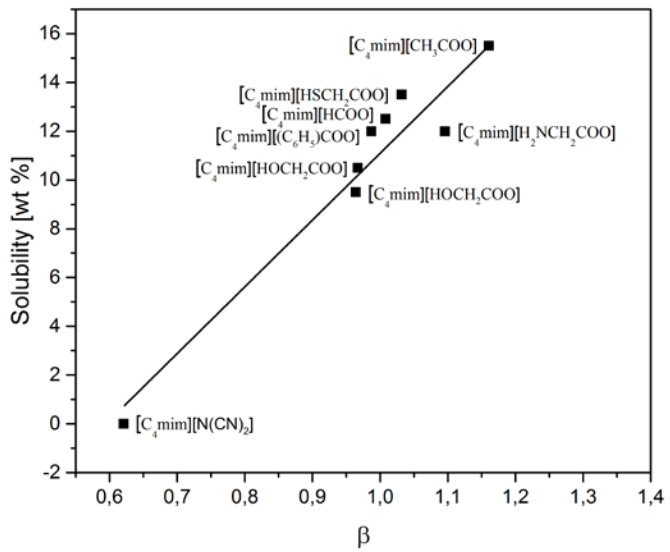


Figure 8: Proposed linear correlation between the Kamlet-Taft β parameter and the cellulose solubility in the IL.[124] (reproduced with the data available in the reference)

The Kamlet-Taft parameters were first introduced in 1976 by Kamlet and Taft. The Kamlet-Taft parameters consist of five parts, i.e. the Kamlet-Taft parameter $E_T(30)$, E_T^N, π^*, α, and β.[125] The $E_T(30)$ and E_T^N describe the interactions between the solvent and the dyes used for the measurements and so express the solvent polarity. The Kamlet-Taft parameter π^* defines the polarizability/dipolarity of a solvent, which is the ability of a solvent to stabilize a charge or a dipole by virtue of its dielectric effect. The Kamlet-Taft α parameter describes the hydrogen bond donating strength, also commonly known as hydrogen bond acidity, while the Kamlet-Taft β parameter is used for describing the hydrogen bond accepting strength, also commonly known as the hydrogen bond basicity.[125]

In general, ILs have a high π^*, a moderate α and high β. Moreover, α depends mainly on the cation, while β depends on the anion. It was found that the Kamlet-Taft β parameter is most important for the dissolution of cellulose. Dissolution of cellulose occurs when the β parameter is higher than approximately 0.8.[8] Furthermore, it can be observed that the solubility is at its maximum with the highest Kamlet-Taft parameter, giving a clear correlation (Figure 8).

A more recent study showed that the electrostatic part of the interaction between cellulose and the anion $[Cl]^-$ is approximately 10 times stronger than the interaction of cellulose with the cation $[C_4mim]^+$.[126] This has been confirmed by another molecular dynamics investigation.[127]

5.1.3. What is the role of the cation?

Tables 1 and 2 present the Avicel cellulose solubility in different ILs with the same anion, but a variation in cation. These data are used to study the effect of the cation on the cellulose solubility. It can be noticed that ILs containing imidazolium, ammonium and morpholium cations can dissolute considerate amounts of cellulose. Previous results indicated that also ILs consisting of a pyridinium or phosphonium as cation are able to dissolve cellulose.[7] However, there is no general consensus on the role of the cation on the ability of the IL to dissolve cellulose. This is partially due to contradictions in literature.

Table 1: Influence of the cation on the dissolution of cellulose at a temperature of 110 °C.[121]

Ionic Liquids	Solubility [wt%]
$[C_2mim][CH_3COO]$	15
$[C_8mim][CH_3COO]$	<1
[AMM110][CH_3COO]	0.5
$[Me(OEt)_2$-Et-Im$][CH_3COO]$	12
$[Me(OEt)_3$-Et-Im$][CH_3COO]$	12
$[Me(OEt)_4$-Et-Im$][CH_3COO]$	10
$[Me(OEt)_7$-Et-Im$][CH_3COO]$	3
$[Me(OEt)_3$-MeOEtOMe-Im$][CH_3COO]$	0.5
$[H(OEt)_2$-Me-Im$][CH_3COO]$	5
$[H(OEt)_3$-Me-Im$][CH_3COO]$	2
$[Me(OPr)_3$-Et-Im$][CH_3COO]$	0.5
$[Me(OEt)_3$-Bu-Im$][CH_3COO]$	<0.5
$[Me(OEt)_3$-$Et_3N][CH_3COO]$	10
$[Me(OEt)_2$-$Et_3N][CH_3COO]$	10
[MM(EtOH)NH][CH_3COO]	<0.5
$[(MeOEt)_2NH_2][CH_3COO]$	<0.5
[MM(MeOEt)NH][CH_3COO]	<0.5
$[M(MeOEt)_2NH][CH_3COO]$	<0.5

Table 2: Influence of the cation on the dissolution of cellulose at 120 °C [128]

Ionic Liquids	Solubility [g·mol^{-1}]
$[C_4mim][CH_3COO]$	58
$[C_1OC_2mim][CH_3COO]$	56
$[C_2OHmim][CH_3COO]$	34
$[C_4dmim][CH_3COO]$	37
$[phC_1min][CH_3COO]$	34
$[C_2mmor][CH_3COO]$	31
$[C=C_2mmor][CH_3COO]$	28
$[C=C_2mpip][CH_3COO]$	19
$[C_4mpip][CH_3COO]$	7
$[C_4mpyr][CH_3COO]$	3
$[C_4ebim][CH_3COO]$	<1
$[C_2ebim][CH_3COO]$	<1

[C_4ebt][CH_3COO]	<1

^{13}C NMR studies on cellobiose and glucose, in respectively 2006 and 2008, concluded that the influence of the cation for the dissolution of cellulose is minor, due to only small interactions between the cationic part of the IL with the sugars.[122,129] However, in both 2010 and 2014, ^{1}H NMR and ^{13}C NMR studies on cellobiose and cellulose suggested that the acidic protons, especially the proton on the H2 position of the imidazole ring, formed hydrogen bonding interactions with the oxygen atoms of cellulose.[130,131] Before any further discussion, it should be noted that some results were questioned in previous articles.[132,133] This because conclusions were mainly based on chemical shift perturbation ($\Delta\delta$) data, which are claimed to be improper indicators, since they only give information about changes in the chemical environment. However, it was shown that replacing the acidic proton on the 2-position of the imidazole ring with a methyl group led to a decrease in cellulose dissolution from 59 g mol^{-1} to 37 g mol^{-1} (comparison between [C_4mim][CH_3COO] and [C_4dmim][CH_3COO]).[128] This can be seen as a strong effect, though the question still remains if this is caused by a lack of hydrogen bonding or as a result of a change in polarity or hydrogen accepting ability of the IL. Unfortunately, the Kamlet-Taft parameters are not given for the [C_4dmim][CH_3COO] IL, so a good comparison between this IL and the [C_4mim][CH_3COO] is rather difficult. Especially a comparison of the Kamlet-Taft β parameters of these two ILs, the parameter that is considered as the most influential, would give some more data for discussion.

The interaction between IL and cellulose, or alternatively between IL and glucose/cellobiose as model compound for cellulose, has also been investigated with molecular dynamics studies. Initial molecular modelling on D-glucose solvation in the IL 1,3-dimethylimidazolium chloride ([C_1mim][Cl]) showed that the cation only has weak interaction with glucose.[134] It was considered that the interaction between the cation and the chloride anions, which are hydrogen-bonded to glucose, resulted in regions of cation density around the sugars as a secondary effect. Their studies were continued with a 1:5 β-glucose:[C_1mim][Cl] ratio to obtain a mixture more representative and comparable to experimental data. In these studies it was observed that some weak hydrogen bonding interactions occurred between the hydrogen on the 2-position of the cation and the oxygen on the 6-position of glucose.[135] They concluded that the decrease in relaxation rates as observed in NMR studies can be attributed to the presence of interactions between the cation and the glucose. From molecular modelling on [C_4mim][Cl] it was concluded that the cation does not directly interact with cellulose. The prevention of interaction between the IL and glucose was attributed to steric hindrance.[136] Furthermore, investigations were conducted to the interactions between [C_2mim][CH_3COO] and 1-4 linked β-D-glucose oligomers with a polymerization degree of 5, 6, 10 and 20. They concluded that the imidazolium ring contributes to the dissolution of cellulose, since they observed that the conjugated ring structure had van der Waals interactions with sugar rings. In the same publication it was also observed that the cations were in close contact with the polysaccharides through hydrophobic effects.[123] In 2013 it was determined that the cation in this research, [C_4mim]$^+$, stacks on the hydrophobic part of the cellulose surface by means of non-polar interactions.[137]

Where previous discussed studies showed that the possible interaction between the cation and the cellulose is mainly via hydrogen bonding, van der Waals interactions and hydrophobic effects, some investigations indicate that there is covalent bonding. The interactions of both [C_2mim][CH_3COO] and [C_2mim][Cl] with cello-oligomer were investigated and it was observed that during the dissolution of cello-oligomer in the IL [C_2mim][CH_3COO] the C-1 carbon signal of the cello-oligomer in NMR disappeared.[138] This was explained as the result of the formation of a covalent bond between the carbon at the 2-position of the [C_2mim][CH_3COO] and the carbon at the 1-position of the cello-oligomer. Interestingly, this disappearance was not detected in the carbon NMR of the cello-oligomer/[C_2mim][Cl] mixture.[138] The discovery of the covalent bonding was verified by an investigation of the formation of the covalent bonds between ILs, butylmethylimidazolium acetate ([C_4mim][CH_3COO]) and 1-(2-napthylmethyl)-3-methyl-imidazolium acetate ([NapMIM][OAc]), and glucose via ^{13}C-isotopic labelling and fluorescence labelling experiments.[139] The results confirmed that the C-2 carbon of the cation of the IL covalently attached to the reducing end of cellulose. Furthermore, it was pointed out that this reaction can be suppressed by the absence of bases.[139]

There is also a clear effect of the length of the alkyl chain on the cellulose dissolution behaviour. Generally, an increase of alkyl chain length beyond C_4 gives a decrease of cellulose solubility. A solubility screening of 1-alkyl-3-methylimidazolium chlorides was performed with a variation of the alkyl chain length from C_2-C_{10}. Surprisingly, the authors found a strong effect between an even and an odd alkyl chain where the even alkyl chains were superior in dissolution ability over the odd alkyl chains. For the even chains the C_4 alkyl chain showed the best dissolution behaviour up to 20 wt% (just after C_2), while for the odd chain this was the C_7 alkyl chain, which dissolved only up to 5 wt%.[140] Reports show that there was no odd/even effect noticed for a variation in alkyl length with bromide as anion, although this conclusion is questioned, since the maximum solubility was only 2-3%.[141] It was reported that the decrease in solubility over an increase of alkyl length might be caused by an increase of viscosity since the solution becomes so viscous that more dissolution is not possible.[121] The authors exemplify this for the increase of viscosity of the methylimidazolium acetate ILs, where an increase of C_2 to C_4 already led to an increase of viscosity of 162 mPa·s to 646 mPa·s.[142,143] Thus, for longer carbon chains this would lead to extreme viscosities and much lower dissolution rates.

