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Dissolution and Hydrolysis of Lignocellulosic Biomass using Tailored Ionic Liquids

Yue Dong, Jana Holm and Ulla Lassi

Additional information is available at the end of the chapter

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1. Introduction

Over the course of the last few decades, the growing demand for energy globally has a wide range of problems associated with it. Anthropogenic emission of greenhouse gases is the severest among these. An increase of carbon dioxide (CO₂) released by burning fossil carbon contributes significantly to the greenhouse effect. Much discussion of limiting CO₂ emission, using renewable energy, generating energy from alternative renewable sources and waste is the primary subject at present [1].

The international Energy Agency (IEA) has reported, approximately 10% of the world's total primary energy supply was biomass-based energy in 2009 [2]. The European Commission aim is to receive 20% of the total energy in the EU from renewable sources (wind, solar and hydropower as well as geothermal energy and biomass) by 2020 [3]. The European Network of Transmission System Operators (ENTSO) expects through The ENTSO-E Ten-Year Network Development Plan (TYNDP) 2014, the total electricity consumption in 34 European countries will integrate up to 60% of renewable energy [4].

The term "biomass" refers to the abiotic organic matter and the living plants that store energy through photosynthesis. Biomass is one of the most plentiful and common utilized sources that is used to generate renewable energy in the world. Biomass-based energy is considered as CO₂ neutral based on the life cycle assessment (LCA) and carbon dynamics in the biosphere. Therefore, biomass-based energy plays an important role in carbon mitigation, especially in the replacement of fossil fuels [5] [6].

Significant research has been made on the conversion of lignocellulosic biomass to biofuel as an alternative replacement of transportation fuel, due to its abundance and low cost. There are three major stages in conventional production of biofuel from lignocellulosic biomass: i)

delignification (pretreatment), ii) hydrolytic depolymerisation (hydrolysis) and iii) fermentation. The amount of sugar that is produced in the former two steps affects the amount of produced biofuel in the latter fermentation process. The pretreatment of lignocellulose is, therefore, an essential step in improving the production of biofuel [7] [8].

Cellulose is an abundant renewable polymer that exists readily in nature, typically combined with lignin and hemicellulose in the cell walls of lignocellulosic biomass. The conception of pretreatment of lignocellulosic biomass is to reduce the crystallinity of cellulose and increase the porosity of biomass so that expanding the accessible surface area of cellulose for hydrolysis. The challenging pretreatment of using available cellulose involves its dissolution [9] [10].

Numerous studies have argued that the dissolution of lignocellulosic biomass with imidazolium-or pyridinium-cation and anions like Cl^- , Br^- , $[\text{OAc}]^-$ and $[\text{CH}_3\text{CH}_2\text{PO}_2]^-$ -based ionic liquids (ILs), such as 1-Butyl-3-methylimidazolium Chloride ([BMIM]Cl) and 1-Allyl-3-methylimidazolium chloride ([AMIM]Cl) would significantly improve sugar conversion in the depolymerisation step [8] [11]. Recently, novel ILs that are especially tailored to combine dissolution and hydrolysis of lignocellulosic biomass simultaneously brings the utilization of lignocellulose to a new scenario.

2. Lignocellulosic biomass

Lignocellulosic biomass accounts for 50% of the world's biomass, such as residues of forest and agriculture, grass and municipal solid waste. It represents an abundant carbon source that stores sunlight energy through photosynthesis. Currently, biomass is the biggest source provider of renewable energy, in all 28 EU countries (See Figure 1) [12] [13].

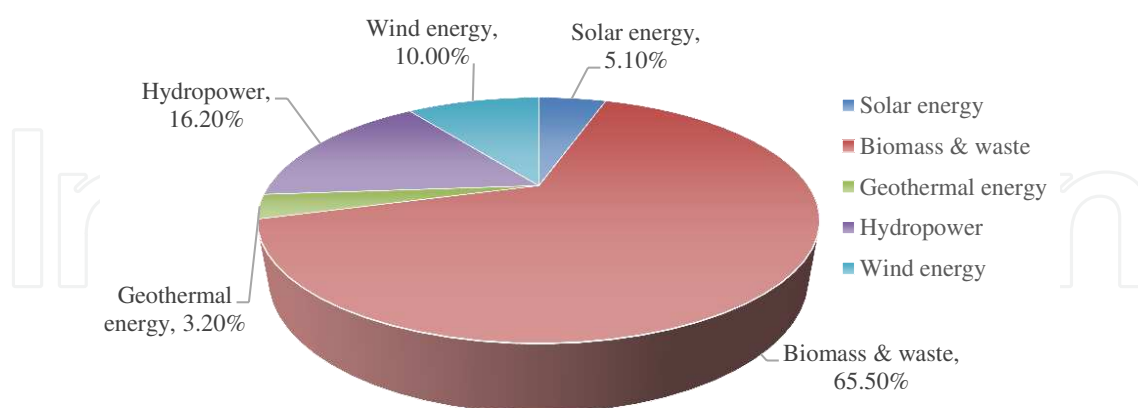


Figure 1. Primary production of renewable energy in the European Union, 2012 [12].

Figure 2 shows the growth of final renewable energy consumption and the renewable energy generated from biomass, wind and solar in all 28 EU countries in the last 12 years. Biomass currently plays a dominant role in renewable energy production and the growth of biomass demand is expected to increase as much as 50% of current demand within the next decade [12].

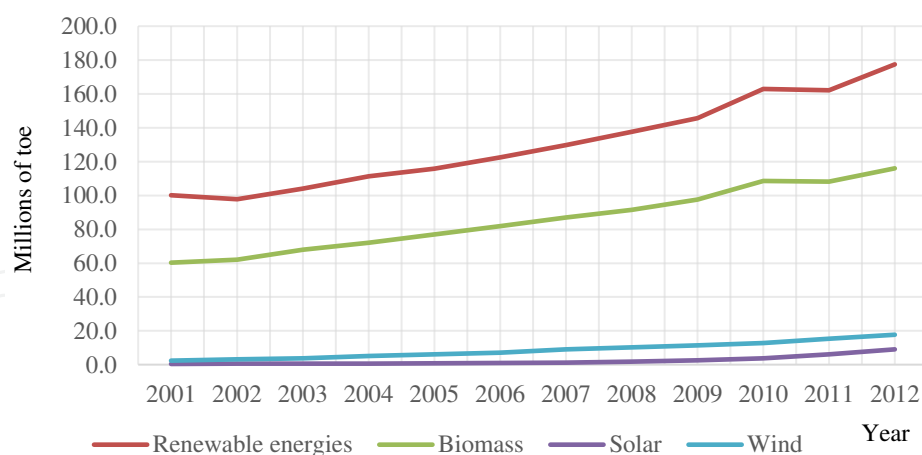


Figure 2. Final renewable energy consumption and renewable energy generated from biomass, solar and wind in all 28 EU countries 2001-2012 [12].

Cellulose (the most abundant organic polymer in terrene), hemicellulose and lignin are the three major organic components that constitute the general rigid structure of lignocellulosic biomass. In general, lignocellulosic biomass contains 30-50% of cellulose by mass, 15-35% of hemicellulose, 10-30% of lignin and small amounts of pectins, starches, extractives, sugars and proteins [8] [14].

Cellulose is a natural linear homopolysaccharide of β -1,4-linked anhydro-D-glucose which accounts for a large proportion of plant biomass. Pure cellulose has crystalline and amorphous regions and is composed of 7000 to 15000 linked glucose ($C_6H_{10}O_5$) monomers. Due to hydrogen bonding between hydroxyl groups and oxygen atoms, cellulose chains form microfibril which further forms cellulosic fiber (See Figure 3 and Figure 4). Approximately 95% of wood derived cellulose is used in papermaking while cellulose derivatives, mainly ethers and esters are also modified in a large-scale [10] [14] [15].

