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Ionic Liquids in the Pretreatment of Lignocellulosic Biomass

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1. Introduction

The fossil fuel-based economy is facing several problems and challenges, as stated by the Intergovernmental Panel on Climate Change IPCC (IPCC, 2007). These challenges involve the increasing emissions of CO₂, decreasing reserves and increasing energy prices. A potential solution to the problem could be in the form of lignocellulosic biomass as an alternative and sustainable energy source of the future. It can be used to produce chemicals and biofuels, which do not compete with food production (Huber et al., 2006; Lynd et al., 1999). Extensive research into the conversion of lignocellulosic biomass is currently being undertaken all over the world.

Biomass as a carbon based material is composed of a mixture of organic molecules containing carbon and hydrogen. It usually possesses atoms of oxygen and nitrogen whilst including small quantities of other elements, such as metals. The carbon used to construct biomass is absorbed from the atmosphere as carbon dioxide (CO₂) by plant life, using energy from the sun. Therefore biomass is the most abundant renewable resource available. The major constituents of lignocellulosic biomass are polymeric carbohydrates (cellulose and hemicellulose) and lignin (Zhang & Zhao, 2010). The term "lignocellulosic biomass" is often used to describe the material that composes the plant cell wall, i.e. cellulose, hemicelluloses and lignin. However, the plant cell contains different layers that differ in structure and chemical composition. As a result of the organisation and interaction between these polymeric structures, the plant cell wall is naturally recalcitrant to the biological degradation (da Costa Sousa et al., 2009). Conventional methods to convert lignocellulosic materials to sugars have been in the form of acid hydrolysis or the use of high pressures and temperatures. These methods are either energy-intensive or require the recirculation of acid. There are several solvents which dissolve cellulose, but these usually degrade the cellulose during the process (Holm et al., 2009; Mosier et al., 2005). Although different process steps are necessary in order to convert the biomass to useful products, the intermediate product is mostly glucose.

As indicated above, the pretreatment of lignocellulosic biomass is a significant tool in the practical conversion processes, and it will be considered in this article.

2. Lignocellulosic biomass

Wood, grass, forestry waste, agricultural residues and municipal solid waste are excellent examples of lignocellulosic materials that can be used in the production of lignocellulosic

biomass. Typically this contains cellulose (30-50 %), hemicellulose (15-35 %) and lignin (10-30 %) of dry weight (Lynd et al., 2002) and is the most abundant renewable organic material on earth (Bhat & Bhat, 1997), with an estimated global production of around 1.0×10^{11} tons/year (Zhang & Zhao, 2010; Sánchez & Cardona, 2008). Against the background of this enormous growth of renewable material, plant biomass offers the most potential platform for energy production.

Cellulose is a crystalline polymer that is made up of glucose units. Cellulose fibre are surrounded by intra and intermolecular hydrogen bonds (Zhbakov, 1992) which makes cellulose insoluble in water and the most organic solvents available (Swatloski et al., 2002). Instead hemicellulose, a polymer of five sugars, is completely amorphous. Lignin as an irregular polymer forms a network in which cellulose and hemicellulose fibre are embedded (Huber et al., 2006). Due to the complex structure of lignocellulose, it is resistant to most chemicals and hydrolysis, which form the barrier for its utilisation (Lynd et al., 2002; Zhu et al., 2006).