Moreover, functional groups within the alkyl chain groups could contribute to an increase or decrease of the cellulose dissolution ability. The higher dissolution ability of 1-ethyl-3-

(2-(2-methoxyethoxy)ethoxy)ethyl)imidazolium acetate ([Me(OEt)$_3$-Et-Im][CH_3COO]) and 1-ethyl-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)ethyl)imidazolium acetate ([Me(OEt)$_4$Et-Im][CH_3COO]) over 1-methyl-3-octylimidazolium acetate ([C_8mim][CH_3COO]) was contributed to the presence of an oxygen atom in the alkyl chain.[121] It was hypothesized that adding oxygen to the alkyl chain of the cation could act as Lewis-base/hydrogen bond acceptor leading to increased hydrogen bonding with cellulose and subsequently more cellulose dissolution.[121] However, Wang *et al.* observed that the solubility of cellulose diminished when the -C_4H_9 alkyl chain was replaced with –$CH_2CH_2OCH_3$ and CH_2CH_2OH. They attributed this decline to the donating electron behaviour of the –OCH_3 and –OH.[128] Thus, adding oxygen can have a positive influence and a negative influence probably explained by the nature of oxygen that can behave as an electron donating group on aromatic groups and withdrawing group in alkyl chains. Zhang *et al.* concluded from molecular dynamics that electron withdrawing groups indeed enhanced the interaction with cellulose and led to an increasing cellulose solubility. They claimed that this phenomena originated from an increase of electronegativity of the cation.[130] Furthermore, there is a possibility that the hydrogen of the hydroxyl undergoes intermolecular hydrogen bonding with the anion.[144] This could lead to competition with the hydrogen bonding of the anion with cellulose. The precise influence of the hydroxyl is not clear yet, but it was suggested that longer alkyl chains containing hydroxyl groups are more flexible than the shorter alkyl groups giving a better possibility for intermolecular hydrogen bonding.[7]

5.1.4. What is the effect of solvent addition?

Many publications have investigated the influence of adding a solvent to the ILs, where both co-solvency as anti-solvency have been investigated. Where co-solvents increase the cellulose dissolution ability, anti-solvents hamper it. In 2011 a paper about the dissolution of cellulose in organic electrolyte solutions was published, which are combinations of molecular solvents with a small to medium molar fraction of IL. A combination of 5 g of 1,3-dimethyl-2-imidazolidinone (DMI) with 5 g of the IL [C_4mim][Cl] was able to dissolute 10 wt% of cellulose (Avicel) after 3 min at 100 °C, where the dissolution of cellulose in the pure IL [C_4mim][Cl] normally takes more than 10 h.[145] Moreover, when [C_4mim][Cl] was replaced with [C_2mim][CH_3COO], an instantaneous dissolution of cellulose occurred with a mole fraction of 0.18 IL. In the same publication DMI was replaced with 14 other molecular solvents. The most striking results, next to that of DMI, were obtained for the combination of the molecular solvents N,N-dimethylformamide (DMF), N-methyl-2-pyrrolidone (NMP) and dimethylsulfoxide (DMSO). In these solvents, respectively, mole fractions of 0.10, 0.16, and 0.08 IL were needed for the direct dissolution of cellulose. In another publication the main focus was on the prediction of suitable co-solvents with the Kamlet-Taft parameters. It was concluded that molecular co-solvents should be rather polar with E_T^N>0.3 and π^*>0.8, have a low HBD ability with α<0.5 and a strong HBA ability with $\beta \geq 0.4$.[146] In 2013 it was speculated that adding an aprotic polar solvent, such as DMSO, to an IL would increase the solvation of the cation, leading to more ‘free’ anions. These anions would then be more accessible for hydrogen bonding interactions with cellulose, increasing its dissolution.[147] They also investigated the dissolution of MCC, with a degree of polymerization (DP) of 229, in pure [C_4mim][CH_3COO], DMSO and a combination of the two. Surprisingly, at 25 °C no dissolution in the pure IL and the pure molecular solvent occurred, while 15% of MCC was dissolved in the mixture. The molar ratio 2.54:1 is the optimal ratio for DMSO:[C_4mim][CH_3COO]. Also cellulose samples with a higher DP were dissolved, i.e. absorbent cotton (DP = 1586) and native cotton (DP = 2179). At 35 °C 6.0% of absorbent cotton and 3.5% of native cotton was dissolved, while this is 12.5% and 11.0% at 85 °C. Moreover, they investigated the co-solvents DMF and dimethylacetamide (DMA), also in a 2.54:1 ratio, where the DMF/[C_4mim][CH_3COO] solvent could dissolve 12.5% and DMA/[C_4mim][CH_3COO] 5.5% of cellulose at 25 °C. The differences in dissolution were contributed to the dipole moment of the aprotic polar solvent, DMSO (3.96D) > DMF (3.86D) > DMA (3.81D), which allows for a higher solvation. A recent publication hypothesized that a pre-treatment of cellulose with DMF would swell the cellulose, leading to increased distances between cellulose strands. This subsequently allows for a quicker interaction between cellulose and IL.[148] This hypothesis was confirmed by NMR studies, in which the interactions between the IL [C_4mim][CH_3COO] and aprotic, organic solvents were investigated.[149] Their investigation showed that ethyl acetate facilitated the most enhanced interaction between the IL and cellulose (Alicell-Super). Moreover, it was shown that the protic formamide had the strongest swelling effect, but also introduced competition between the IL and cellulose. DMSO in combination with a crown ether (18-crown-6) and the IL tetrabutylammonium acetate was able to dissolve 8% cellulose (DP_w = 830) within 5 min and 12% in 30 min, both at 40 °C.[150] Moreover, it was claimed that cellulose was molecularly dissolved, no degradation occurred, with a combination of the co-solvents chloroform, DCM, DMF, acetonitrile and propylene carbonate with the IL [C_2mim][CH_3COO] up to co-solvent/IL molar ratios of 10:1.[151] They made this conclusion after analysis with static light scattering (SLS) and Small angle neutron scattering (SANS), which showed no molecular aggregation.[151] It was found that a novel method, in which the co-solvent was rapidly evaporated, ensured high solubilities up to 27 wt% in pure [C_2mim][CH_3COO]. [151] Finally, it was concluded that an almost instantaneous dissolution occurred in the solvent mixture with the highest electrical conductivity.[151] An investigation, both theoretically as experimentally, concluded that DMSO improves the dissolution of cellulose in [C_4mim][CH_3COO] + DMSO mixtures due to an enhancement of mass transfer caused by the decrease in viscosity.[152] Furthermore, it was concluded that DMSO had no interactions with the cation and the anion. This was confirmed by another investigation solely

based on molecular dynamics.[153] Since 2013 more molecular simulations were conducted into the dissolution of cellulose with ILs and molecular co-solvents. It was shown that the interaction between the anion $[Cl]^-$ enhances upon addition of DMSO, while for water the contrary happens due to the hydrogen bonding between the anion and water.[126]

The addition of anti-solvents has also been investigated, which can lead to the precipitation of cellulose and consequently to its regeneration. Arguably, the most investigated anti-solvent is water, which has two reasons. Firstly, ILs often contain hygroscopic parts taking up water from air. Secondly, most biomass comprises a low percentage of water. Thus, it is of major importance to gain knowledge of the influence of water. The first publication in the field of cellulose dissolution with ILs showed that more than 1 wt% of water hampered the cellulose dissolution. The authors explained this by competitive hydrogen bonding between the water molecules and cellulose.[119] The authors also indicated that for this reason water is an excellent anti-solvent, inducing the precipitation of cellulose. The fact that water decreases the dissolution of cellulose was acknowledged by multiple publications, although the amount of water at which turbidity and/or precipitation occurred varied.[119,141,146,154,155,147,156] A publication in 2009 investigated the influence of water and cellulose solubility in the IL $[C_4mim][Cl]$.[157] The more water is added, the lower the solubility of cellulose in $[C_4mim][Cl]$.[157] Water is a protic solvent with a high Kamlet-Taft α parameter (1.17) and a moderate Kamlet-Taft β parameter (0.47). The high Kamlet-Taft α parameter could indicate that it interacts with the hydrogen bond accepting anions.[146] Determination of the Kamlet-Taft parameters of ILs containing 1 wt% of water showed a decrease in hydrogen accepting ability, a lower Kamlet-Taft β parameter, which might indicate that this is caused by hydrogen bonding interactions of the anion with water.[155] Furthermore, it was found that the water uptake was dependent on the anion, decreasing in the following order: $[CH_3COO]^- > [Et_2PO_4]^- > [(CN)_2N]^- > [CF_3SO_3S]^- > [BF_4]^- > [PF_6]^-$.[141] Remarkably, tetrabutylphosphonium hydroxide (TBPH) and tetrabutylammonium hydroxide (TBAH) were able to dissolve 20 wt% of MCC with a staggering 40 wt% of water in respectively 5 and 6 min at 25 °C. Though, it should be mentioned that it is thought that water is essential for the stabilization of these IL.

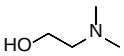
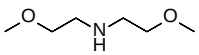
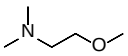
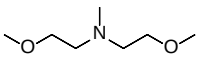
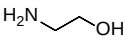
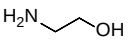
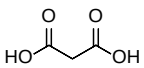
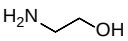
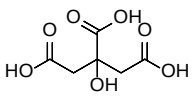
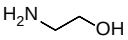
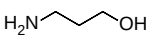
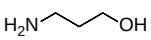
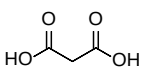
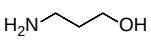
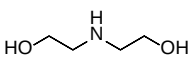
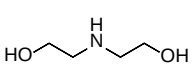
More recently, it was concluded that the water content had a small influence on the recovery in comparison to the temperature. At 90 °C it was found that both $[C_4mim][Cl]$ and $[C_4mim][Cl]$ with water behave as a non-derivatizing solvent, while at 120 °C they behave as derivatizing solvent.[158] Furthermore, the effect of different amounts of water (0%, 20%, 50%, 80%) on the regeneration was investigated at 40 °C. The effect of temperature was further explored at 60 °C and 80 °C with 50 wt% of water.[127] It was concluded that with an increase of water content the cellulose regenerates due to aggregation of cellulose chains in the mixture of the IL $[C_4mim][CH_3COO]$ and cellulose. The increase of water led to a decrease of hydrogen bonding between the acetate group of the IL and cellulose. Consequently, the number of hydrogen bond interactions between the cellulose chains increased. The influence of temperature showed that at higher temperatures the cellulose-cellulose interactions are stronger, which has a positive effect on the regeneration.