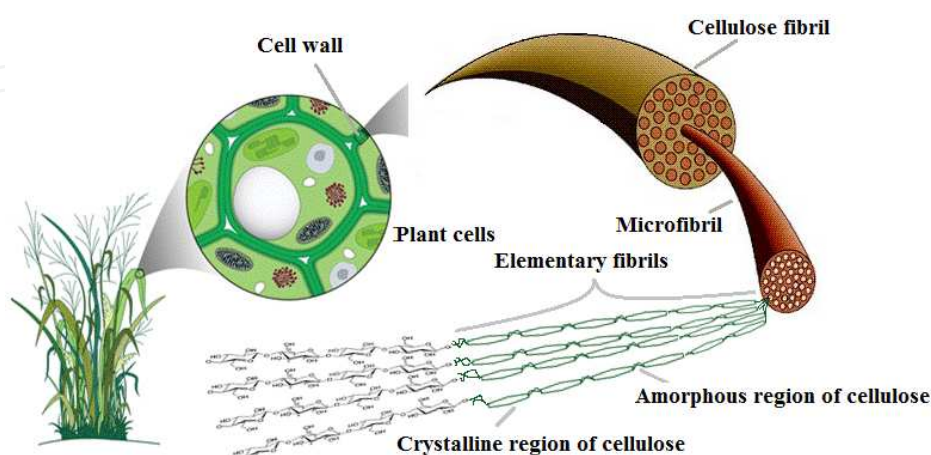


Figure 3. Cellulosic fiber structure with emphasis on the cellulose microfibril adopted and redrawn from Quiroz-Castañeda and Folch-Mallol and Lavoine, et al [16] [17]

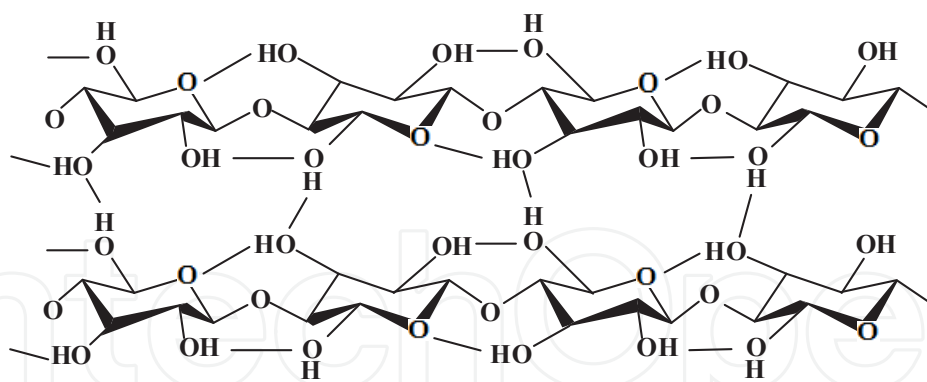


Figure 4. Intra- and intermolecular hydrogen bonds in cellulose redrawn from Pinkert et al. [18].

Cellulose has an amphiphilic property, which has become a more recent perspective highlight in the dissolution of lignocellulosic biomass. Three hydroxyl groups are located on the equatorial positions of the glucopyranose ring which causes the hydrophilic character of cellulose. Whereas, a hydrophobic character is observed on the axial direction since the hydrogen atoms of C-H bonds are located axially (See Figure 5). Cellulose molecules therefore have an intrinsically structural anisotropy [10] [19] [20] [21].

Bergensträhle et al. have estimated the contributions of both hydrophobic stacking and hydrogen bonding to the insolubility of crystalline cellulose by calculating the potentials of mean force for separating the short cellulose oligomer in an aqueous solution through molecular dynamic simulations [22]. A significant hydrophobic pairing energy was found to favor a crystal-like association of cellulose oligomers over solution. Furthermore, the magnitude of hydrophobic pairing energy was estimated to be much higher than that of the hydrogen bond contribution [19] [21] [22].

As discussed above, hydrogen bonding and hydrophobic interactions are the major forces to have influence on both the interactions and solubility of cellulose. However, most of the time hydrophobic interactions are neglected [19] [21] [22].

In contrast to cellulose, the hemicellulose fraction of lignocellulosic biomass is an amorphous heterogeneous polymer which comprises of five and six carbon sugars, abundant D-xylose, L-arabinose, D-galactose, D-glucose and D-mannose monomers. Hemicellulose is characterized as a non-bonding steric repulsion and consequently it is more reactive than hydrogen bonded cellulose. In the cell wall, hemicellulose interlaces with cellulose fibers and keeps microfibrils separate (See Figure 6) [14] [23] [24].

The main non-carbohydrate component of lignocellulosic biomass, lignin, is usually a highly branched aromatic polymer, which has a random complex and cross-linked network structure. The basic building blocks of lignin are *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. The unmodified structure of lignin is therefore not well defined. Lignin fraction of lignocellulosic biomass is usually found in plant cells and is always associated with hemicellulose by covalent bonds. In a rigid three-dimensional structure of the cell wall, lignin works as cement in cross-linking cellulose and hemicellulose. Hemicellulose and cellulose are

shielded by lignin from, such as enzymatic and chemical degradation. Thus, the major barrier of utilizing lignocellulosic biomass more widely in energy is its strong structure. To achieve this, its structure can be broken through dissolution to further dissolve cellulose and hemicelluloses [14] [26] [27].

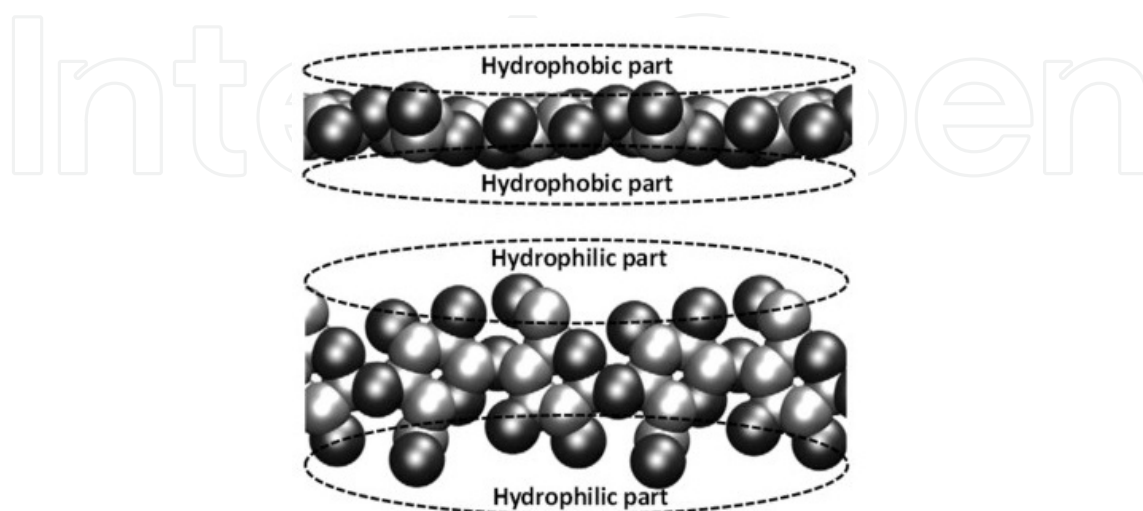


Figure 5. Hydrophilic and hydrophobic parts in cellulose molecules adopted from Medronho et al. [21].