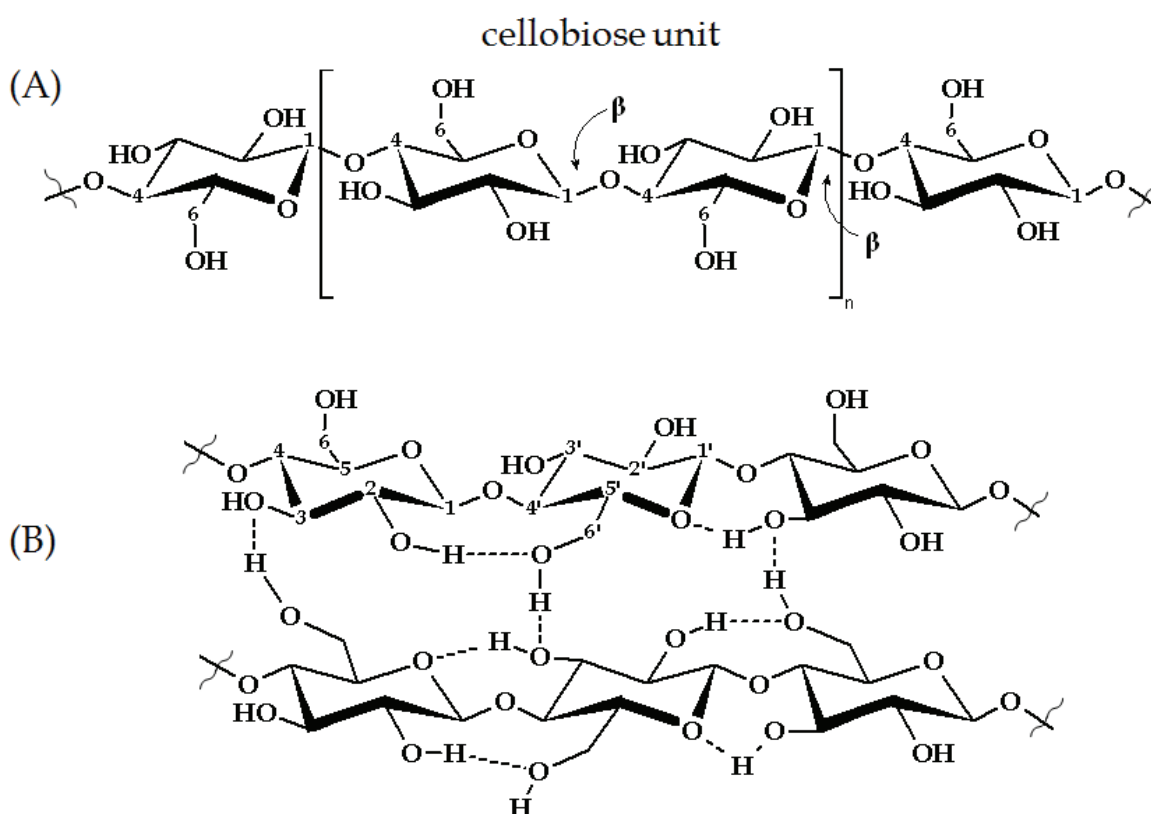


Fig. 1. The cellulose network (A is the cellulose chain and B shows inter and intra H-bonds present in cellulose) adopted from Olivier-Bourdigu et al., 2010.

Cellulose forms the skeleton in which other substances, hemicelluloses (matrix) and lignin (encrust) surround it. Cellulose, hemicelluloses and lignin are closely attached and covalent cross-linkages occur between lignin and the polysaccharides (Rogalinski et al., 2008).

3. Aims of biomass pretreatment

Since different lignocellulosic materials have different physio-chemical characteristics, it is necessary to adopt suitable pretreatment technologies based on the lignocellulosic biomass

properties of each raw material (Alvira et al., 2010). Biomass pretreatment is needed for several reasons. The main goal is to alter the structure of cellulosic biomass, and thus to make the cellulose structure more accessible to adsorbates (enzymes and/or chemicals). The lignin seal of the cellulose must be broken and then the crystalline structure of cellulose can be disrupted.