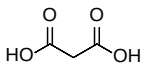
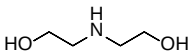
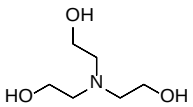
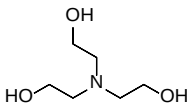
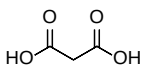
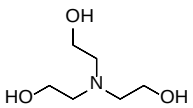
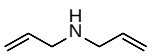
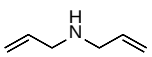
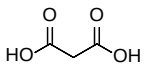
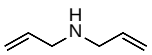
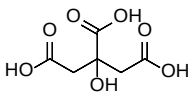
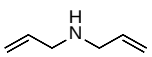
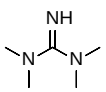
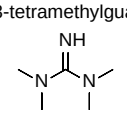
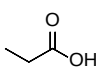
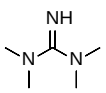
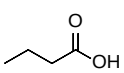
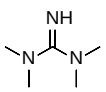
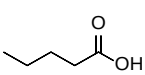
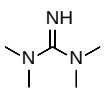
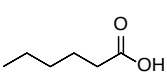
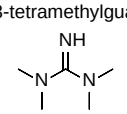
Next to water, different anti-solvents have been reported. In general, it is believed that protic solvents are excellent anti-solvents. Examples are ethanol, methanol, 2-propanol, acetone and acetonitrile. In terms of mechanism, it is thought that they work the same as water. Thus, hydrogen bonding will occur with the anion of the IL or with the cellulose. An investigation into the regeneration with acetone, ethanol and water showed that the strength of cellulose with $[CH_3COO]^-$ decrease from acetone > ethanol > water.[159] Furthermore, there is an increase of hydrogen bonding interactions between cellulose and $[CH_3COO]^-$ over water > ethanol > acetone.[159]

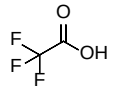
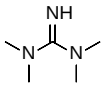
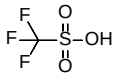
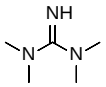
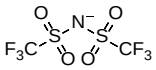
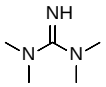
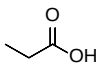
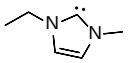
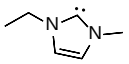
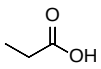
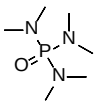
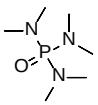
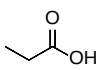
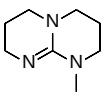
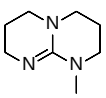
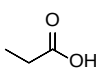
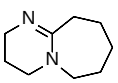
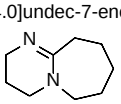
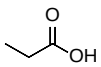
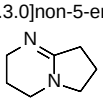
5.1.5. Protic ionic liquids

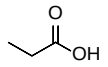
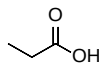
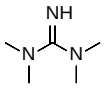
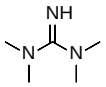
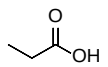
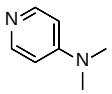
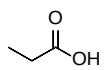
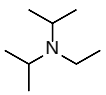
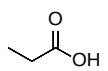
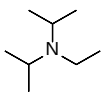
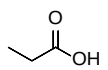
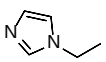
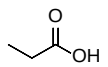
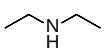
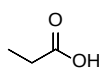
The main difference between (AILs) and (PILs) is the cationic part, which is aprotic for AILs and protic for the PILs. So far, the dissolution of cellulose in AILs was described. In this paragraph the dissolution of cellulose in PILs is presented (see Table 3). The first research into the dissolution of cellulose with PILs originates from 2008 when ILs were presented that could both dissolve carbohydrates and were compatible with enzymes. In that work, the authors investigated 32 AILs and 4 PILs. The PILs used in this investigation were acetic acid in combination with N,N-dimethylethanolammonium acetate ($[MM(EtOH)NH][CH_3COO]$), Bis(2-methoxyethyl)ammonium acetate ($[(MeOEt)_2NH_2][CH_3COO]$), N,N-dimethyl-2-methoxyethylammonium acetate $[MM(MeOEt)NH][CH_3COO]$ and N-methyl-bis(2-methoxyethyl)ammonium acetate $[M(MeOEt)_2NH][CH_3COO]$.[121] All four PILs showed cellulose (Avicel PH-101) dissolution ability lower than 0.5 wt% at a temperature of 110 °C. In 2010 an investigation regarding the dissolution of cellulose in alkanolammonium-based PILs was published.[160] The alkanolammonium PILs were prepared by combining an organic acid with amines. The organic acids used were formic acid, acetic acid, malonic acid and citric acid. The amines used were 3-hydroxypropylamine, diallylamine, 2-hydroxyethylamine, bis(2-hydroxyoethyl)amine (diethanolamine) and tris(2-hydroxyethyl)amine (triethanolamine). For the PILs that were formed, no cellulose dissolution was observed (less than 0.1 wt%).

Table 3: Protic ionic liquids for the dissolution of cellulose

Acids	Base	Source Of cellulose	T (°C)	t [h]	Sol [wt%]	Ref
 Acetic acid	 2-Dimethylaminoethanol	MCC (DP 225)	110	1	<0.5	[121]
 Acetic acid	 bis(2-methoxyethyl)amine	MCC (DP 225)	110	1	<0.5	[121]
 Acetic acid	 2-methoxy-*N*',*N*-dimethylethan-1-amine	MCC (DP 225)	110	1	<0.5	[121]
 Acetic acid	 2-methoxy-*N*-(2-methoxyethyl)-*N*-methylethan-1-amine	MCC (DP 225)	110	1	<0.5	[121]
 Formic acid	 2-hydroxyethylamine	MCC (DP 163)	80	24	<0.1	[160]
 Acetic acid	 2-hydroxyethylamine	MCC (DP 163)	80	24	<0.1	[160]
 Malonic acid	 2-hydroxyethylamine	MCC (DP 163)	80	24	<0.1	[160]
 Citric acid	 2-hydroxyethylamine	MCC (DP 163)	80	24	<0.1	[160]
 Formic acid	 3-hydroxypropylamine	MCC (DP 163)	80	24	<0.1	[160]
 Acetic acid	 3-hydroxypropylamine	MCC (DP 163)	80	24	<0.1	[160]
 Malonic acid	 3-hydroxypropylamine	MCC (DP 163)	80	24	<0.1	[160]
 Formic acid	 Bis(2-hydroxyethyl)amine	MCC (DP 163)	80	24	<0.1	[160]
 Acetic acid	 Bis(2-hydroxyethyl)amine	MCC (DP 163)	80	24	<0.1	[160]

 Malonic acid	 Bis(2-hydroxyethyl)amine	MCC (DP 163)	80	24	<0.1	[160]
 Formic acid	 Tris(2-hydroxyethyl)amine	MCC (DP 163)	80	24	<0.1	[160]
 Acetic acid	 Tris(2-hydroxyethyl)amine	MCC (DP 163)	80	24	<0.1	[160]
 Malonic acid	 Tris(2-hydroxyethyl)amine	MCC (DP 163)	80	24	<0.1	[160]
 Formic acid	 Diallylamine	MCC (DP 163)	80	24	<0.1	[160]
 Acetic acid	 Diallylamine	MCC (DP 163)	80	24	<0.1	[160]
 Malonic acid	 Diallylamine	MCC (DP 163)	80	24	<0.1	[160]
 Citric acid	 Diallylamine	MCC (DP 163)	80	24	<0.1	[160]
 Formic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	5	[161]
 Acetic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100 105	10 min 20	5 10	[161]
 Propionic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	10 min	5	[161]
 Butanoic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	5	[161]
 Valeric acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	NO	[161]
 Hexanoic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	NO	[161]

 Trifluoroacetic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	NO	[161]
 Triflic acid	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	NO	[161]
 bis(trifluoromethylsulfonyl)imide	 1,1,3,3-tetramethylguanidine	MCC (DP 381)	100	18	NO	[161a]
 Propionic acid	 1-ethyl-3-methylimidazol -2-ylidene carbene	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Acetic acid	 1-ethyl-3-methylimidazol -2-ylidene carbene	Eucalyptus PHK-dissolving pulp	90	N.G.	18	[162]
 Propionic acid	 Hexamethylphosphoramide	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Acetic acid	 Hexamethylphosphoramide	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Propionic acid	 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Acetic acid	 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Propionic acid	 1,8-diazabicyclo[5.4.0]undec-7-ene	Eucalyptus PHK-dissolving pulp	80	N.G.	16	[162]
 Acetic acid	 1,8-diazabicyclo[5.4.0]undec-7-ene	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Propionic acid	 1,5-diazabicyclo [4.3.0]non-5-ene	Eucalyptus PHK-dissolving pulp	80	N.G.	16	[162]
 Acetic acid	 1,5-diazabicyclo [4.3.0]non-5-ene	Eucalyptus PHK-dissolving pulp	80	18	5	[162]

 Propionic acid	 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Acetic acid	 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Propionic acid	 1,1,3,3-tetramethylguanidine	Eucalyptus PHK-dissolving pulp	80	N.G.	15	[162]
 Acetic acid	 1,1,3,3-tetramethylguanidine	Eucalyptus PHK-dissolving pulp	80	18	5	[162]
 Propionic acid	 4-(dimethylamino)-pyridine	Eucalyptus PHK-dissolving pulp	80	18	NO	[162]
 Propionic acid	 N,N-di-iso-propylethylamine	Eucalyptus PHK-dissolving pulp	80	18	NO	[162]
 Propionic acid	 N,N-di-iso-propylethylamine	Eucalyptus PHK-dissolving pulp	80	18	NO	[162]
 Propionic acid	 1-ethylimidazole	Eucalyptus PHK-dissolving pulp	80	18	NO	[162]
 Propionic acid	 N,N-diethylamine	Eucalyptus PHK-dissolving pulp	80	18	NO	[162]
 Propionic acid	 Pyridine	Eucalyptus PHK-dissolving pulp	80	18	NO	[162]

[a]Acid is already depicted in deprotonated form due to multi-step reaction

Only in 2011 the first publication involving successful (> 5 wt%) cellulose dissolution in PILs was published.[161] Combinations of the superbase 1,1,3,3-tetramethylguanidine (TMG) with carboxylic acids being formic acid, acetic acid, propionic acid, butanoic acid, valeric acid, trifluoroacetic acid and triflic acid were presented. The combination of these acids with the super base led to [TMGH][CO_2H], [TMGH][OAc], [TMGH][CO_2Et], [TMGH][CO_2nPr], [TMGH][CO_2nBu], [TMGH][CO_2nAm], [TMGH][CO_2CF_3], [TMGH][OTf] respectively. Furthermore, 1,1,3,3-tetramethylguanidinium bistriflimide ([TMGH][NTf_2]) was prepared and tested for the dissolution of cellulose. The results showed that cellulose could be dissolved with [TMGH][CO_2H], [TMGH][OAc], [TMGH][CO_2Et] and [TMGH][CO_2nPr]. The most rapid dissolution occurred within 10 min at 100 °C with the anions acetate and propionate. Dissolution was also observed with PILs composed of formic acid and butanoic acid as anion, where formic acid as anion has a faster dissolution than butanoic acid.

The Kamlet-Taft parameters of two of the above mentioned PILs, [TMGH][OAc] and [TMGH][CO_2Et], were investigated as a function of water content.[155] It was found that the β parameter decreased, as also within the research in ILs, upon addition of water, leading to lower cellulose dissolution. Furthermore, the polarizability/dipolarity (π^*) increased upon water addition, while the Kamlet-Taft α parameter and the $E_T(30)$ parameter remained constant. It was concluded that only the Kamlet-Taft β value played an important role in the

explanation of the lower solubility of cellulose, while this was not enough for the regeneration. For this reason the authors introduced a second criterion for both the dissolution and the regeneration of cellulose, which they generalized for both AILs as PILs. The criteria for cellulose dissolution that they introduced were $0.35 < \beta - \alpha < 0.9$ and $0.80 < \beta < 1.20$.