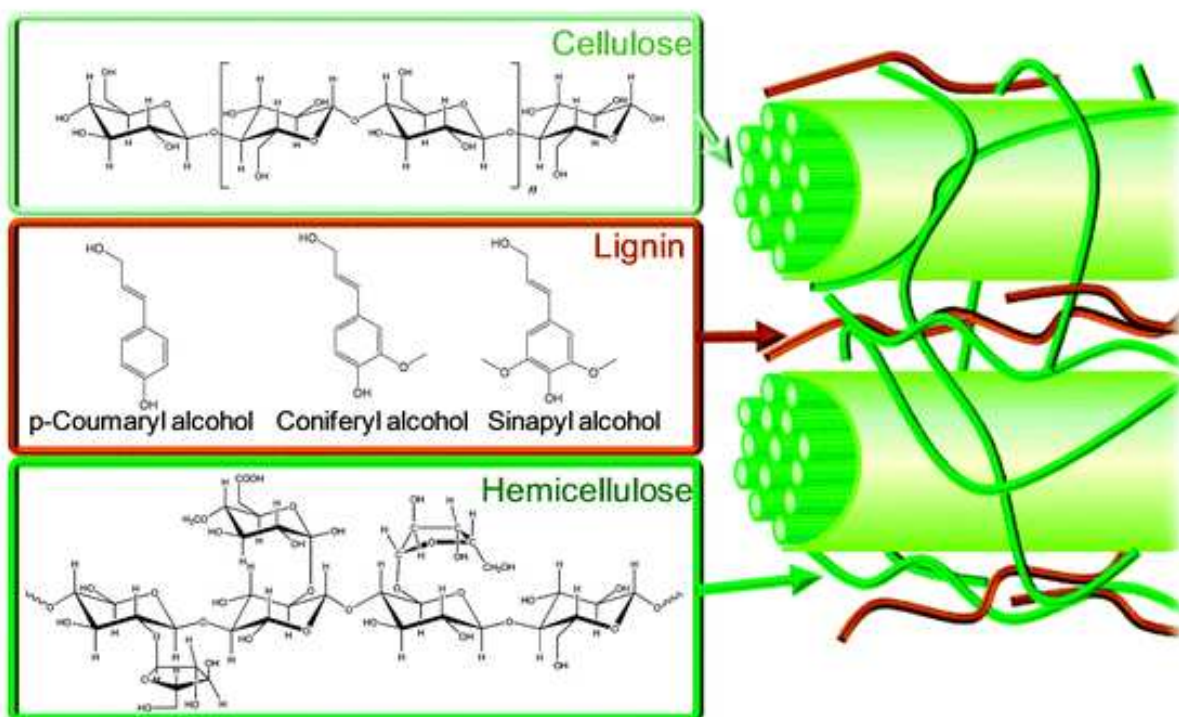


Figure 6. Lignocellulosic biomass structure adopted from Alonso, et al. [25]

3. Ionic liquid

Ionic liquids (ILs) are traditionally defined as liquids that consist exclusively or almost exclusively of ions as well as molten salts or fused salts. In contrast to molten salts, ILs have lower melting points. Hence, ILs are more or less defined as salts that have melting points below the boiling point of water (100°C). Aqueous solutions of salts are not classified as ILs due to the purity of ions. [28].

ILs are usually comprised of organic cations and organic or inorganic anions. Due to the existence of a bulky and asymmetrical cation structure in ILs, there is a low tendency for ILs to crystallize. Since the properties of ILs can be tailored for a particular need, ILs are also known as “designer solvents” or “task-specific ionic liquid” (TSIL) [29] [30].

In general, it is possible to tailor the properties of ILs with almost infinite combinations of suitable cations and anions. For instance, anions are responsible for such qualities such as air and water stability while cations are responsible for organic solubility and melting temperature. Figure 7 and Figure 8 represent the structures of commonly used cations and suitable anions. In comparison to volatile organic compounds (VOCs), ILs are considered as remarkable “greener” solvents in chemical processes, due to, for instance, their high thermal stability, negligible vapour pressure and their ability to remain in a liquid form over a wide temperature range. However with an increase of research on the utilization and toxicity of ILs, these “greener solvents” have been questioned. [29] [30].

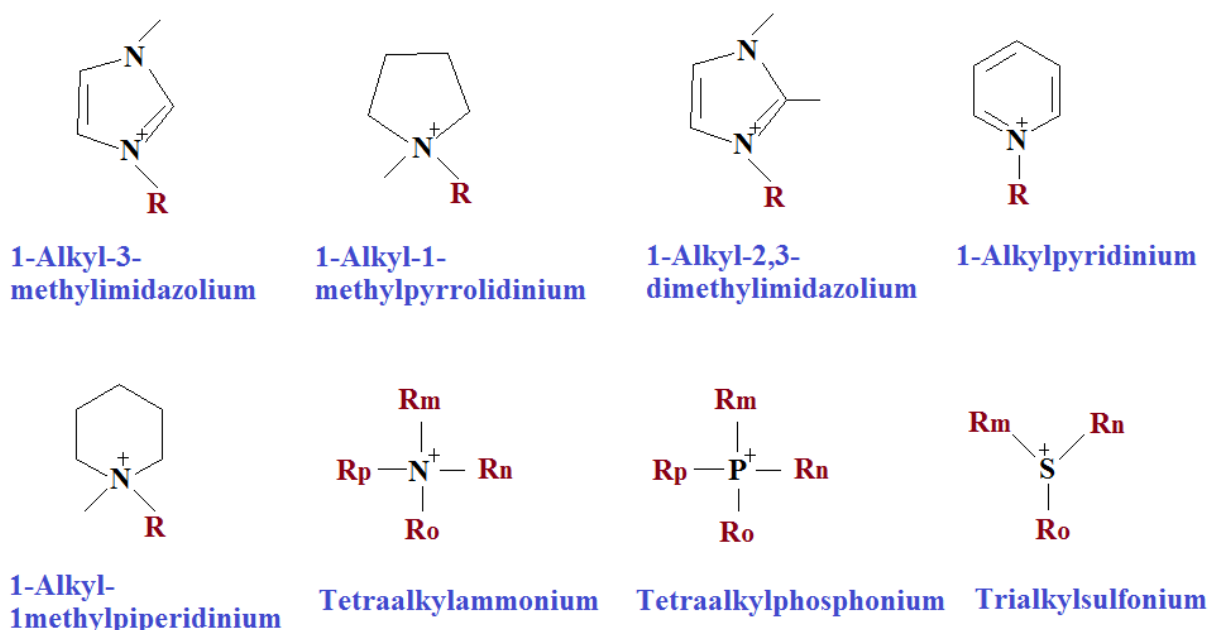
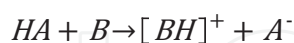


Figure 7. Commonly used cations in modern ionic liquids redrawn from Brandt, et al. [31].

For the commonly used ILs, it is possible for them to be classified as two groups based on their cation structures: aprotic (AILs) and protic (PILs) ionic liquids. PILs can be easily synthesized by the transfer of a proton from an acid which can donate a proton (Brønsted acid HA) to a base which can accept a proton (Brønsted base B):



The reaction shows the basic formation of PIL through proton transfer from a Brønsted Acid (A) to a Brønsted Base (B). PILs do not necessarily contain entirely of ions, for instance, a small amount of molecular species can be found in PILs, due to the incomplete proton transfer [28] [32].

AILs have been used as “classic” or “conventional” ILs for more than a decade. The main difference between AILs and PILs is that AILs are not protonated but based on substitution [29] [33] [34].