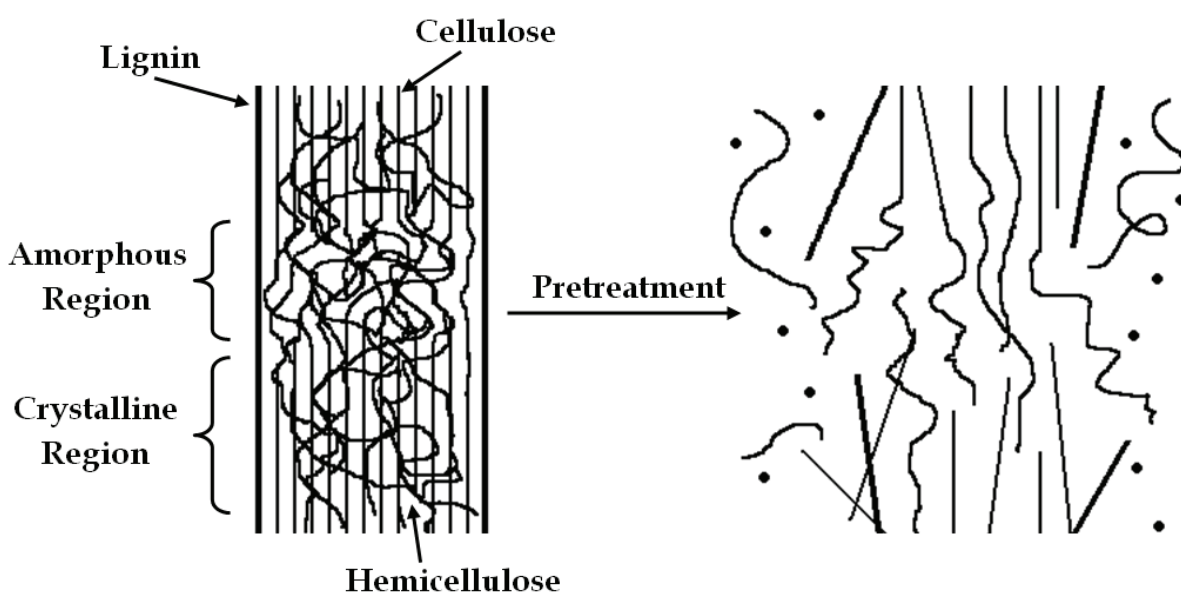


Fig. 2. Goals of the pretreatment adopted from Mosier et al., 2005.

Recently, much research has been undertaken worldwide to convert lignocellulosic biomass (forestry waste, agricultural residues and energy crops) through a sugar platform. Lignocellulose serves as a sustainable feedstock for the production of future valuable products, such as biofuels and chemicals. Pretreatment of biomass is required to decompose the fibre structure of lignocelluloses and to utilise all the components (Kuo & Lee, 2009). Pretreatment alters the structure of cellulosic biomass to make cellulose more accessible to the enzymes that convert carbohydrate polymers. Subsequently, when lignocellulose is separated into its components, it can be hydrolysed to fermentable sugars (monosaccharides) using mineral acids or enzymes. Monosaccharides can then be further converted to valuable bio-based chemicals (Kamm & Kamm, 2004).

The aim of pretreatment is to break the lignin shield and the crystalline structure of cellulose whilst increasing the porosity of cellulose. Pretreatment can be considered as a very important tool for practical cellulose conversion processes. Pretreatment methods are usually categorised into physical, chemical, physiochemical and biological (Zhao et al., 2009) however each of these methods have their own specific drawbacks (Chandra et al., 2007).

The effectiveness of lignocelluloses pretreatment is one of the key factors to a successful conversion of the originally low-cost material into sugars and further into biofuel or biofuel intermediates. The pretreatment of cellulosic materials can affect its physical properties such as its degree of polymerisation, its crystallinity and even the surface area of the substrate accessible in the case of further enzymatic hydrolysis (Olivier-Bourbigou et al., 2010). Pretreatment methods increase the surface area accessible to water and cellulases are expected to generate improvements in hydrolysis kinetics and conversion of cellulose to glucose.

Pretreatment is a significant tool for practical cellulose conversion processes. Several pretreatment procedures for lignocelluloses have been successfully developed (Mosier et al., 2005; Wyman et al., 2005), i.e. after mechanical comminution for chemical and hydrothermal pretreatments have been applied. The most commonly applied methods involved, for example include steam (Cara et al., 2008) or carbon dioxide (Zheng et al., 1998) explosions and hot water treatment (Mosier et al., 2005). Chemical processes involve acid (Lloyd & Wyman, 2005) or alkali treatments (Kaar & Holtzapple, 2000) and organosolv process for example however, all these pretreatment methods have several disadvantages. They are tailored to a specific type of lignocelluloses (Mosier et al., 2005) and some of the solvents cause the degradation of lignocelluloses upon dissolving. These unwanted by-products can inhibit a subsequent hydrolysis or fermentation step (Larsson et al., 1999; Weil et al., 1994). Cellulose solvents should have most of the features listed below (Olivier-Bourbigou et al., 2010). They have to:

1. be able to dissolve cellulose at low temperatures,
2. be non volatile, non toxic and chemically stable,
3. no decompose cellulose,
4. be easy to regenerate,
5. be recyclable,
6. be cost effective and easily processed
7. non-toxic to enzymatic and microbial fermentation.

As indicated in the list above, solvent use and recovery increases the total cost of pretreatment. Some pretreatment methods are too slow (even weeks), and these methods cannot be considered as “green” since hazardous or toxic compounds are released (Zhu 2008). Therefore, more efficient pretreatment procedures are required. One potential alternative is the use of ionic liquids.