In 2013 12 bases were used for the formation of PILs in combination with acetic acid and propionic acid.[162] They were tested for cellulose dissolution, of which 14 were successful. The reported PILs able to dissolve cellulose are the two before mentioned acids in combination with 7 bases, being 1-ethyl-3-methylimidazole-2-ylidene carbene (emim-y), *N*,*N*,*N*,*N*,*N*,*N*-hexamethylphosphorimidetriamide (HMPI), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine (DMP) and 1,1,3,3-tetramethylguanidine (TMG). All these PILs were able to dissolve 5 wt% cellulose in the form of pre-hydrolysed Kraft (PHK) pulp at 100 °C. [TMGH][CO_2Et], [DBUH][CO_2Et], [DBNH][CO_2Et] and the AIL [C_2mim][CH_3COO] were further investigated to find the maximum loading of cellulose still dissolvable, which were 15, 16, 16 and 18 wt% respectively.

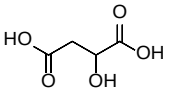
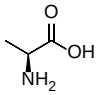
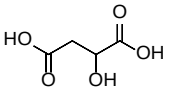
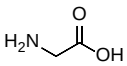
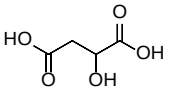
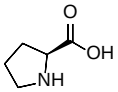
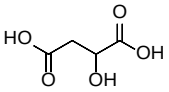
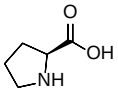
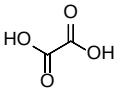
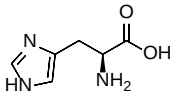
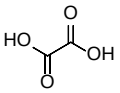
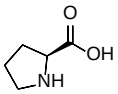
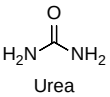
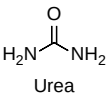
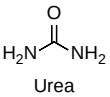
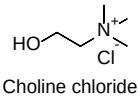
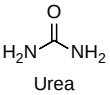
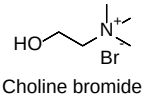
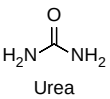
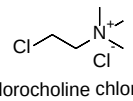
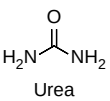
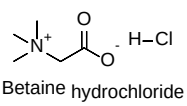
5.2. Cellulose dissolution with deep eutectic solvents

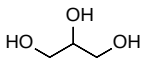
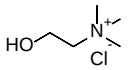
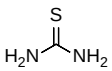
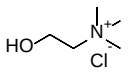
The research into the dissolution of cellulose with DESs started in 2012 when 26 DESs were tested for the dissolution of lignin, starch and cellulose.[65] Despite that up to 14.9 wt% of lignin could be dissolved with the tested DESs, only minor amounts of cellulose could be dissolved. The lowest solubility, 0.11 wt%, was observed with the DES consisting of malic acid as hydrogen bond donor (HBD) and alanine as hydrogen bond acceptor (HBA) in a 1:1 ratio. The DESs comprised of malic acid:glycine and oxalic acid (anhydrous):proline, both in a 1:1 ratio, dissolved 0.14 wt% and 0.15 wt%, respectively. Slightly higher amounts of cellulose, 0.24 wt% and 0.25 wt%, were dissolved with different ratios of malic acid:proline (1:2 ratio) and oxalic acid (anhydrous):histidine (9:1 ratio). The highest solubility was achieved with the DES composed of malic acid and proline in a 1:3 ratio, namely 0.78 wt%. An interesting fact was the increase of cellulose dissolvability over an increase of the ratio of proline in the malic acid:proline DES. Especially the question how the interactions vary over a change in ratio from 1:2 to 1:3 is very interesting, since this ratio change led to a tripling of cellulose dissolution. Furthermore, it should be mentioned that various temperatures were used for the dissolution, which influenced the amount of cellulose that could be dissolved. The dissolution experiments of the DESs oxalic acid (anhydrous):proline (1:1 ratio) and oxalic acid (anhydrous):histidine were conducted at 60 °C, while the experiments for the DESs malic acid:alanine (1:1 ratio), malic acid:glycine (1:1 ratio), malic acid:proline (both the 1:2 and the 1:3 ratio) were performed at 100 °C.

In 2013, a report mainly discussing chitin dissolution showed 6 DESs that were also able to dissolve cellulose.[163] The 6 DESs showing cellulose dissolvability were urea:choline chloride (2:1 ratio), urea:choline bromide (2:1 ratio), urea:chlorocholine chloride (2:1 ratio), urea:betaine hydrochloride (4:1 ratio), glycerol:choline chloride (2:1 ratio) and thiourea:choline chloride (2:1). Different methods were used as dissolution technique varying between heating at 100 °C for 10 h, ultrasonication and heating at 80 °C for 1 h and microwave irradiation at 80 °C for 2 h. The results showed that the dissolution of cellulose in the DESs urea:betaine hydrochloride and glycerol:choline chloride were relatively low in comparison to the 4 other DESs with maxima of 2.5 and 3.5 wt%. The DESs constituted of urea with choline chloride and urea with betaine hydrochloride had cellulose dissolution abilities varying from 3.0-5.0 wt% and 5.0-6.0 wt% respectively. Remarkably, the cellulose dissolution in the DES constituting urea and choline chloride varied between 1.5 wt% and 8.0 wt%. Especially the low cellulose solubility with the microwave irradiation was surprising. The DES composed of thiourea and choline chloride dissolved up to 10 wt% of cellulose with heating at 100 °C, while ultrasonication and heating at 80 °C still led to a dissolution of 6.0 wt%. However, we were not able to reproduce the high dissolution of cellulose in the DES consisting of urea and choline chloride in a 2 to 1 molar ratio.

In 2014, a publication showed three DESs with a varying between 1.03 and 2.83 wt% solubility of cellulose.[164] Three DESs were used in this investigation being urea:acetamide (1:2 ratio), caprolactam:acetamide (1:1 ratio) and urea:caprolactam (1:3 ratio). They showed, in the order as depicted above, solubilities of 1.03, 1.79 and 2.83 wt%. However, the temperature applied is not completely clear. In the experimental part it is mentioned that a dissolution temperature of 120 °C is used, while in Table 2 it is said that 50 °C is used. Furthermore, two of the reported eutectic mixtures have melting points higher than room temperature. Thus, it is debatable to define these two eutectic mixtures as DESs. An overview of cellulose solubilities is presented in different DESs is presented in Table 4. .

Table 4: Deep eutectic solvents for the dissolution of cellulose

HBD	HBA	Ratio	Source of cellulose?	T [°C]	t [h]	Sol [wt%]	Ref
 Malic acid	 Alanine	1:1	Cellulose (90%)	100	24	0.11	[65]
 Malic acid	 Glycine	1:1	Cellulose (90%)	100	24	0.14	[65]
 Malic acid	 Proline	1:2	Cellulose (90%)	100	24	0.24	[65]
 Malic acid	 Proline	1:3	Cellulose (90%)	100	24	0.78	[65]
 Oxalic acid	 Histidine	9:1	Cellulose (90%)	60	24	0.25	[65]
 Oxalic acid	 Proline	1:1	Cellulose (90%)	60	24	0.15	[65]
 Urea	 Acetamide	1:2	Cotton-ramie pulp (DP = 517)	120	NA[c]	1.03	[164]
 Caprolactam	 Acetamide	1:1	Cotton-ramie pulp (DP = 517)	120	NA[c]	1.79	[164]
 Urea	 Caprolactam	1:3	Cotton-ramie pulp (DP = 517)	120	NA[c]	2.83	[164]
 Urea	 Choline chloride	2:1	MCC (MW = 3.12 x 10^5 Da)	100 80[a] 100[b]	10 1 2	8.0 6.0 1.5	[163]
 Urea	 Choline bromide	2:1	MCC (MW = 3.12 x 10^5 Da)	100 80[a] 100[b]	10 1 2	5.0 6.0 6.0	[163]
 Urea	 Chlorocholine chloride	2:1	MCC (MW = 3.12 x 10^5 Da)	100 80[a] 100[b]	10 1 2	5.0 5.0 3.0	[163]
 Urea	 Betaine hydrochloride	4:1	MCC (MW = 3.12 x 10^5 Da)	100 80[a]	10 1	2.5 2.5	[163]

 Glycerol	 Choline chloride	2:1	MCC (MW = 3.12 x 10^5 Da)	100 80[a] 100[b]	10 1 2	3.0 2.5 3.5	[163]
 Thiourea	 Choline chloride	2:1	MCC (MW = 3.12 x 10^5 Da)	100 80[a] 100[b]	10 1 2	10.0 6.0 7.0	[163]

[a]Ultrasonic treatment, [b]Microwave treatment, [c]Not Adressed

5.3. Lignin dissolution with ionic liquids

A considerate amount of research has been performed on finding efficient and non-destructive methods to separate lignin from lignocellulosic biomass. A promising method is its extraction from lignocellulosic biomass with innovative solvents such as ILs. The interest in ILs for the fractionation of lignocellulosic biomass is mainly based on the tunability of the physical properties by a proper selection of their cation/anion, their low volatility and high thermal stability.[57]

The solubility of lignin is most commonly tested using alkaline, Kraft or Organosolv lignin. Despite the fact that native lignin differs significantly from lignin obtained via these commercial methods, it gives valuable information. However, it does not guarantee that an IL with high commercial lignin solubility will also achieve high lignin extractability from lignocellulosic biomass.[8]

5.3.1. Which ionic liquids can dissolve lignin?

A number of ILs, both AILs and PILs, have shown to dissolve lignin to a certain extent (Table 5).[165–168] There is evidence, experimentally and theoretically, that both the cation and anion play an important role in the dissolution of lignin and lignocellulose. It was found that increased p-conjugation in the anions or cations of ILs enhances lignin solubility.[169]

5.3.2. What is the role of the anion?

Generally, it is assumed that lignin is only soluble in polar ILs with mid-range basic anions.[170,167] An investigation into the effect of the anion showed that lignin was insoluble in the combination of $[Emim]^+$ as cation with weakly-coordinating anions such as $[BF_4]^-$, $[PF_6]^-$, and $[(SO_2CF_3)_2N]^-$.[171]

The highly coordinating anions ($[O_2P(OCH_2CH_3)_2]$, $[MeSO_4]^-$, $[MeCO_2]^-$, $[CNS]^-$, as well as the moderately coordinating anion triflate CF_3SO_2, all showed a solubility of approximately 50 wt%. The halide anions with high hydrogen bonding capacity, chloride and bromide, show moderate lignin solubility of 10-15 wt%.[166,167]