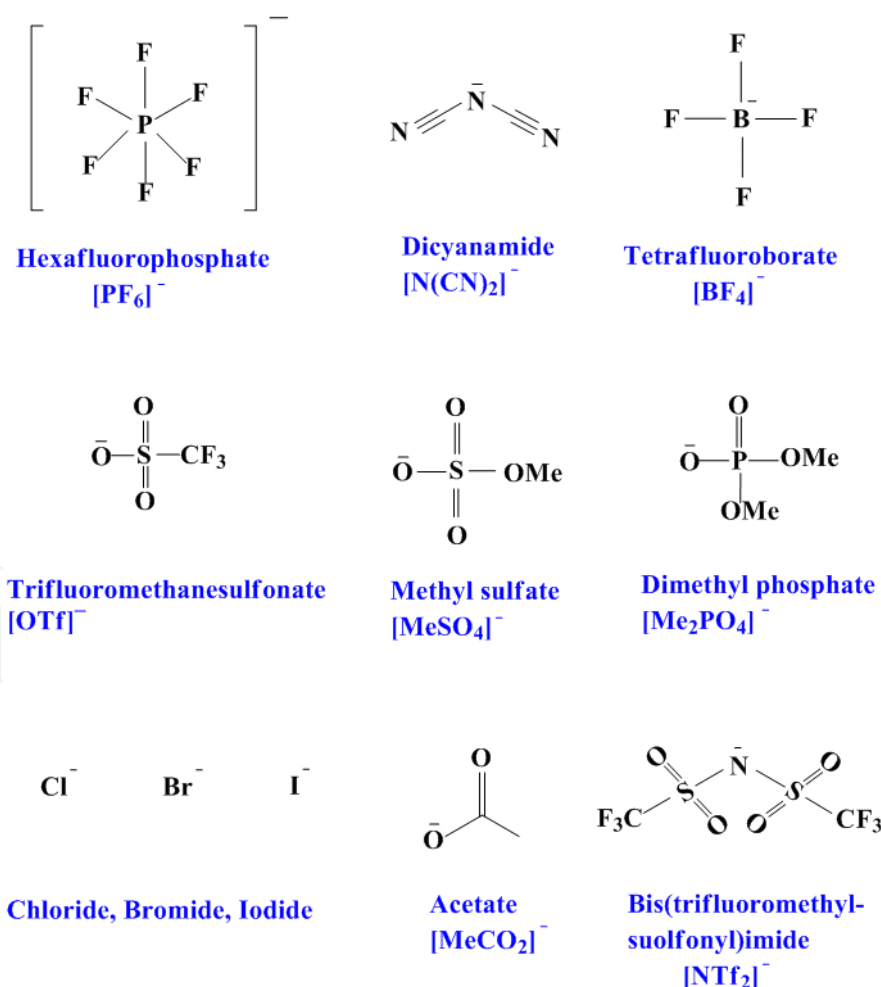
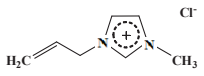
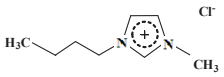
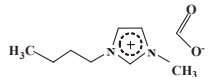
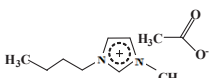
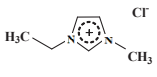
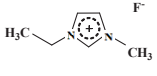
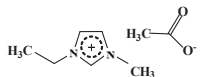
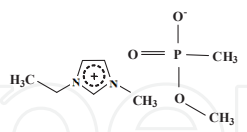
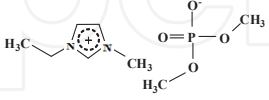
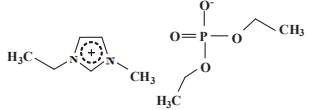
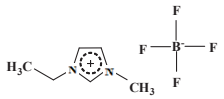
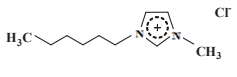


Figure 8. Commonly used anions in modern ionic liquids redrawn from Brandt, et al. [31].

In dissolving lignocellulosic biomass, the dissolution of the major component, cellulose, is mostly discussed, due to its structure and abroad applications. Imidazolium-or pyridinium-cation and anions like Cl⁻, Br⁻, [OAc]⁻ and [CH₃CH₂PO₂]⁻-based ILs have been identified as a good combination in dissolving cellulose. Table 1 lists some of the tested ILs used in cellulose dissolution and their dissolving abilities [8] [11].

Regarding dissolution of hemicellulose and lignin, no great differences from dissolution of cellulose are expected. However, the efficiency of lignin dissolution is not as good compared to cellulose dissolution [8] [11] [35].

	Ionic Liquid	Substrate	Solubility wt/wt	T (°C)	Structure of ionic liquid	Ref.
1	[AMIM]Cl	Cellulose (Avicel) 9%		120		[36]
		Cellulose (Pulp) 14%		80		[37]
2	[BMIM]Cl	Cellulose (Avicel) 13%		110		[38]
		Cellulose (Pulp) 18%		83		[39]
3	[BMIM][HCOO]	Cellulose (Avicel) 8%		110		[40]
4	[BMIM][OAc]	Cellulose (Avicel) 12%		100		[41]
6	[EMIM]Cl	Cellulose (Avicel) 12%		80		[42]
7	[EMIM][F]	Cellulose (Avicel) 2%		100		[41]
8	[EMIM][OAc]	Cellulose (Avicel) 15%		110		[40]
		Cellulose (Avicel) 5%		90		[43]
9	[EMIM][MePO ₃ Me]	Microcrystalline cellulose	10%	45		[44]
10	[EMIM][(MeO) ₂ PO ₂]	Microcrystalline cellulose	10%	65		[44]
11	[EMIM][(EtO) ₂ PO ₂]	Cellulose (Avicel) 12-14%		100		[41]
12	[EMIM][BF ₄]	Cellulose (Avicel) Insoluble		90		[43]
13	[HexMIM][Cl]	Cellulose (Avicel) 5%		50		[43]
		Cellulose (Avicel) 7%		100		[45]

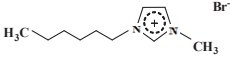
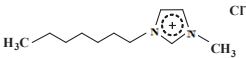
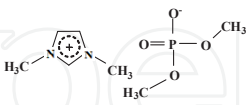
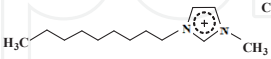
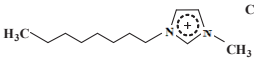
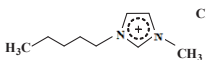
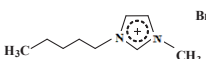
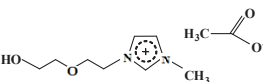
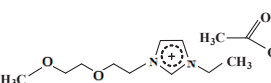
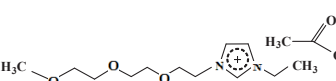
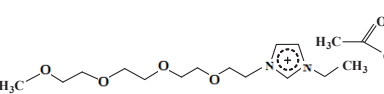
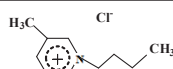
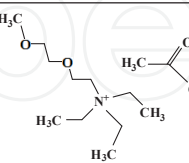
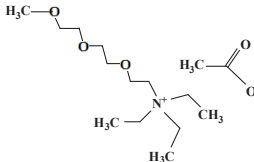
	Ionic Liquid	Substrate	Solubility wt/wt	T (°C)	Structure of ionic liquid	Ref.
14	[HexMIM][Br]	Cellulose (Avicel) 1-2%		100		[41]
15	[HepMIM][Cl]	Cellulose (Avicel) 5%		100		[45]
16	[MMIM][(MeO) ₂ PO ₂]	Cellulose (Avicel) 10%		100		[41]
17	[NMIM][Cl]	Cellulose (Avicel) 2%		100		[45]
18	[OMIM][Cl]	Cellulose (Avicel) 4%		100		[45]
19	[PeMIM][Cl]	Cellulose (Avicel) 1%		100		[41]
20	[PeMIM][Br]	Cellulose (Avicel) 1-2%		100		[41]
21	1-(3,6-dioxaheptyl)-3-methylimidazolium acetate	Cellulose (Avicel) 5%		110		[40]
22	1-ethyl-3-(3,6-dioxaheptyl)imidazolium acetate	Cellulose (Avicel) 12%		110		[40]
23	1-ethyl-3-(3,6,9-trioxadecyl)imidazolium acetate	Cellulose (Avicel) 12%		110		[40]
24	1-ethyl-3-(3,6,9,12-tetraoxatridecyl)imidazolium acetate	Cellulose (Avicel) 10%		110		[40]
25	[3MBPy][Cl]	Cellulose (Pulp) 39%		105		[46]
26	<i>N,N,N</i> -triethyl-3,6-dioxaheptylammonium acetate	Cellulose (Avicel) 10%		110		[40]
27	<i>N,N,N</i> -triethyl-3,6,9-trioxadecylammonium acetate	Cellulose (Avicel) 10%		110		[40]

Table 1. Commonly tested ionic liquids in cellulose dissolution and their dissolving capacities.