4. Ionic liquids

4.1 General

Ionic liquids (ILs) are a group of new organic salts that are liquids at relative low temperatures (below 100°C). As the name suggest they are completely ionic with most ionic liquids consisting of an organic cation and an inorganic anion. Many ionic liquids are also liquids at room temperature making it an ideal solvent to work with. Compared with traditional molecular solvents, ionic liquids express very interesting properties like broad liquid regions, high thermal stabilities and negligible vapour pressures (Brennecke & Maginn, 2001). Ionic liquids are also called green solvents because no toxic or explosive gases are formed when used (Anderson et al., 2002). Depending on which anion and cation is chosen, their physical and chemical properties such as melting points, viscosity, hydrophobicity and hydrolysis stability are affected (Huddleston et al., 2001). Therefore, optimal ionic liquids for a special application can be designed. Simply by making changes to the structure of either the anion or the cation, or both, properties such as solubility, density, refractive index and viscosity can be adjusted to meet the requirements of the user or experiment. The tuning of properties is possible by varying the length and branching of the alkyl groups that are incorporated to the cation. There is also the potential for task-specific ionic liquids (TSILs) to be produced.

When observing the physical properties of ionic liquids, studies have shown that the melting point is influenced by the charge distribution on the ions, H-bonding ability,

symmetry of the ions and van der Waals interactions. When comparing the melting points between NaCl and 1-propyl-3-methylimidazolium chloride, 803 °C and 60 °C respectively, it is clear that the reduction in the melting temperature is caused by replacing the small inorganic cations by bulky asymmetric organic cations. Many ionic liquids undergo supercooling which make their melting point rather uncertain. Many RTILs (room temperature ionic liquid) can be supercooled to more than 100 K below the melting point and in many cases they then form a glass (Marsh et al., 2004).

Most of the known ionic liquids are denser than water, with values between 1-1.6 g/cm³. The density decreases with increasing length of the alkyl chain in a systematic manner (Marsh et al., 2004). In most cases ionic liquids are viscous, similar to that of oils. Their high viscosity is a disadvantage because it will negatively affect the mass transfer and power requirements for mixing heterogeneous liquid-liquid systems. An increase in length of one or both alkyl chains in the cation does not automatically result in a direct increase of the viscosity.

The first published report of dissolution of cellulose in an ionic liquid ([N-ethylpyridinium][Cl] in the presence of a nitrogen base) dates back to 1934 (Graenacher 1934).

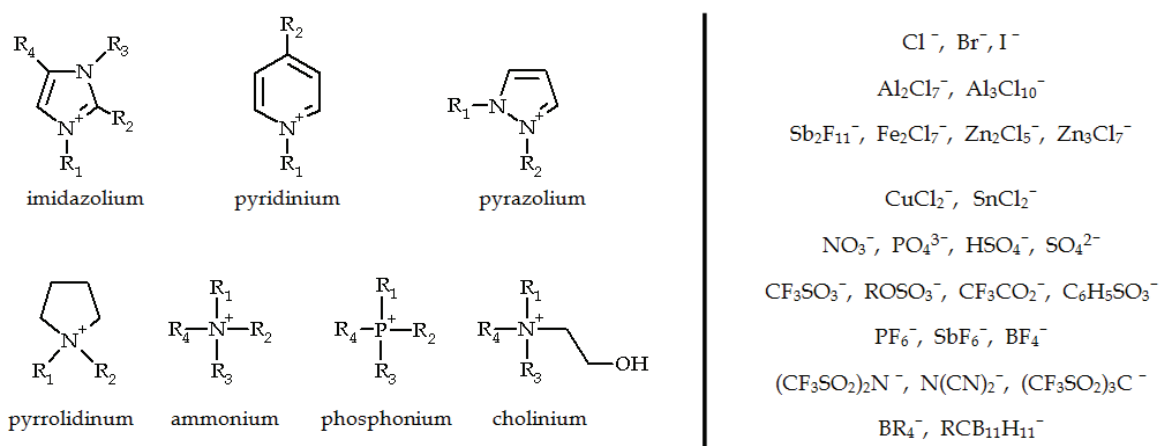


Fig. 3. Main cations and anions described in literature adopted from Olivier-Bourdigou et al., 2010.

Today, there are more than 20 ionic liquids which are known to dissolve cellulose (Barthel & Heinze, 2006). Ionic liquids are also able to dissolve other biomaterials (Fort et al., 2006), such as lignin and lignocelluloses (Kilpeläinen et al., 2007). Dissolved cellulose can be precipitated and separated from lignin and hemicelluloses by the addition of anti-solvents, such as water (Fort et al., 2006). Recent patents also prove that the pretreatment of lignocellulose using ionic liquids (ILs) is of industrial interest, and the commercialisation of such processes is underway (Myllymäki & Aksela, 2008; Zhu, 2008).