Table 5: Ionic liquids able to dissolve commercial available lignin

Ionic Liquid	T [°C]	Sol. [w%]	Lignin Source	Ref
$[C_4mim][PF_6]$	120	0	Softwood Kraft	[166]
$[Bmpyrr][PF_6]$	120	0	Softwood Kraft	[166]
$[C_4mim][BF_4]$	100	12	Softwood Kraft	[166]
$[C_1mim][MeSO_4]$	90	50	Indulin AT	[167]
$[C_4mim][CF_3SO_3]$	90	50	Indulin AT	[167]
[Amim][Cl]	90	30	Indulin AT	[167]
$[C_2mim][CH_3COO]$	90	30	Indulin AT	[167]
$[C_2C_2IM][MeCO_2]$	90	30	Indulin AT	[168]
DMEAF	90	28	Indulin AT	[168]
DMEAA	90	19	Indulin AT	[168]
DMEAG	90	17	Indulin AT	[168]
DMEAS	90	10	Indulin AT	[168]
$[C_4mim][Cl]$	90	10	Indulin AT	[168]
[Bzmim][Cl]	90	10	Indulin AT	[167]
$[C_4mim][Cl]$	90	10	Indulin AT	[167]
$[C_4mim]Br$	90	10	Softwood Kraft	[167]
$[C_4mim][BF_4]$	90	4	Indulin AT	[167]
$[C_4mim][PF_6]$	90	1	Indulin AT	[167]
$[C_4mim][PF_6]$	90	1	Softwood Kraft	[168]
$[Bmmim][BF_4]$	75	14	Softwood Kraft	[166]
$[C_4mim]Cl$	75	13	Softwood Kraft	[166]
$[C_6mim][CF_3SO_3]$	70	22	Softwood Kraft	[166]
$[C_4mim][MeSO_4]$	50	26	Softwood Kraft	[166]
$[C_2C_2IM][MeSO_4]$	50	26	Softwood Kraft	[166]
$[C_2C_2IM][MeSO_4]$	25	6	Softwood Kraft	[166]
$[C_4mim][MeSO_4]$	25	6	Softwood Kraft	[166]
$[Py][CH_3COO]$	90	>50	Kraft lignin	[165]
$[C_1mim][CH_3COO]$	90	>50	Kraft lignin	[165]
$[Pyrr][CH_3COO]$	90	>50	Kraft lignin	[165]

This observation is backed up by DFT calculations, which show that $[C_1mim][PF_6]$ is 6 kcal·mol^{-1} more weakly complexated with a model lignin compound than $[C_1mim][Cl]$.[169] However, a more recent study proposed that the influence of the anion on the degree of dissolution is negligible beyond a critical point.[171]

5.3.2. What is the role of the cation?

Also, the cation was found to have an influence on the lignin solubility.[167] Highest lignin solubilities were found in aromatic cations (e.g. imidazolium). A significant reduction in lignin solubility was observed upon methylation of the C2 carbon on the imidazolium ring (e.g. $[Bm_2im][CF_3SO_3]$ vs. $[C_4mim][CF_3SO_3]$).[171] Furthermore, the IL without any aromatic groups, $[N_{4448}][CF_3SO_3]$, showed evidently the lowest solubility.[171] Replacing the $[C_4mim]^+$ in the IL $[C_4mim][Cl]$ with 1-benzyl-3-methylimidazolium ($[Benzylmim]^+$) improved the dissolution of lignocellulose.

A theoretical study concluded that hydrogen bonding and pi-stacking interactions between lignin and the cation of the IL play an important role in the dissolution of lignin and lignocellulose in ILs.[169] This is consistent with the results that imidazolium cations with p-conjugated substituents, such as benzyl and allyl,[172,173] yield more successful lignocellulose solubility. A theoretical model found that imidazolium cations are particularly suitable for lignin solubilisation, as the cation can favourably interact with the lignin phenyl rings via the aromatic rings.[169] A high-throughput screening found that the best IL solvent for lignin combined $[Cl]^-$ anions and *p*-conjugated $[Amim]^+$ cations.[173]

5.3.3. What is the effect of the polarity of the ionic liquid?

Lignin dissolution capacities of ILs can be predicted by comparing their Hildebrandt solubility parameters (δH), as a measure of their polarities, with those of lignin. Maximum solubility is observed when the δH values of the biopolymer and solvent are identical, since the solubility of two materials is facilitated when their intermolecular attractive forces are similar.[174] Thus, the high solubility of lignin in $[C_4mim][CF_3SO_3]$ is not surprising given the similarity of the δH values for both the IL and lignin (24.9 and 24.6, respectively). Moreover, the δH values for $[C_4mim][PF_6]$ and $[C_4mim][BF_4]$ are 30.2 and 31.6, respectively,[175] which are sufficiently different from that of lignin, and therefore do not facilitate high lignin solubility.[167]

Another measure to correlate the lignin solubilities is Kamlet-Taft β parameter for hydrogen bond basicity. Mid to high range basic ILs seem to be better solvents for lignin than low hydrogen-bond basic ILs, although hydrogen-bond basicity does not need to be as high as for cellulose (> 1), see Figure 9.[125]

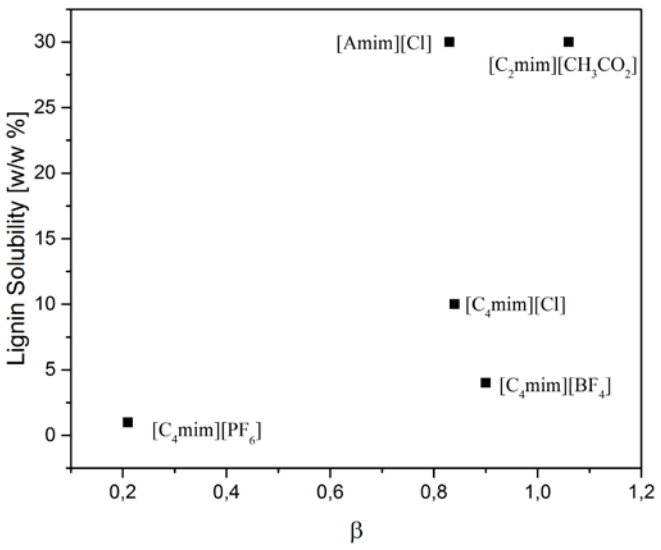


Figure 9: Lignin solubility over the Kamlet-Taft β parameter.[146,176,177]

5.4. Lignin extraction from lignocellulosic biomass with ionic liquids

Lignin extracted with commercial methods is considerately different from its native form. Although solubility tests give valuable information, the solubility of such model compounds for lignin in an IL do not guarantee that the same IL will also excel at extraction of native lignin from a biomass substrate. For this reason, several studies were performed aiming for the reduction of lignin content in real lignocellulosic biomass using ILs. It should be mentioned that for the extraction of lignin, cellulose, and starch from biomass, the H-bonding between solute and solvent molecules must be strong enough to break down inter- and intramolecular H-bonds in the biomass. Only ILs with anions with a strong H-bond accepting ability, e.g. halides and acetate, were found to work well.

In a recent study the ILs $[C_2CNBzim][Cl]$, $[C_2CNAim][Cl]$ and $[C_4mim][Cl]$ were found to be effective to extract lignin with 53%, 47% and 38%, respectively.[178] Furthermore, a mixture of the IL $[C_2mim][CH_3COO]$ and water demonstrated to be effective for the pretreatment of lignocellulosic biomass, removing 75 wt% of the lignin.[179] The most effective mixture so far was found to be the combination of monoethanol (MEA), sulfurdioxide (SO_2), 1,8-diazabicyclo-[5.4.0]-undec-7-ene (DBU). This combination was depicted as MEA-SO2-SIL, where SIL stands for switchable ionic liquid. The results showed 80 wt% lignin extraction.[180]

The cation species has an effect on the extraction efficiency similar to that on lignin dissolution. ILs that have cations with an electron-rich aromatic π-system have been observed to produce stronger interactions with polarizable solute molecules, such as lignin.[181,182] The extraction yield of phenolic compounds proved to be a little higher for [BPy][Cl] than $[C_4mim][Cl]$ and the lowest yield was observed for $[(CH_3)_4N][Cl]$. This can be explained by the more aromatic character of the $[BPy]^+$ in comparison with $[C_4mim]^+$.[183] A longer alkyl chain length of the cation enhances the extraction yield of lignin, as its hydrophobicity increases with increasing alkyl chain length. Apart from the hydrophobicity, the viscosity increases. Hence, the longer chain length benefits the extraction of some middle to less polar compounds, while the increase in viscosity limits their diffusion.[183–186]

A method to overcome the limits caused by viscosity is the usage of a co-solvent. For example, the addition of DMSO has proven to be beneficial for the extraction of lignin from wood, increasing the extraction efficiency by almost 50%.[187] The improvement in extraction yield in the presence of DMSO is only partially due to decreased viscosity, since it also has the potential to loosen the hydrogen bond network of the wood cellulosics, enhancing the penetration of the IL.

Another studied co-solvent is water, mainly since the presence of water is often inevitable during biomass treatments. Small amounts of water, <0.5 wt%, in the IL do not have a high impact on the extraction efficiency.[187] Higher amounts decrease the viscosity significantly, but are also detrimental for extraction yields. In fact, water at high concentrations is an

anti-solvent for lignin. Sun et al. completely dissolved wood in [C_2mim][CH_3COO], isolating up to 0.3 mass fraction of the initial wood lignin by selective precipitation in a mixture of acetone and water.[187]

5.5. Lignin dissolution and extraction from lignocellulosic biomass with deep eutectic solvents

In the search for an efficient and non-destructive process for lignocellulosic biomass fractionation, DESs have shown the first promising steps towards this goal.[65] In 2012 some DESs have been evaluated for biopolymer dissolution, showing remarkably high lignin solubilities compared to cellulose.[65] Especially DESs with lactic acid as HBD show high selective solubilities, up to 12.03 w%, for lignin and no detectable solubility for cellulose (Table 6). Moreover, the DES consisting of malic acid and proline showed high lignin solubilities. This suggests that DESs could very well be employed to design a selective lignin extraction for lignocellulosic biomass.

Kumar *et al.* recently reported extracting up to 60±5% of the total lignin in rice straw biomass with a maximum of 10% solids loading.[188] The DES based delignification of this rice straw had no significant effect on the cellulose and hemicellulose fractions.[188]

Procentese *et al.* have reported an 88 wt% decrease of acid insoluble lignin of corncob biomass samples after treatment at 150 °C and 43 wt% at 80 °C with a choline chloride – imidazole DES.[189] The crystallinity index of the biomass sample was measured before and after treatment, and was found unchanged for treatment at 80 °C, which implies that the DES pretreatment resulted in a reduction of the cellulose crystallinity, since the amorphous lignin has been reduced.

Addition of small amounts of water during pretreatment significantly enhanced the total lignin extraction, and nearly 22±3 % more lignin was released from the residual biomass into the DES extract. However, additional results showed that water contents above 5 % (w/v) affected the lignin extractability negatively.[188] An overview of the lignin extractability using DES is presented in Table 7.