4. Dissolution of lignocellulosic biomass in an ionic liquid

4.1. Aim of dissolution

Different types of lignocellulosic biomass contains different components of cellulose, hemicellulose, lignin and other extractives. However, the three major components are cellulose, hemicellulose and lignin. In any lignocellulosic biomass, cellulose is present in the form of amorphous and crystalline structures. The form of crystalline cellulose in a cell wall is tightly packed and highly resistant to chemical and biological hydrolysis, due to a complex biopolymeric network [9] [10].

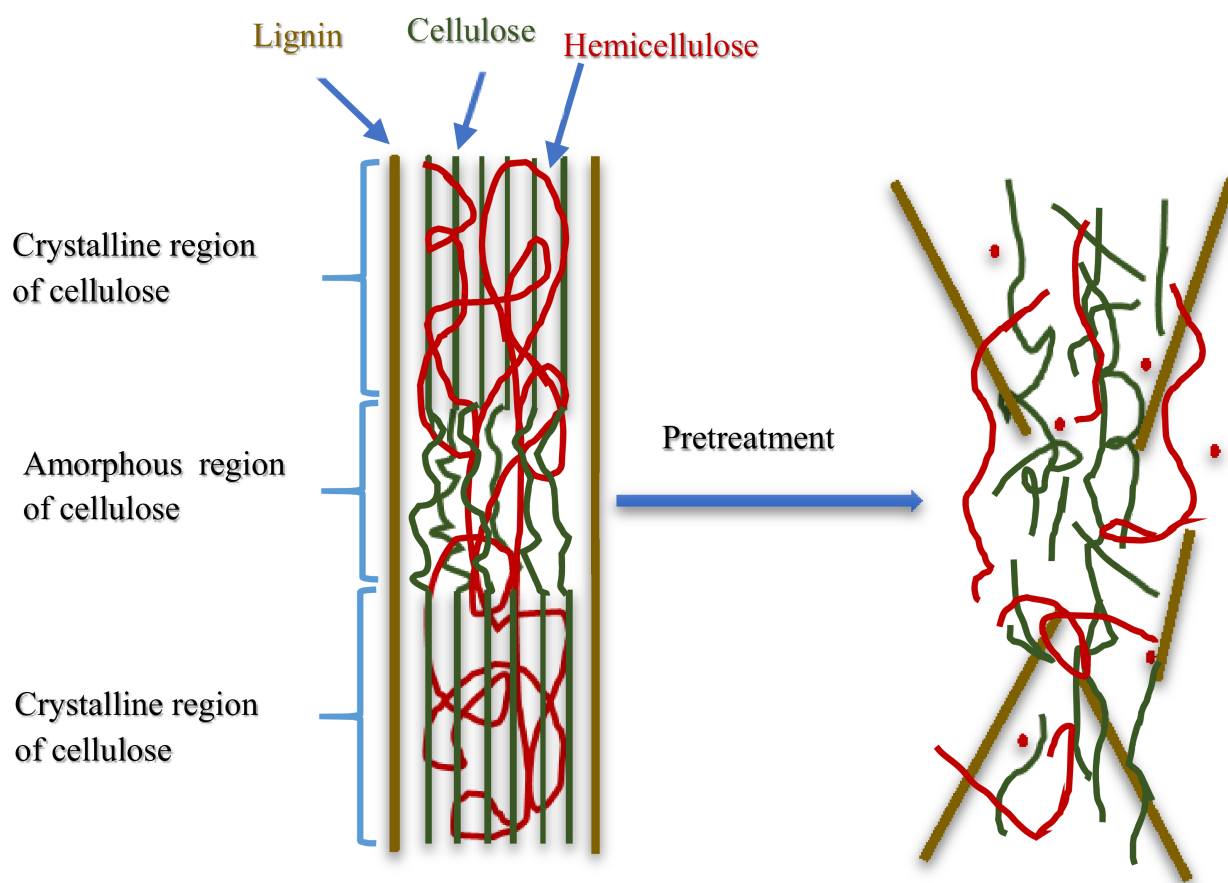


Figure 9. Pretreatment of lignocellulosic biomass redrawn from Holm and Lassi [8].

Cellulose has a clear amphiphilic nature and it is insoluble in common aqueous or organic solvents, though polysaccharide is soluble. The hydrophobicity of crystalline cellulose forms, together with acid, a dense layer of water on the hydrated cellulose surface, which resists to further acidic hydrolysis. The strong intra-and intermolecular hydrogen bonding network in crystalline cellulose obstructs enzymatic hydrolysis, whereas amorphous hemicellulose and cellulose are possibly hydrolyzed. Thus, many applications of cellulose can be applied through its dissolution to break the intra-and intermolecular hydrogen bond network, in order to

increase the active accessible surface area of cellulose (See Figure 9). Other minor factors of interactions among cellulose molecules have been mostly ignored [9] [10].

5. Anion and cation of ionic liquids and effects on dissolution of cellulose

The design of ILs for a specific application is critical to determine the properties of an IL. One of the extraordinary features of ILs is their wide adjustable properties, such as the variations of acid-base character, hydrophilicity and melting temperature. Designing properties and trends of ILs can be achieved by modifying cation and anion independently. However, the impurities, like water, halide anions and organic bases that are mainly from preparations of ILs, may have an effect on the properties as well, which might lead to an unexpected side reaction [18] [47] [48].

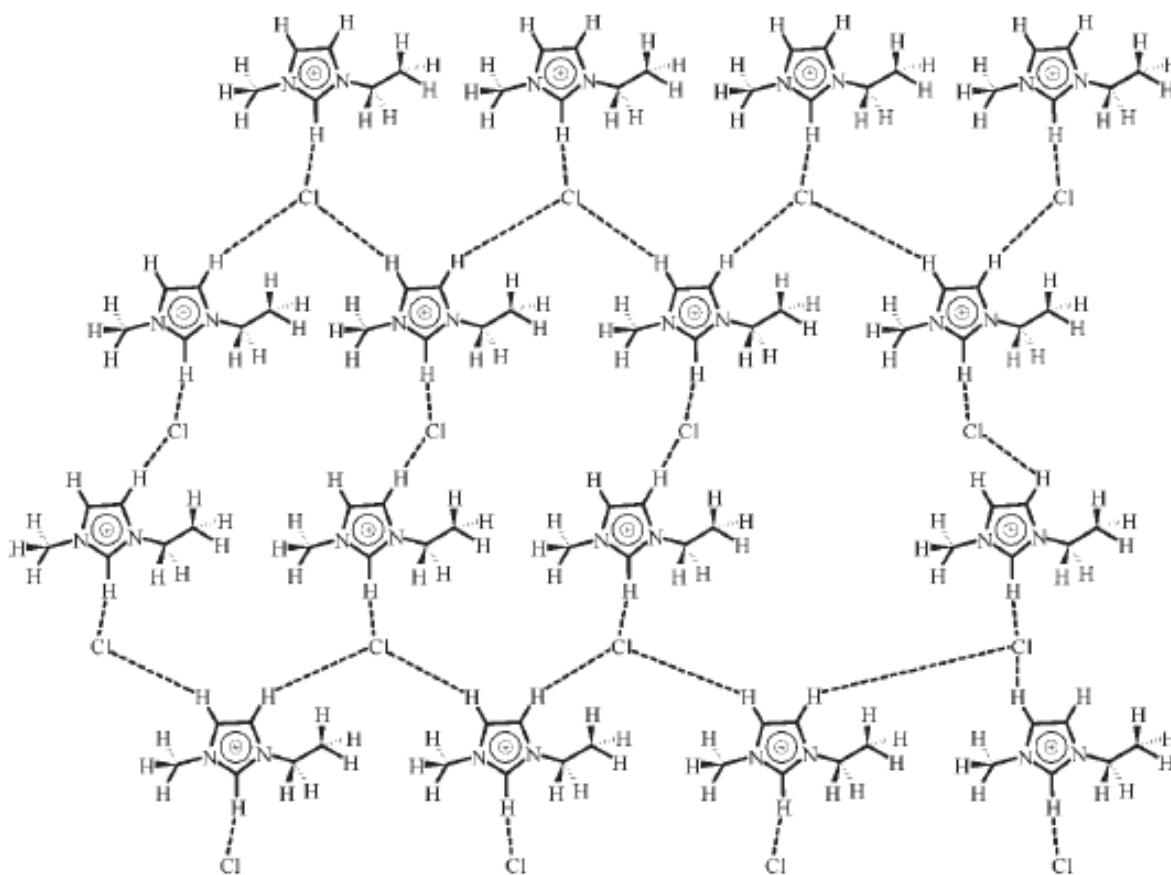


Figure 10. Schematic representation of hydrogen bonding in [EMIM]Cl adapted from Heinze, et al. [46]