The ability of ionic liquids to dissolve cellulose depends on the nature of the native cellulose (its DP and crystallinity) on the operating conditions (temperature, reaction time, initial concentration of cellulose in the IL) and the presence of impurities (water). The use of a non-dried ionic liquid can affect the solubility of cellulose, so much that severely dried ionic liquid is needed to achieve an optimal dissolution (Vitz et al., 2009).

The ionic liquids which are most commonly considered for extraction and synthesis are those with cations based on an imidazolium or pyridinium ring with one or more alkyl groups attached to the nitrogen or carbon atoms. Quaternary ammonium salts have been widely used for electrochemical synthesis (Marsh et al., 2004).

4.2 Impurities in ionic liquids

Ionic liquids may contain several impurities, such as halides, water and volatiles. Volatile impurities, primary originating from starting materials or solvents used in synthesis, can easily be removed from the non-volatile ionic liquid by evaporation.

In ionic liquids possessing halide impurities, these can be removed by halide exchange reactions that precede more or less quantitatively causing residual amounts of halide impurities in the final product. Residual halide can seriously affect the usefulness of the ionic liquid as a solvent for a given chemical reaction (Fukaya et al., 2006). Some physiochemical properties are strongly dependent on the presence of halide impurities, e.g. in the biomass dissolution. The halide can act as a catalyst poison, as a stabilising ligand, nucleophile or reactant, depending on the chemical nature of the reaction (Wagner & Hilgers, 2008).

Protic impurities have to be considered for ionic liquids which have been produced by an exchange reaction using a strong acid and for ionic liquids that are sensitive to hydrolysis. It is easy to control if there are acidic impurities in an ionic liquid that is not fully hydrophilic. The ionic liquid is added to water and the pH is measured in the aqueous phase. If the pH is below seven (acidic solution), the ionic liquid needs to be washed with water until it becomes neutral (Wagner & Hilgers, 2008).

Impurities from incomplete metathesis reactions can also contaminate the ionic liquid. This can occur if the alkali salt that is used in the metathesis reaction shows significant solubility in the formed ionic liquid. This may not be a problem for some catalytic reactions (the alkali cation may not affect the catalytic cycle of a transition metal catalyst), but it is of great relevance for the physicochemical properties of the ionic liquid (Wagner & Hilgers, 2008).

Water is found in all ionic liquids however this may or may not be a problem for some applications. In all cases, the approximate amount of water in the used ionic liquid should be known. The fact is that water in an ionic liquid may not be inert. The presence of water can have significant influence on the physicochemical properties of the ionic liquid, on its stability and on the reactivity of catalysts dissolved in the ionic liquid (Swatloski et al., 2002; Liebert & Heinze, 2008).

Before researching with the aid of a specific ionic liquid, one should be aware of the level of impurities present. A good commercial ionic liquid should be free of organic volatiles, halides (if not a halide of IL) and all ionic impurities. Though, it may be coloured and contain some traces of water.

To remove water, the ionic liquid should be dried at 60 °C over night in a vacuum. The water content should then be checked with IR before use and recorded in any descriptions or documentation that is relevant to the ionic liquid used in experiments.

If a colourless ionic liquid is required, the colour can be removed by chromatography/filtration over silica 60. For this purification method, the ionic liquid is dissolved in a volatile solvent such as CH₂Cl₂ (Wagner & Hilgers, 2008).

Finally, the purity of an ionic liquid is a very important issue when measuring the physical properties.

4.3 Effect of the anion on the dissolution

Whilst attempting to dissolve carbohydrates, many different ionic liquids were explored and it was concluded that good dissolution of cellulose may be obtained using halide based ionic liquids as presented in Table 1. It is well known that higher the anion concentration the better the solubilisation become. Other advantages include the strong electronegativity of

the chloride anion and its small size (Dadi et al., 2006). This is especially important since the chloride anion, being a small hydrogen-bond acceptor, is a good selection in cellulose