Table 6: Solubility of lignin and cellulose in various DESs[65]

HBD	HBA	Ratio	T [°C]	Lignin [wt%]	Cellulose [wt%]
Lactic Acid	Proline	2:1	60	7.56	0.00
Lactic Acid	Betaine	2:1	60	12.03	0.00
Lactic Acid	Choline Chloride	1.3:1	60	4.55	0.00
Lactic Acid	Choline Chloride	2:1	60	5.38	0.00
Lactic Acid	Choline Chloride	5:1	60	7.77	0.00
Lactic Acid	Choline Chloride	10:1	60	11.82	0.00
Lactic Acid	Histidine	9:1	60	11.88	0.00
Lactic Acid	Glycine	9:1	60	8.77	0.00
Lactic Acid	Alanine	9:1	60	8.47	0.00
Malic Acid	Alanine	1:1	100	1.75	0.11
Malic Acid	Betaine	1:1	100	0.00	0.00
Malic Acid	Choline Chloride	1:1	100	3.40	0.00
Malic Acid	Glycine	1:1	100	1.46	0.14
Malic Acid	Proline	1:1	100	0.00	0.00
Malic Acid	Proline	1:2	100	6.09	0.24
Malic Acid	Proline	1:3	100	14.90	0.78
Malic Acid	Histidine	2:1	85	0.00	0.00
Malic Acid	Nicotinic Acid	9:1	85	0.00	0.00
Oxalic Acid[1]	Betaine	1:1	60	0.66	0.00
Oxalic Acid[1]	Proline	1:1	60	1.25	0.00
Oxalic Acid[1]	Choline Chloride	1:1	60	3.62	0.00
Oxalic Acid[1]	Glycine	3:1	85	0.28	0.00
Oxalic Acid[1]	Nicotinic Acid	9:1	60	0.00	0.00
Oxalic Acid[1]	Histidine	9:1	60	0.00	0.25
Oxalic Acid[2]	Choline Chloride	1:1	60	0.00	0.00
Oxalic Acid[2]	Proline	1:1	60	0.00	0.15

Table 7: Extractability of lignin of various DESs:

HBD	HBA	ratio	T [°C]	Extracted [wt%]	ref
Glycerol	Choline Chloride	2:1	80	4,4%	189
Glycerol	Choline Chloride	2:1	115	8,8%	189
Glycerol	Choline Chloride	2:1	150	24,8%	189
Urea	Choline Chloride	2:1	80	8,0%	189
Urea	Choline Chloride	2:1	115	24,8%	189
Imidazole	Choline Chloride	7:3	80	43,1%	189
Imidazole	Choline Chloride	7:3	115	70,8%	189
Imidazole	Choline Chloride	7:3	150	88,3%	189
Lactic Acid	Betaine	2:1	60	52,0%	188
Lactic Acid	Betaine	5:1	60	56,0%	188
Lactic Acid	Choline Chloride	2:1	60	51,0%	188
Lactic Acid	Choline Chloride	5:1	60	60,0%	188
Lactic Acid	Choline Chloride	9:1	60	59,0%	188

5.6. Lignocellulosic biomass dissolution and regeneration with ionic liquids

The research into the dissolution of lignocellulosic biomass with ILs started in 2007 when two publications regarding this topic arose in literature. The first publication showed partial dissolution of 5 wt% wood chips in the mixture of the AIL [C_4mim][Cl] and the co-solvent DMSO-d_6 at 100 °C.[190] The types of woods used in this investigation were pine, poplar, eucalyptus and oak, and dissolution times varied from 2 to 24 h. It was shown that dissolution was easier for softwoods than for hardwoods. To investigate the dissolved wood, it was regenerated with either a mixture of water and acetone (1:1), dichloromethane, or acetonitrile. The other publication in 2007 used [C_4mim][Cl], [Amim][Cl], 1-methyl-3-benzylimidazolium chloride ([benzylmim][Cl]), 1-Methyl-3-m-methoxylbenzylimidazolium chloride ([methoxybenzylmim][Cl]), 1-Methyl-3-methylbenzylimidazolium chloride ([methylbenzylmim][Cl]) and 1-Methyl-3-benzyl-imidazolium 1-Methyl-3-benzyl-imidazolium dicyanamide ([benzylmim][Dca]) for testing the dissolution of unbleached Norway spruce thermomechanical pulp (TMP), Southern pine TMP, Norway spruce dust and ball-milled Southern pine powder and wood chips.[172] The results demonstrated that especially [C_4mim][Cl] and [Amim][Cl] had high ability for dissolving the wood-based lignocellulosic

biomass. The best results were obtained for the dissolution of Norway spruce sawdust at heating to 100 °C for 8 h, being 8 wt% for both [C_4mim][Cl] and [Amim][Cl]. Moreover, 8 wt% of ball-milled Southern pine powder could be dissolved with the AIL [Amim][Cl]. The dissolved wood was regenerated with distilled water.

In 2009 investigations showed several other AILs able to dissolve wood. The AILs [Amim][Cl], [C_2mim][Cl], [C_4mim][Cl], [ECOENG][1111P] and [C_2mim][CH_3COO] were tested for the dissolution of 5 wt% wood chips of the species spruce, silver fir, common beech and chestnut at 90 °C, while shaking for 12 h.[173] The results indicated that [C_2mim][Cl], [C_4mim][Cl] and [ECOENG][1111P] partially dissolved all the wood species, while [C_2mim][CH_3COO] could completely dissolve the four wood chips expect for the silver fir, which was only partially dissolved. All four types of wood chips could be dissolved with the AIL [Amim][Cl]. It was hypothesized that the π-electrons of the side chain of the cation play an important role, since it has the capability to undergo π-π interactions with the aromatic compounds of lignin contributing to the dissolution ability of this AIL.[173] Furthermore, the low viscosity could play a role. Another investigation in 2009 aimed at full dissolution of lignocellulosic biomass with [C_2mim][CH_3COO] in comparison to [C_4mim][Cl].[191] [C_2mim][CH_3COO] was chosen for its higher hydrogen bond basicity, which was hypothesized to be a more effective solvent for dissolving the lignocellulosic biomass. A softwood, southern yellow pine, and a hardwood, red oak, were used for the investigation. The results demonstrated that red oak can be fully dissolved within 25 h and southern yellow pine 46 h, both at 110 °C. It was observed that smaller particle sizes led to an easier dissolution, which can be explained by the increased surface area and the breaking down of the structure due to the pre-treatment.

Continued investigations showed that viscosity, water content and temperature played an important role in the swelling and the partial dissolution of pine sapwood.[192] Kamlet-Taft parameters were investigated to correlate the dissolution behaviour. The results indicated that especially the Kamlet-Taft β parameter needs to be higher than 0.8.

In 2011 research continued with the dissolution of different wood sorts with aforementioned AILs. [Amim][Cl] in combination with 16 wt% of DMSO was used for the dissolution of approximately 5 wt% of pine, poplar, Chinese parasol or catalpa wood samples at different temperatures.[193] Since a colour change and an increase of viscosity was observed, it was assumed that wood was fully dissolved. As found before, softwood, in this case pine, can be easier dissolved than the hardwoods. The authors further indicated that a reduction of dissolution time was possible by the use of microwave irradiation instead of heating in an oil bath. In another publication the disintegration and dissolution kinetics of wood chips, beech and spruce wood, were investigated for the AIL [C_2mim][CH_3COO].[194] Wood particles varying from 0.1-0.5 mm were used. The results showed that approximately 40% of spruce and 75% of the beech could be dissolved at 115 °C. No full dissolution was observed after 72 h. It was observed that the kinetics can be considered as a first order reaction. An interesting research showed the dissolution of bagasse within 5-15 min at temperatures up to 195 °C and approximately 90% dissolution of southern yellow pine at 175 °C after 30 min.[195] These dissolution temperatures are both above the glass transition temperature of lignin. Despite the major decrease of the dissolution times, the AIL disintegrated for about 15%, which contributes to a lower overall efficiency when recycling is taken into account. Later in 2011, a combination of acetic acid with the ILs [C_2mim][CH_3COO], [C_2mim][Cl] and [C_4mim][Cl] was used for the dissolution of wheat straw and pine wood.[6] It was shown that not only dissolution occurs, but also hydrolysis.

It was also tried to dissolve pinus radiata (0.35 g) with the AIL [C_2mim][CH_3COO] (7.0 g) at temperatures of 120 °C and 155 °C.[196] It was observed that after 3 h the wood particles swelled and partially dissolved, but no complete dissolution was achieved. In 2012 4 wt% of pinus radiata and eucalyptus globulus were dissolved in the IL [AMIM][Cl].[197] The extractives from these woods were removed with acetone and water, after which dissolutions were conducted in a microwave oven first 10 min at 110 °C, continued by heating at 120 °C for 20 min. After dissolution, DMSO is added to decrease the viscosity of the system, after which the mixtures were filtered to remove the parts that were not dissolved (34%). The solutions were added to 200 mL methanol to precipitate the cellulose via stirring at 300 RPM for 10 min and a temperature of 40 °C. FTIR analysis showed that the precipitated cellulose was comparable to MCC, while XRD and ^{13}C NMR proved that crystallinity of the regenerated cellulose decreased due to the dissolution and regeneration processes. In 2013 this paper was continued with the same two sorts of wood, where in this case both raw wood and extractive-free wood were used.[198] The solutions of the mixtures of wood and IL were first heated at 110 °C for 10 min, after which the temperatures were increased to 120, 140 or 170 °C for approximately 20, 40 or 60 min. Methanol was used as anti-solvent to regenerate cellulose and lignin. It was found that by varying the regeneration temperature and time, either pure cellulose, both cellulose and lignin, or pure lignin can be regenerated. Later in that year, three methods were described for regeneration.[199] A brief summary is depicted, but for a broad description the reader is redirected to the original publication.[199] The 1st method was based on the dissolution of 250 mg of wheat straw particles (<0.5 mm) in 5 g of the IL [C_2mim][CH_3COO] for 6 h under continuous stirring and heating at 120 °C.[199] After the dissolution, 0.1 M NaOH was used for the precipitation of the carbohydrate material. This material was collected by filtration and washing with ultrapure water, after which the lignin was precipitated from it with 1 M HCl and heating the mixture up to 70 °C during 30 min. The lignin was washed with 10 mL of ultrapure water and both the lignin as the carbohydrate materials were dried for 24 h at 60 °C. The 2nd method describes the dissolution of 100 mg of the before mentioned wheat straw in 5 grams of [C_2mim]CH_3COO] for 4 h at a

temperature of 110 °C.[199] In this method regeneration is performed upon addition of a mixture consisting of acetone/water (9:1, v/v), after which the solution was centrifuged at 4000 RPM for 15 min at 22 °C. The phase containing the carbohydrate-rich phase was filtered and then washed again in a 1:1 (v:v) mixture of acetone/water after it was centrifuged at 9000 RPM for 30 min at 4 °C, after which the carbohydrates were dried for 18 h at 60 °C. From the lignin containing phase acetone was removed via reduced pressure, after which the pH was lowered to 2.0 upon addition of 1 M HCl. This step was conducted to precipitate lignin-rich material, which was subsequently washed with 0.01 M HCl. The third method was an optimized regeneration by combining the two previous mentioned methods.[199]

Another publication in 2013 presented ILs based on amino acids.[200] It was observed that the IL N-methyl-N-(2-methoxyethyl)-pyrolidin-1-ium 2,6-diaminohexanoate ([P1ME][Lys]) was able to dissolve lignin at 60 °C and not cellulose, while both could be dissolved at 80 °C. With this IL, the authors extracted lignin from Japanese cedar (Cryptomeria japonica). They added 1.0 g of the lignocellulosic biomass to the IL and stirred it for 12 h at 60 °C. The lignin precipitated upon addition of methanol or ethanol. In general, this IL could even be used to fully dissolve the lignocellulosic biomass at the higher temperatures, after which cellulose could be precipitated upon decreasing the temperature of the mixture. Furthermore, cellulose was dissolved originating from ammonia fiber expansion (AFEX) pretreated Zoysia japonica.[201] It was shown that AFEX pretreatment reduces the amount of lignin and hemicellulose in the biomass and thus breaks the structure of the lignocellulose. For the dissolution, 2 g of the pretreated Zoysia japonica was dissolved in 50 g of the IL [Amim][Cl]. Moreover, the results indicated that approximately 97% of the cellulose could be regenerated. Wood was also pretreated with autohydrolysis to increase the fractionation of the birchwood.[202] The results showed that with the pretreatment 15 wt% of the birchwood could be dissolved, while this was unrenderable without. Upon precipitation, it was shown that the cellulose-to-lignin ratio changed from 2.7 to 5.7 (comparison of non-treated with pre-treated). A more fundamental research gave physical insight into the dissolution of switchgrass in the IL [C_2mim][CH_3COO] with small-angle neutron scattering.[203] The results showed that although dissolution of the cellulose fibrils occurs, the supramolecular network of the biopolymer stays intact. However, this is not present in solutions of the individually biopolymers, and thus, no self-assembly occurs. Finally, a recent paper showed the complete dissolution of switchgrass in [C_4mim][Cl] via ultrasonification.[204] An overview of all ionic liquids that have been used to dissolve lignocellulosic biomass can be found in Table 8.