The structure of IL is the critical factor that influences the outcome of the dissolution. As known, ILs consist of anion and cation, and both can be varied, in order to provide different functions of ILs. The size, symmetry, hydrogen bond interactions and charge delocalization

of ILs judge van der Waals force and electrostatic interaction which govern the thermal properties of ILs. Anion type shows greater significant effects on the melting temperature and viscosity of ILs than cation. Recently, many researches have pointed out that dissolution in ILs is driven mainly by the formation of hydrogen bonds between cellulose and anions and hydrophobic interactions with cations. The reduction of anion size leads to the increase of the melting point of IL, due to the increase of the Coulombic attraction contributions to the lattice energy of the crystal and of the covalency of the ions. Hydrogen bonds that are present or absent in ILs influence the melting temperature as well. In addition, greater charge delocalizations can be caused by larger anions. The symmetry of the ions also have a direct relationship to the melting points. Reducing symmetry in the ions reduces the melting points and therefore, lowers the freezing point of ILs [18] [49] [50].

Similarly to many solvents, the viscosities of many ILs strongly depend on temperature. Nevertheless, anion and cation properties, such as the anion's ability of forming weak hydrogen bonds with a cation, and the impurities in the ILs also vary the viscosity. Mantz et al. have described that a series of non-haloaluminate ILs have the same cation, but with changes in the anion, the viscosity can be clearly effected, however, not according to the size of the anions. Conversely, for ILs with the same anion, but different cations, the larger the cation size, the greater the viscosity. Another contributing factor on the effect of viscosity is the asymmetric substitution of a cation. It has been identified as a highly asymmetric substitution obtaining a low viscosity IL [51]. The low viscosity of an IL identifies high mobility of ions which promote the dissolution process [10] [52] [53].

The solubility of water in ILs can be varied by changing cation substitution and anion types present in ILs. Generally, coordinating anions relate to the miscibility of ILs with water and conversely, large, non-coordinating, charge-diffuse anions produce hydrophobic ILs. As organic solvents, ILs usually appear with high polarity, due to their ionic nature and respect to organic solutes. Lignocellulosic biomass can be dissolved in ILs while the solubility of cellulose increases in more polar ILs. The interactions between solvent and solute are greater when the ILs have a better hydrogen bond acceptor capability, such as chloride. ILs become more lipophilic with increasing alkyl substitution to reduce further the Coulombic ion-ion interactions, resulting in an increasing solubility of hydrocarbons and non-polar organics [54].

Up to now, it has been reported that the ILs' ability of dissolving cellulose is governed by the interactions between anion and oligomers, although cations are of minor influence. Therefore, theoretically, good hydrogen bond accepting anions bring better influence in the dissolution of cellulose. Figure 10 demonstrates the strong hydrogen bonded network of [EMIM]Cl that are formed by three imidazolium ring protons in three dimensions. Whereas paring with certain cations can also create negative effects [10] [52] [53].

6. Effect of water in an ionic liquid

Water always exists in ILs, even in a neat IL. The role of water in an IL is rather complex. It is considered as an impurity, which influences the properties of ILs. Stark, et al. reported that a

hydrogen bonding network exists in a 'neat' IL due to the interactions between cations and anions [55] [56] [57].

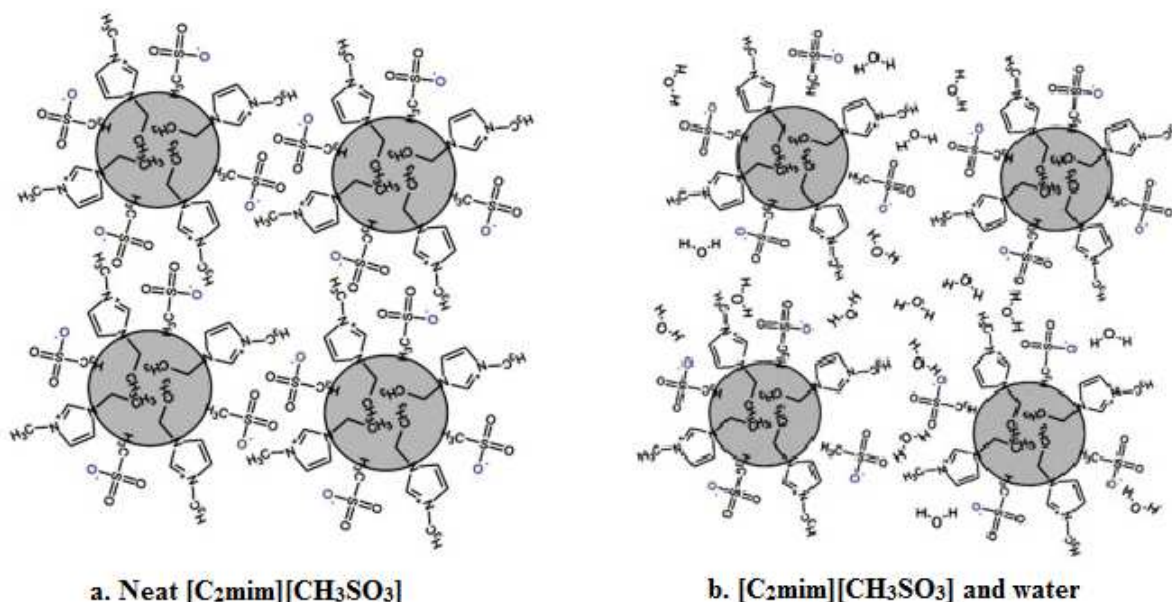


Figure 11. Graphical representation of the structural domains of [C₂mim][CH₃SO₃] and its mixtures with water (tail-tail aggregates, water–anion hydrogen-bonding) adopted from Stark [56].

Depending on the properties of anions and cations in an IL, water can have either positive or negative effects in the utilization of ILs. Figure 11a illustrates that in [C₂mim][OAc] cations' ring plane a cation interacts with several anions to form a hydrogen bonding network [55] [56] [57].

When water is added into the IL, the order of the cation–anion hydrogen bonding network is disturbed. A strong hydrogen bond acceptor [OAc] is disrupted which interacts with water and becomes tightly incorporated into the hydrogen bond network of water. Hence, the amount of water in [C₂mim][OAc] reduces the ability of interactions between ions and cellulose (See Figure 11b) [55] [56] [57].

7. Methods and considerations of cellulose dissolution using a tailored ionic liquid

The conversion of lignocellulosic biomass to biofuel as an alternative replacement of transportation fuel can be proceeded through dissolution, hydrolysis and fermentation processes. Dissolution plays a major role among these steps and such methods have been previously discussed. The dissolution of lignocellulosic biomass breaks down intra- and intermolecular hydrogen bonds, which mainly increases the accessible surface area of cellulose for further hydrolysis [9] [10].

Tailored ILs refer to the ILs that are designed for specific needs. In our early research, three ILs (See Figure 12) were tailored to combine dissolution and hydrolysis of cellulose in a single step (See Figure 13). As can be seen in Figure 12, besides common properties of ILs, these tailored ILs also provide an acidic nature, which can simultaneously dissolve and acid hydrolyze lignocellulosic biomass. Similar to the ILs that are used in lignocellulosic dissolution, it is possible for tailored ILs to be recycled and reused again, based on our previous study, but more research is required.