Substrate	DP (cellulose)	Solvent	Solubility	T (°C)
Cellulose	286	[BMI][Cl]	18 (wt%)	83
Cellulose	593	[BMI][Cl]	13 (wt%)	83
Cellulose	~1000	[BMI][Cl]	3 (wt%)	70
Cellulose	~1000	[BMI][Cl]	10 (wt%)	100
Cellulose	~1000	[BMI][Cl]	25 (wt%)	110
Cellulose	1108	[BMI][Cl]	10 (wt%)	83
Cellulose	6500	[BMI][Cl]	6 (wt%)	80
Cellulose	225	[BMI][Fm]	8 (wt%)	110
Cellulose	250	[BMMI][Cl]	4.5 (wt%)	110
Cellulose	286	[BMI][Cl]	9 (wt%)	80
	593	[BMI][Cl]	6 (wt%)	80
	1198	[BMI][Cl]	4 (wt%)	80
Cellulose	650	[AMI][Cl]	14.5 (wt%)	80
	1600	[AMI][Cl]	8 (wt%)	80
Cellulose	286	[AMI][Br]	12 (wt%)	80
	593	[AMI][Br]	4 (wt%)	80
	1198	[AMI][Br]	4 (wt%)	80
Cellulose	250	[AMI][Fm]	10 (wt%)	60
	250	[AMI][Fm]	22 (wt%)	85
Cellulose	286	[EMI][Cl]	12 (wt%)	80
	593	[EMI][Cl]	6 (wt%)	80
	1198	[EMI][Cl]	4 (wt%)	80
Cellulose	795	[EMI][Ac]	20 (wt%)	80
Cellulose	200-250	[EMI][PO ₂ (H)(OMe)]	10 (wt%)	45
Cellulose	200-250	[EMI][PO ₂ (Me)(OMe)]	10 (wt%)	55
Cellulose	200-250	[EMI][PO ₂ (OMe) ₂]	10 (wt%)	65
Cellulose	200-250	[EMI][PO ₂ (OEt) ₂]	14 (wt%)	100
Cellulose	200-250	[MMI][PO ₂ (OMe) ₂]	10 (wt%)	100
Cellulose	286	[BMPy][Cl]	39 (wt%)	105
	593	[BMPy][Cl]	37 (wt%)	105
	1198	[BMPy][Cl]	12 (wt%)	105
Cellulose	200-250	[(HO(CH ₂) ₂)MI][Cl]	6.8 (wt%)	70

Table 1. Examples of solubility of cellulose in ILs adopted from Olivier-Bourdigou et al., 2010.

dissolution (Holm, 2010 unpublished data; Swatloski et al., 2002). The halogen anion containing ionic liquids, such as [BMIM][Br] and [BMIM][I], have been found not to be good solvents for cellulose (Zavrel et al., 2009). The fairly high melting point ($> 70\text{ }^{\circ}\text{C}$ for [BMIM][Cl]) of ionic liquids containing the chloride anion could be a technical drawback and possibly limit their practical applications in cellulose processing (Wu et al., 2009). Very high dissolution temperatures (mainly above $80\text{ }^{\circ}\text{C}$) are often required for dissolving cellulose. This may result in cellulose modification by ionic liquids themselves and in thermal decomposition of ionic liquids. Some organohalogenides which have uncertain toxicity and are hazardousness can be produced. In general, high viscosity of [BMIM][Cl] and the high hygroscopicity of halide in ionic liquids make their handling more difficult (Vitz et al., 2009).

Formate, acetate or phosphate based imidazolium ionic liquids have also been studied. They have shown potential to dissolve cellulose under mild conditions such as ionic liquids containing formate anions were found to be good solvents for dissolving cellulose (Olivier-Bourdigou et al., 2010). Formate ionic liquids generally exhibit low thermal stability due to decarboxylation (Fukaya et al., 2008) and they are known to be basic and unsuitable for enzymes (Zhao et al., 2009). Acetate-based ionic liquids were found to be interesting due to their low melting point, lower viscosity and have a less toxic and corrosive character compared with the chloride-based ionic liquids (Feng & Chen, 2008). Furthermore, phosphate-based ionic liquids provide high thermal stability in the $260\text{--}290\text{ }^{\circ}\text{C}$ range and low viscosities (Olivier-Bourdigou et al., 2010).

In general, acetate based ionic liquids are less viscous than chloride based ionic liquids and are thermally more stable than formate based ionic liquids (Fukaya et al., 2008).