Table 8: Ionic liquids that can dissolve lignocellulosic biomass

IL	Biomass type	Recovery solvent(s)	T [°C]	t [min]	Particle size [mm]	Ref
[C_4mim][Cl][a]	Pine Poplar Eucalyptus Oak	1:1 acetone-water Dichloromethane Acetonitrile	100	120 360 720 1440	5	190
[C_4mim][Cl]	Wood chips	Distilled water	130	900	N.A.	172
[C_4mim][Cl]	Norway spruce sawdust	Distilled water	110	480	0.1-2	172
[C_4mim][Cl]	Southern pine TMP	Distilled water	130	480	N.A.	172
[Amim][Cl]	Ball-milled Southern pine powder	Distilled water	110	480	N.A.	172
[Amim][Cl]	Norway spruce sawdust	Distilled water	110	480	0.1-2	172
[Amim][Cl]	Norway spruce dust	Distilled water	80	1440	0.1-2	172
[Amim][Cl]	Norway spruce TMP	Distilled water	130	480	N.A.	172
[Amim][Cl]	Southern pine TMP	Distilled water	110	480	N.A.	172
[Amim][Cl]	Southern pine TMP	Distilled water	130	480	N.A.	172
[bzmim][Cl]	Southern pine TMP	Distilled water	130	480	N.A.	172
[bzmim][Cl]	Norway spruce TMP	Distilled water	130	480	N.A.	172
[bz-ome-mim][Cl]	Southern pine TMP	Distilled water	130	480	N.A.	172
[benzylmim][Dca]	Southern pine TMP	Distilled water	130	480	N.A.	172
[Amim][Cl]	Spruce Silver fir Common beech Chestnut	N.A.	90	1080	1-2	173
[C_2mim][Cl]	Spruce Silver fir Common beech Chestnut	N.A.	90	1080	1-2	173
[C_4mim][Cl]	Spruce Silver fir Common beech Chestnut	N.A.	90	1080	1-2	173
[ECOENG][1111P]	Spruce Silver fir Common beech Chestnut	N.A.	90	1080	1-2	173
[C_2mim][CH_3COO]	Spruce Silver fir Common beech Chestnut	N.A.	105	1080	1-2	173
[C_2mim][CH_3COO]	Southern yellow pine Red oak	Acetone/water (1:1 v/v)	110	2760 1500	0.125 0.125-0.250 0.250-0.500 0.500-1.000	195
[C_4mim][OTf] [C_4mim][$N(CN)_2$] [C_4mim][$MeSO_4$] [C_4mim][Cl] [C_4mim][Me_2PO_4] [C_4mim][$MeCO_2$]	Pine	N.A.	60-120	≤ 60 h	10x10x5	192
[Amim][Cl]	Pine Poplar Chinese parasol Catalpa	DSMO/water	90 120	min-h	0.45-0.65	193
[C_2mim][CH_3COO]	Spruce Beech	N.A.	115	≤ 72 h	0.1-0.5	194
[C_2mim][CH_3COO]	Bagasse	Acetone:water (1:1 v/v)	110	900-960	<0.125	195
[C_2mim][CH_3COO]	Bagasse	Acetone:water (1:1 v/v)	175-195	5-15	<0.125	195
[C_2mim][CH_3COO]	Pine	Acetone:water (1:1 v/v)	175	30	<0.25	195
[C_2mim][CH_3COO]	Wheat straw Pine	Water	100	1440	<0.1	6
[C_2mim][Cl]	Wheat straw Pine	Water	100	1440	<0.1	6
[C_4mim][Cl]	Wheat straw Pine	Water	100	1440	<0.1	6

$[C_2mim][CH_3COO]^b$	Wheat straw Pine	Ethanol (cellulose) Water (lignin)	100 125	300	<0.1	[6]
$[C_2mim][Cl]^b$	Wheat straw Pine	Ethanol (cellulose) Water (lignin)	100 125	300	<0.1	[6]
$[C_4mim][Cl]^b$	Wheat straw Pine	Ethanol (cellulose) Water (lignin)	100 125	300	<0.1	[6]
$[C_2mim][OAc]$	Pinus radiata	Water	120 155	180	0.420 - 0.841	[196]
[Amim][Cl]	Pinus radiata and Eucalyptus globulus woods	Methanol	110-120	10 20	N.A.	[197]
[Amim][Cl]	Pinus radiatia and Eucaltyptus globulus	Methanol	110-120 140 170	10 20 40 60	N.A.	[198]
$[C_2mim][CH_3COO]$	Wheat straw	0.1 M NaOH 1.0 M HCl NaOH pelleter Acetonitrile Acetone/water (9:1, v/v) Acetone/water (1:1, v/v)	120	360	<0.5 mm	[199]
$[C_2mim][CH_3COO]$	Wheat straw	Ultrapure water 1.0 M HCl 3% (w/w) NaOH 4 M HCl 96% (v/v) ethanol 0.1 M NaOH distilled water HCl 4 M HCl 1 M 96% (v/v) ethanol HCl 0.02 M 3% (w/w) NaOH	110	240	<0.5 mm	[199]
$[C_2mim][CH_3COO]$	Wheat straw		120	360	<0.5 mm	[199]
$[C_2mim][Cl]$	Zoysia japonica	Deionized water	80	30	<0.7 mm	[201]
$[C_2mim][CH_3COO]$	Birchwood	Acetone/water (1:1 v/v)	100	N.A.	<0.125 mm	[201,202]
[C4mim][Cl]	Switchgrass	Acetone Water	130 100-150[b]	720-1440 2-4	N.A.	[204]

[a]Not Adressed [b]Ultrasonification

6. Other extractables

Apart from the three most obvious lignocellulosic biomass constituents – lignin, cellulose and hemicellulose – alternative biomass components can be valorised. These components are typically located outside the plant's stem, for instance in fruits, seeds or leaves. Attempts have been made to process, isolate and/or valorise these components with both ILs and DESs. The treatment of plant materials with ILs was extensively reviewed in literature,[205,206] therefore the focus of the following paragraphs will be on DESs. Consequently, the performance of DESs will be compared to that of ILs for each particular application where both solvent categories have been studied.

6.1. Starch processing

Together with (hemi)celluloses, starch is an omnipresent polysaccharide found in vegetal sources. Several studies present notable starch solubilities in DESs (see Table 9), while starch is poorly soluble in water and most other polar solvents.[207] Since DESs exhibit strong affinities with starch, they were explored for the plasticisation of thermoplastic starch. A DES and starch were introduced to an extruder resulting in plastic pallets that can be moulded into films. Plasticisers (conventionally glycerol, urea, ethanolamine or formamide) are added to starch films to decrease some of its weaknesses, such as recrystallization and moisture absorption, both leading to reduced mechanical properties.[208,209] Starch plasticised with glycerol:ChCl 2:1 resulted in a colourless translucent film, while the incorporation of urea/ChCl based DESs resulted in a transparent slightly yellow film with better material properties.[208,209]

Table 9: Starch solubility in several ILs and DESs

Solvent	Sol [wt%]	T [°C]	t [h]	Ref
[Amim][Cl]	15	80	0.66	[210]
	20	100	15	
	50	100	n.r.	
$[C_4mim][Cl]$	15.0	80	n.r.	[207]
$ZnCl_2$:ChCl 1.9:1	4.6	98	n.r.	[207]
Urea:$CaCl_2$ 4:1[a]	16.7	80	n.r.	[207]
Urea:ChCl 1:1[a]	9.1	100	n.r.	[207]
Citric acid:ChCl 1.4:1[a]	8.3	100	n.r.	[207]
Oxalic acid:ChCl 1:1.6[a]	9.1	100,	n.r.	[207]
Oxalic acid:ChCl 1:1	0.15	60	<24	[65]
Glucose:ChCl 1:1	17.2[c]	n.r.	n.r.	[56]
Lactic acid:ChCl 10:1	0.13	60	< 24	[65]
Lactic acid:Histidine 9:1	0.13	60	< 24	[65]

Lactic acid:Alanine 9:1	0.26	60	< 24	[65]
Malic acid:Alanine 1:1	0.29	100	< 24	[65]
Malic acid:Betaine 1:1	0.81	100	< 24	[65]
Malic acid:ChCl 1:1	7.10	100	< 24	[65]
Malic acid:Glycine 1:1	7.65	100	< 24	[65]
Malic acid:Proline 1:2	0.32	100	< 24	[65]
Malic acid:Proline 1:3	5.90	100	< 24	[65]
Oxalic acid:Nicotinic acid 9:1	2.83	60	< 24	[65]
Oxalic acid: Proline 1:1	0.15	60	< 24	[65]

In addition to DESs, ILs can act as plasticisers at low concentrations (< 25 wt%). Similarly, the inclusion of [Amim][Cl] or [C_4mim][Cl] lowers the hygroscopicity of the starch film and improves its material properties compared to the conventional glycerol.[211] An advantage of [C_4mim][Cl] over the tested DESs and glycerol is that it allows the starch films to be compatible with zein.[212] Zein is a hydrophobic protein that is abundant in corn. This allows the production of films from corn starch with higher zein impurities, reducing the level of corn flour refining necessary. The two tested ChCl containing DESs showed less compatibility with zein than [C_4mim][Cl].[212]

Another advantage of using ILs as starch plasticisers over DESs is that the resulting film has a relatively high electrical conductivity.[211] Polymer electrolytes made with IL plasticized starch have conductivities in the range of 10^{-5} – $10^{-1.5}$ $S \cdot cm^{-1}$, while conductivities for DES based starch films show conductivities in the order of 10^{-7} $S \cdot cm^{-1}$.[205,208,211] The advantages of the DES (cheap, easy preparation) were combined with the advantages of lithium bis(trifluoromenthanesulfonyl)imide (LITFSI) plasticised starch. The conductivities of these DES-LITFSI-starch films were in the order of 10^{-5} – 10^{-3}.[213] However, not many details were given on other material properties. A more elaborated discussion on ILs and starch plasticisation, dissolution and modification can be found in an earlier review.[205]