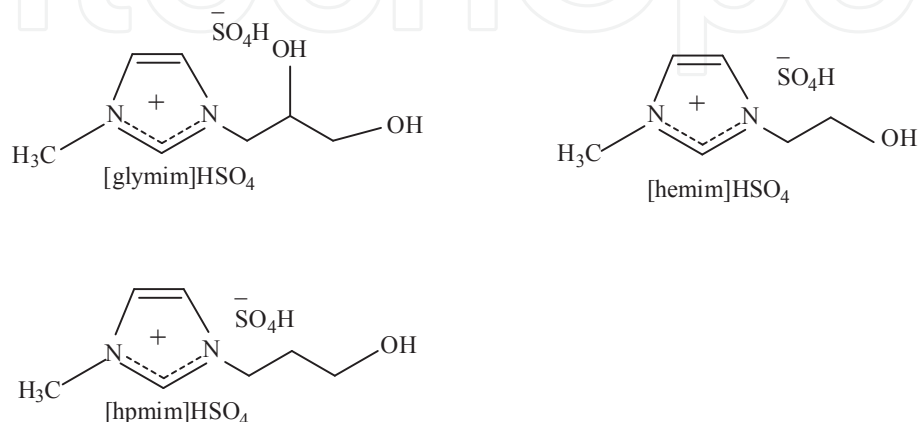


Figure 12. Structures of tailored ionic liquids, [glymim]HSO₄, [hemim]HSO₄ and [hpmim]HSO₄.

Fiber sludge is a by-product from chemical pulping, which was used as the cellulose sample. According to chemical analysis, fiber sludge contained a mass fraction of approximately 93-94% cellulose and 6-7% hemicelluloses of total carbon materials. In addition, water content in fiber sludge is around 53% of the total mass.

The method is rather similar to conventional dissolution of lignocellulosic biomass. Besides dissolution of cellulose, cellulose is hydrolyzed simultaneously (See Figure 14). Thus, the regenerated cellulose solution (Figure 14, right) consists of reducing sugars, tailored IL, anti-solvent and regenerated cellulose. Based on the DNS method, the total reducing sugar yield was measured which indicated that approximately up to 30% of the dry mass sample was converted to sugars.

A couple of factors influence the outcome of lignocellulosic biomass pretreatment with ILs. Certainly, the type of lignocellulosic biomass and IL are key considerations. The temperature and reaction time should be controlled accordingly. The temperatures of typically used ILs in lignocellulosic biomass pretreatment are between 70 and 150°C, with reaction times from 20 mins up to 15 hours. It is suggested that the temperature of dissolution should be controlled approximately 10°C above the melting point of the IL. Too long a dissolution time and high temperature runs the risk of degradation [18].

The production of derivatives are also possible as a by-product due to the unexpected side reactions caused by impurities in ILs or feedstock [18]. In our early research, a gel formed during the reaction and it is thought that the gelation is possibly caused by methylcellulose

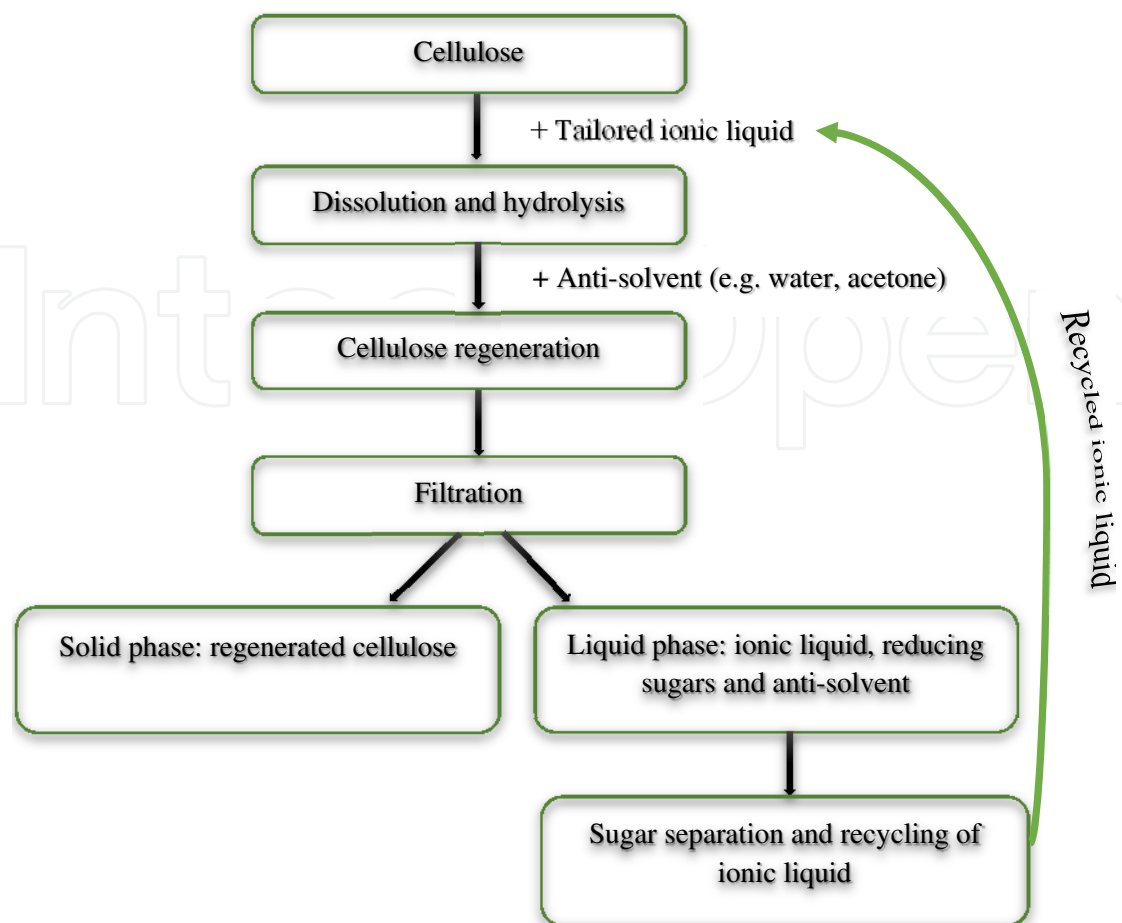


Figure 13. Fractionation scheme in one-step dissolution and hydrolysis of cellulose in a tailored ionic liquid.

that is a derivative of cellulose. In the pulp mill industry, pulp is soaked and cooked in a solution of sodium hydroxide (NaOH) for softening before the resulting pulp is subjected to further processes. Fiber sludge, the residual from a pulp mill, consists of hydroxyl groups and was rapidly dissolved in the ILs. This resulted in methylcellulose as the by-product in the substitution reaction by replacing hydrophilic hydroxyl groups (-OH) with hydrophobic methoxide groups (-OCH₃) [58] [59] [60]. Based on the experimental data, it is reasonable to believe that the impurities in the ILs had a side reaction with the fiber sludge and produced methylcellulose. Methylcellulose has thermo-sensitive properties that allow it to be dissolved in water at low temperature (approximately under 40°C) and it displays reversible gelation at a particular temperature [61] [62] which may block further reactions.

According to the experimental results, cellulose dissolution using tailored ILs with a certain amount of water gave higher yields of reducing sugars. Interestingly, the amount of water in ILs also improved the efficiency of cellulose dissolution. Figure 15 presents images of filtrated regenerated cellulose after dissolution (filter paper) with (right) and without (left) water in a tailored IL. Almost no cellulose dissolution could be found in cellulose without water (Figure 15 left), but significant dissolution occurred when additional water was added (Figure 15 right).



Figure 14. One-step dissolution and hydrolysis of fiber sludge (left) using tailored ionic liquid (middle, tailored IL and fiber sludge) and regeneration of cellulose (right).