4.4 Effect of the cation on the dissolution

Studies have shown the existence of weak interaction between cation of ionic liquids and cellulose (El Seoud et al., 2007). The cations interact in the dissolution process while their role in the dissolution mechanism should not be neglected (Dadi et al., 2006). When increasing the length of the alkyl chain on the dialkyl imidazolium cation (with chloride anion) this leads to a decrease in the cellulose solubilisation (Olivier-Bourdigou et al., 2010). The introduction of an allyl group on the imidazolium cation has been shown to provide excellent improvements in dissolving of cellulose. 14.5 % of cellulose can be dissolved using [AMIM][Cl] compared to, 13 % of the same cellulose when [BMIM][Cl] was used (Olivier-Bourdigou et al., 2010). We can also report similar results (Holm et al., 2010 unpublished data). [AMIM][Cl] is a smaller cation because it contains only three carbon atoms in the side chain, while the strong polar of the double bond seems to be an essential part of the cation (Feng & Chen, 2008). Overall, it can be said that relatively small cations are efficient in dissolving cellulose. Zhang et al., 2005 discovered that [AMIM]⁺ is more powerful in the dissolution of cellulose than [BMIM]⁺ due to its smaller size. Kosan et al., 2008 published that [EMIM][Cl] was a better choice (i.e. is smaller) than [BMIM][Cl], because of the size of the cation. If the cation is large it decreases the ability to form hydrogen bonds with cellulose (Zhao et al., 2008). Vitz et al., 2009 was able to show [EMIM][Br] to have a poor dissolution effect on the cellulose while Zavrel et al., 2009 indicated that [EMIM][Ac] is the most efficient solvent for cellulose and [AMIM][Cl] is the most suitable ionic liquid for dissolution of hardwood and softwood.

Functional groups in the cation can also be crucial for the dissolution of cellulose. The presence of a hydroxyl end-group in the cation decreases the solubility of cellulose in the corresponding ionic liquid (Mäki-Arvela et al., 2010). The longer-chain substituted ionic liquids ($[\text{C}_6\text{MIM}][\text{Cl}]$ and $[\text{C}_8\text{MIM}][\text{Cl}]$) appear to be less efficient at dissolving cellulose. This can be due to the reduced effective chloride concentration within these liquids (Swatloski et al., 2002).

4.5 Dissolution process in ionic liquids

The main properties of ILs affecting the dissolution and functional modification of cellulose and carbohydrates are their polar characteristics, the basic form of the ionic liquid anions and their ability to generate H-bonds. The most important contribution is due to the hydrogen's bonding ability that the IL anion has (chlorine forms an H-bond with the hydroxyl groups of the biomolecule) (Olivier-Bourbigou et al., 2010). In a typical process when dissolving cellulose, the reaction medium has to be heated. Therefore, thermal stability is also an important aspect. Depending on the purity of the IL, the melting points of IL can differ.

In order to dissolve cellulose, the ionic liquid should satisfy the following three conditions: 1) the anion must be a good hydrogen bond acceptor; 2) the cation should be a moderate hydrogen bond donator because the cation has the most moderate activated hydrogen for forming hydrogen bonding with oxygen atoms of the hydroxyls of cellulose and 3) the size of the cation should not be too large (Zhang et al., 2010). The IL solutions become increasingly viscous as the length of the dissolved cellulose oligomer increases (Moulthorp et al., 2005).

Zhang et al., 2005 speculated that the small cation $[\text{AMIM}]^+$ favours the attack on the oxygen atom of the hydroxyl group in cellulose and that the less electronic chemical structure