6.2. Plant extractives

Two main plant material valorisation routes can be distinguished: (1) utilising the pervasive biopolymers, isolate and/or modify them into moderate added-value materials or chemicals and (2) isolating specific, low amounts of valuable components present in the biomass. The last route creates extensive added-value to the biomass and circumvents the often costly synthesis necessary to obtain the components artificially. However, it requires an extractant with high selectivity towards the solute. Designer solvents like DESs and ILs can offer this feature. A detailed overview of viable extraction pathways for value-added compounds originating from biomass utilising ILs is given in a recent review.[206]

In 2013, the extraction, stabilisation and recovery of yellow and red pigments from safflower with DESs were studied.[214,215] It was found that the main hurdle to successful extraction was the DESs' inherent high viscosity. Increasing the extraction temperature from ambient to 40 °C could decrease the viscosity of a DES significantly.[68,82] However, the biggest reduction of viscosity was obtained by the addition of 10-25 wt% water. Extraction yields of the diluted DESs were analysed for polar and less polar pigments at multiple water contents. The optimum DES-water mixtures displayed comparable or better extraction results than the reference solvents water, ethanol and the 60/40 (v/v) water/ethanol mixture.[214] This emphasises once more the tunability of DESs and their compatibility with water. The stability and solubility of the pigment could also be controlled by the DESs' water content, decreasing water contents yielded improved stability and the solubility had an optimum at 10% (v/v) water.[68,215]

The same strategy was applied for the extraction of compounds from traditional Chinese medicines (TCM), which usually originate from plant roots, leaves or blossoms. Recently, the extraction of bioactive compounds from pigeon pea roots (*Cajanus Cajan*)[216] and sophora flowers (*Flos Sophorae*)[217], flavonoids from skullcap root (*Radix Scutellariae*)[218] and marsh horsetail (*Equisetum Palustre*)[219] and phenolics from *Pyrola incarnata Fisch*[220] and dried sprouts of the redstem wormwood (*Herba Artemisiae Scopariae*)[221] was studied. The aim of the extraction experiments is to either isolate or quantify the active components that are present in the often complex matrices of TCMs. The extraction efficiencies of the DESs were optimised through statistical analysis using microwave (MAE),[216,218,220] ultrasound (UAE)[216,217] and negative pressure cavitation (NPCAE)[219] assisted extraction. The optimisation process typically focuses on a series of single factor experiments. Herein, the DESs' components, ratio and water content are optimised followed by the extraction conditions (temperature, time, sample loading). In all cases, the extraction process was more effective compared to the common extractants, often (a mixture of water and) an alcohol.

In the aforementioned publications the performance of DESs was not directly compared to that of ILs, probably since the biomass source was not the same or because the optimisation process focussed on different techniques. Pigeon pea roots have, for instance, also been treated with ILs, but only using NPCAE.[222] Lab-scale DES-MAE could obtain yields of 0.449, 0.617 and 0.221 $mg/g_{dryweight}$ for genistin, genistein and apigenin,[216] respectively, while the yields for those flavonoids were 0.482, 0.496 and 0.291 $mg/g_{dryweight}$, respectively, for IL-NPCAE[222]. The yields are in the same order of magnitude, but since no IL-MAE or DES-NPCAE studies were performed, it is questionable whether it is a fair comparison. For redstem wormwood no comparable direct extraction was performed with ILs, but a supported IL showed interaction with the phenolic acids that could be extracted with DESs.[221,223] This allows the alternative analysis of four bioactive components in a redstem wormwood extract.

Another analytical chemistry related application of designer solvents is the headspace single droplet microextraction (HSDME) using DESs and ILs. In this technique, a single micro droplet of a low-volatile solvent with a known volume is brought into contact with the headspace of a liquid or solid containing volatile compounds. The volatiles are extracted from the headspace into the micro droplet and the droplet is

subsequently injected in a gas chromatograph for qualification or quantification of the volatiles.[224] Both DESs and ILs are described to have low volatility and could act as selective extractant for headspace samples.[225,226] The first application of DESs in a HSDME setup is the analysis of terpenoids in Japanese cypress (*Chamaecyparis obtuse*) leaves with ethylene glycol:ChCl mixtures.[225] Hence, in combination with HSDME, DESs can be used for the analysis of specific compounds in biomass samples.

DESs were also applied to the extraction of saponins from sisal waste and juá bark.[227] Saponins are plant metabolites that can be applied as bioinsecticide, surfactant and act as a basis for steroidal drugs.[227,228] ChCl based DESs and cholininium based ILs were mixed with water or a water/ethanol mixture and consecutively tested for saponin extraction.[227] The ILs were generally performing slightly better than, or similar to their corresponding DESs.[227] Nevertheless, the cholinium based ILs were omitted during extraction optimization since their estimated price is typically an order of magnitude higher than that of their corresponding DESs. After several optimisation steps, the most effective DES based extractants appeared to be the mixtures consisting of 58 % propionic acid:ChCl 2:1 + 42% ethanol and 81% acetic acid:ChCl 2:1 + 19% water for juá bark and sisal waste, respectively. The DESs showed high selectivities and they could improve the extraction efficiency with a factor 1.7 and 2.5 compared to ethanol and water, respectively. It has to be noted, however, that the pure acid constituents used in the DESs are liquid at room temperature and their eutectic behaviour was not reviewed.

By the use of ILs, other sources for saponins were explored. Dried leaves and aerial parts of mate (*Ilex paraguariensis*) and tea (*Camellia sinensis*) were treated with aqueous imidazolium and cholinium based ILs and with aqueous solutions of ChCl.[228] In another research ginseng roots were subjected to aqueous imidazolium ionic liquid based ultrasonic assisted extraction experiments.[229] In both studies the influence of the imidazolium alkyl chain length on the extraction efficiency and selectivity was investigated. The alkyl chain length of the imidazolium cations affected the extraction performance, but the effect was different per saponin source. [C_3mim][Br] clearly showed the highest extraction efficiency for ginseng roots, while for shorter and longer alkyl chains the efficiencies are significantly lower, although similar among them.[229] For tea a different trend was observed: [C_2mim][Cl] and [C_4mim][Cl] had comparable extraction efficiencies, but increasing the alkyl chain length more resulted in an obvious decrease. The extraction results of mate did not show a clear tendency with increasing cation chain length.[228] The influence of the extractants' anions on the extraction efficiencies of mate, tea, ginseng, juá bark and sisal waste was studied.[227–229] The anions of imidazolium based ILs did not appear to be vital for the extraction process, while for cholinium based ILs the efficiencies were strongly influenced by changing the anion. Again, different behaviours were observed for the distinct biomass sources.

It has to be noted that the saponins in tea, ginseng, juá bark, sisal waste and mate consist of different glycoside and terpene groups. This obviously influences the solute-solvent interactions.[227–229] Additionally, the solute accessibility changes with the biomass type and process conditions. This is expressed in the different temperature profiles for extraction efficiencies of saponins with ChCl from mate and tea. For mate the efficiencies increased significantly with temperature, while for tea they remained constant.[228] The size and polarity of the DESs' components and ILs' ions play different roles depending on the biomass variety. This highlights that a tailor-made extractant is often needed for the selective extraction of value-added components from biomass sources. Both DESs and ILs offer the versatility to exploit efficient, cheap and renewable extraction routes from biomass sources.

7. Challenges and outlook

The innovative solvents as discussed in this review show great promise for the processing of lignocellulosic biomass. With the current information available in literature, AILs have the potential of overtaking the conventional methods used in the bio refinery industry, which is shown by their possibilities of large removal of lignin from the lignocellulosic biomass, up to 50 wt%, in combination with the large cellulose dissolution, up to 25 wt%. Next to their high extraction and dissolution capacity, various studies show their high thermal stability ensuring the usage of the AILs at the high temperatures needed for the extraction of lignin and the solvability of cellulose. Nevertheless, AILs also have some disadvantages, which should be resolved or further investigated before scale-up or implementation in industry is possible. Probably the biggest disadvantage of AILs is their production price. The combination of the low reaction yields and the use of conventional solvents leads to the need of extended purification steps increasing their price per ton. Thus, better procedures should be devised to decrease the production price. Next to their high production price, AILs often have moderate to high viscosities hampering their full potential due to a lower ability of dissolution caused by a large decrease of mass transfer. This problem could be overcome by the addition of conventional solvents such as DMSO. However, this introduces other problems related to toxicity and the separation of these co-solvents from the AIL for their use in the regeneration.

A promising alternative for the AILs are the PILs, which are able to dissolve cellulose (18 wt%) in combination with their ability to extract lignin (80 wt%) from lignocellulosic biomass. The major advantage of PILs over AILs is their easy preparation. While for the AILs a complete synthesis with extended purification is needed, only mixing of the acid and base is needed for the preparation of a PIL. A disadvantage of the preparation is the fact that it is exothermic, which introduces the need for cooling. At a lab scale this is a minor problem, but heat development can cause major problems during the upscaling process. Moreover, the thermal stability and the recycling of PILs should be further investigated. The ability of PILs to evaporate is often noted as a big advantage, and could be a method for recycling, but the boiling points are

so high that enhanced temperatures would be needed. In our opinion, this will make applications such as distillation too energy-costly. Furthermore, only few publications discussed the handling of cellulose and lignocellulosic biomass with PILs. Thus, in general it can be concluded that further investigation is needed before a concrete conclusion can be made, though until now they show great potential for a future in the bio refinery industry.

The last class of solvents that was discussed for its future use of treating lignocellulosic biomass and its constituents are the DESs. As mentioned before, DESs were only published for the first time in 2003. Thus, until now only a fraction of the work in the field of DESs has been done. Despite, DESs show already great promise for a future use in the bio refinery industry. As published by our group in 2012, DESs can be used for dissolving up to 14.9 wt% lignin. More recent work has shown the potential of DESs when lignin was extracted from lignocellulosic biomass. It should be mentioned that the amounts of cellulose that can be dissolved are not high yet and in some cases the results are not reproducible. Therefore, at the moment the performance of DESs for biomass processing is still inferior to that of ILs. However, we think this is just a matter of time and finding the right functional groups and constituents. A major advantage of DESs is their easy preparation being mixing at moderate temperatures. No cooling and no purification steps are needed, which makes them cheaper than ILs. Furthermore, the constituents of DESs are in most cases described as readily available and ‘green’. We agree with this, although synergy/additivity effects should be investigated before calling a DES ‘green’. A disadvantage already known in literature is the viscosity of DESs, which is often rather high. Currently, there is also still a lack of fundamental knowledge about the formation of DESs and their interaction with solutes. Furthermore, more research should also be conducted into the thermal stability of the DESs to obtain a deeper inside in this topic.

For both the PILs and DESs it is the question if only dissolution or also acid hydrolysis occurs. Up until now, only minor knowledge is present in literature regarding the acidity of the PILs and the DESs. Thus, this should be addressed first before more discussion is possible.

In general, all three innovative solvents have potential for a future use in the bio refinery for the valorisation of lignocellulosic biomass and the alternative biomass constituents. However, scale up experiments should be conducted to investigate their full potential. Questions that still arise from the literature are: i) How is the recyclability of these innovative solvents? ii) What is the influence of water on their performance? iii) Are the particular solvents proposed to use in the bio refinery industry as ‘green’ as thought? iv) Can they be produced on the large scale needed for the bio-refinery (ton/year scale)?

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