Presumably, the hydrophilic and hydrophobic parts of cellulose adjusted their conformation in water while the contacts between hydrophobic parts and water was reduced [48]. It is possible the IL in water disassociated and weaken the hydrophobic interactions in cellulose. The anion of HSO_4^- can also be further disassociated in water and provide H^+ in hydrolysis.

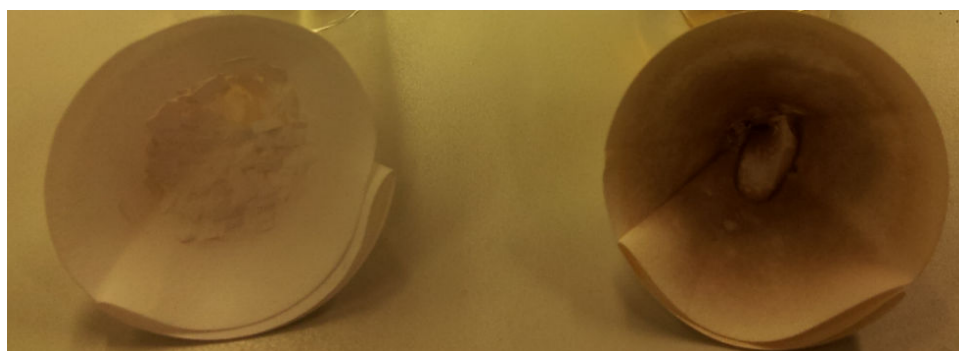


Figure 15. Filtrated regenerated cellulose (dry filter paper) after dissolution of cellulose with (right) and without (left) water in a tailored ionic liquids.

8. Cellulose regeneration

The shape of regenerated cellulose depends on the method and conditions of regeneration. Typically, the dissolved cellulose is precipitated in a polar anti-solvent, such as water, ethanol and acetone however distilled water is often preferred for clear economic reasoning. When the crystalline cellulose is broken down, the regenerated cellulose is usually in the form of amorphous and cellulose II. [11] [18].

There have been a significant number of studies published on the dissolution of cellulose in an IL, however, only a few of these discussed the mechanism of cellulose regeneration. The mechanistic understanding of the interactions between an IL, water and cellulose still remains

elusive. For example, Liu, et al. used molecular dynamics simulations to study the structural and dynamic properties of water, IL and cellulose in cellulose regeneration [11].

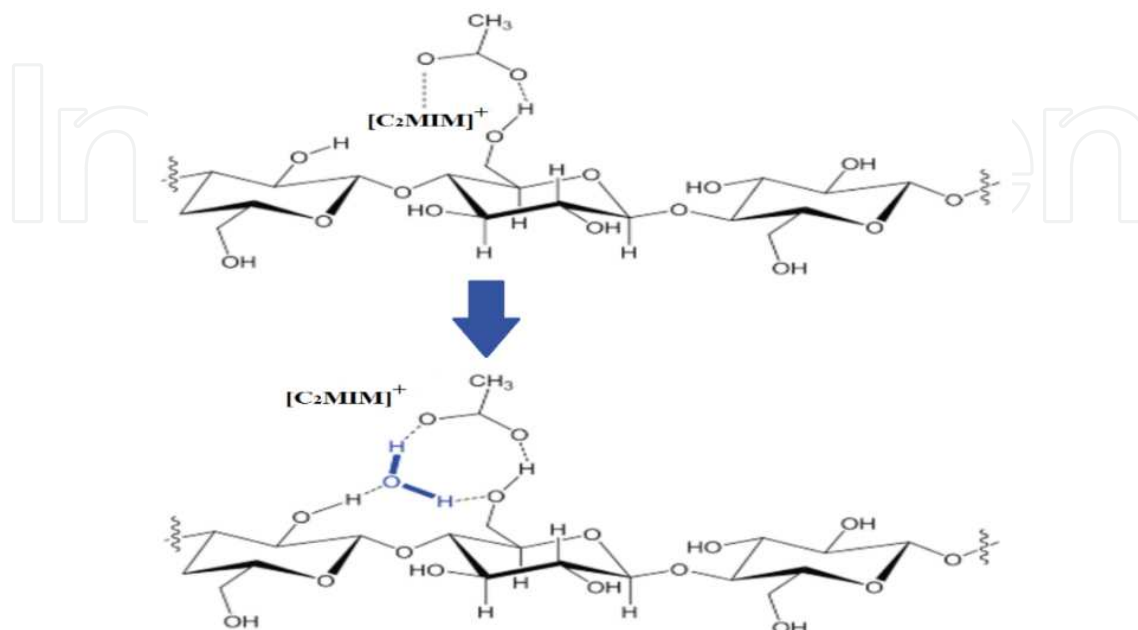


Figure 16. Intermediate structure of cellulose regeneration from [C₂MIM][OAc] in water adopted from Liu, et al. [11]

It has been proposed that the regeneration of cellulose should go through a key intermediate process due to the strong ion-ion interaction between cation and anion in the IL. The number of hydrogen bonds among water molecules and polymer increases and form an anion-water-cellulose hydrogen bonding network, when water diffuses inside the first solvation shell of cellulose. Presumably, water forms hydrogen bonds with cellulose and acts as both a hydrogen bond donor and a hydrogen bond acceptor, which displaces cation out of the first solvation shell to the second solvation shell. However, existing anions in the second solvation shell bond displaces cations in the second solvation shell through strong electrostatic interactions. The hydrogen bonds' bonded anions are liberated from dissolved cellulose into the water solution, because the hydrogen bonds are pushed out to the first solvation shell. The formation of this new hydrogen bonding network finally leads to cellulose precipitation [11].

9. Conclusion

The major barrier in many applications of lignocellulosic biomass is the crystal-like structure and solubility of cellulose for water, acid or enzymes. With a good understanding of the lignocellulose's structure, the solubility of cellulose is mainly affected by intra- and intermolecular hydrogen bonds in cellulose and hydrophobic interactions. Hydrophobic interactions have shown a significant contribution on the solubility of cellulose, as well as on its crystal-

like structure, that is even stronger than hydrogen bonding. Hydrophobic interaction is, therefore, a perspective highlight in lignocellulosic biomass dissolution.

Cellulose has an intrinsic structural anisotropy which shows an amphiphilic nature, due to the intra- and intermolecular hydrogen bonding. It is reasonable to think that an amphiphilic IL would facilitate the dissolution of cellulose.

The properties of ILs can be designed for specific lignocellulosic biomass by carefully choosing suitable cations and anions. Based on the ILs' properties, water may promote or obstruct the dissolution. In our research, we have tailored three types of acidic ILs to perform dissolution and hydrolysis in a single step, and the total reducing sugar yield in the regenerated cellulose solution was calculated, up to 30% of the dry mass, based on the DNS method. The water content in tailored ILs is not as critical as in usual ILs in dissolution, due to the simultaneous hydrolysis reaction.

The mechanistic understanding of interactions between IL, water and cellulose has been barely discussed, however, water as an anti-solvent, is also expected to play an important role in cellulose regeneration. According to molecular dynamics simulations, a key intermediate process between cation and anion in the IL is performed.

Clearly, tailored ILs can be used in a one-step dissolution and hydrolysis of lignocellulosic biomass. This is especially the case for wet lignocellulosic biomass which can be directly used in tailored ILs that also differ from general ILs. The existing impurities in ILs or substrates can cause side reaction in dissolution, which may obstruct or promote further reaction. A longer reaction time could cause sugar degradation in tailored ILs.

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Author details

Yue Dong^{1,2*}, Jana Holm³ and Ulla Lassi^{1,2}

*Address all correspondence to: yue.dong@chydenius.fi

1 University of Oulu, Department of Chemistry, University of Oulu, Finland

2 University of Jyväskylä/Kokkola University Consortium Chydenius, Kokkola, Finland

3 Centria University of Applied Sciences, Kokkola, Finland

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