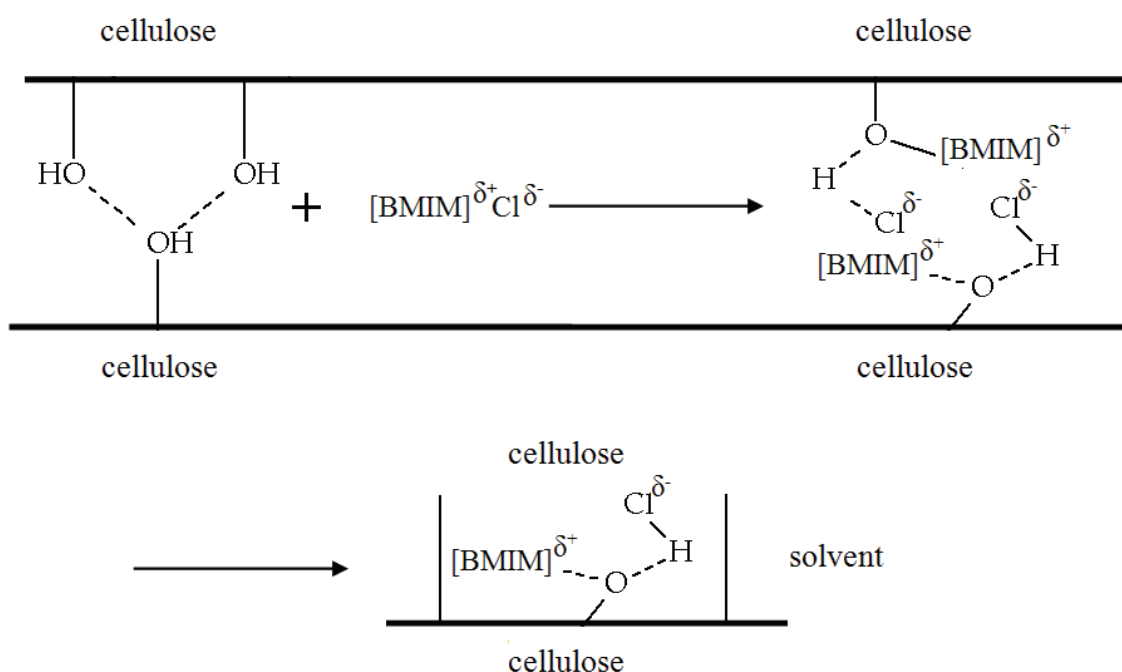


Fig. 4. Dissolution mechanism of cellulose in $[\text{BMIM}][\text{Cl}]$ adopted from Feng & Chen, 2008.

caused by the alkyl group also enhances the interaction between cations in ionic liquid and oxygen atoms of the hydroxide group in cellulose. Above the critical temperature, the ions in [AMIM][Cl] dissociate to individual [AMIM]⁺ and Cl⁻ ions. The free Cl⁻ ions associate with the cellulose hydroxyl proton and the free cations complex with the cellulose hydroxyl oxygen. This leads to the disruption of hydrogen bonds in cellulose and to the dissolution of cellulose. Fukaya et al., 2006 discovered the same mechanism occurring in their studies.

Demonstrated by Zhang et al., 2010, studies showed that the hydrogen bonding of hydroxyls in cellulose with the [CH₃COO⁻] anion and [AMIM]⁺ cation is the major force behind cellulose dissolution in an ionic liquid. The relatively small acetate anion favours the formation of a hydrogen bond with hydrogen atoms in hydroxyls, while the aromatic protons in the bulky cation imidazolium (especially H2) prefer to associate with the oxygen atoms of hydroxyls with less steric hindrance.

The carbohydrate dissolving ionic liquids usually contain anions such as Cl⁻, HCOO⁻ and OAc⁻, which form strong hydrogen bonds with carbohydrates when being dissolved. For this reason, these ionic liquids are more likely to denature the enzymes and thereby preventing a further enzymatic modification of dissolved carbohydrates in ionic liquids. To overcome this problem, development over the past two years has been in the form of synthesizing new glycol-substituted ionic liquids that are capable of dissolving carbohydrates but not denature lipase (Zhao et al., 2008).

When using ionic liquids as cellulose solvents, it is important to investigate if any structural changes occur in the cellulose molecule during the cellulose dissolution, i.e. if any derivatisation or depolymeration of cellulose takes place. Ionic liquids, such as 1-butyl-3-methylimidazolium chloride, 1-methyl-3-methylpyridinium chloride and N-benzyl-N,N-dimethyltetradecylammonium chloride, were found to be non-derivative solvents for cellulose (Heinze et al., 2005). When dissolving dry fibre sludge (fibre sludge is pure cellulose) from a pulp mill in 1-butyl-3-methylimidazolium chloride, the IL was found to be non-derivative (Holm, 2010, unpublished data).

Zavrel et al., 2009 reported that a structural change of cellulose was observed when dissolved cellulose was precipitated with water. This could potentially enhance subsequent hydrolysis. The cellulose regenerated from ionic liquids was essentially found to be amorphous and porous, which was much more prone to degradation by cellulases (Dadi et al., 2006). The celluloses regenerated by rapid precipitation of the dissolved cellulose dopes with an anti-solvent (water) have demonstrated a great improvement on enzymatic hydrolysis kinetics (Kuo & Lee, 2009).

Glucose degradation products observed with acid pretreatment or hydrolysis include hydroxymethyl furfural (HMF) and furfural (Dadi et al., 2006). In the presence of water, HMF produces levulinic and formic acid that inhibit downstream fermentation. For example, if a [BMIM][Cl] pretreated fibre sludge sample is left standing for a long period of time (weeks) before analysis, 5-HMF and levulinic acid can be found in the solution (Holm, 2010 unpublished data).

Following on from this, the dissolved cellulose in the ionic liquid, can be precipitated from its solution by the addition of a non-solvent (anti-solvent), such as water, methanol, ethanol or acetone (Swatloski et al., 2002; Kosan et al., 2008). When the anti-solvent (e.g. water) is added to the solution the ions in the ionic liquid are extracted into an aqueous phase (Mäki-Arvela et al., 2010). The resulting regenerated cellulose can then be separated by filtration or

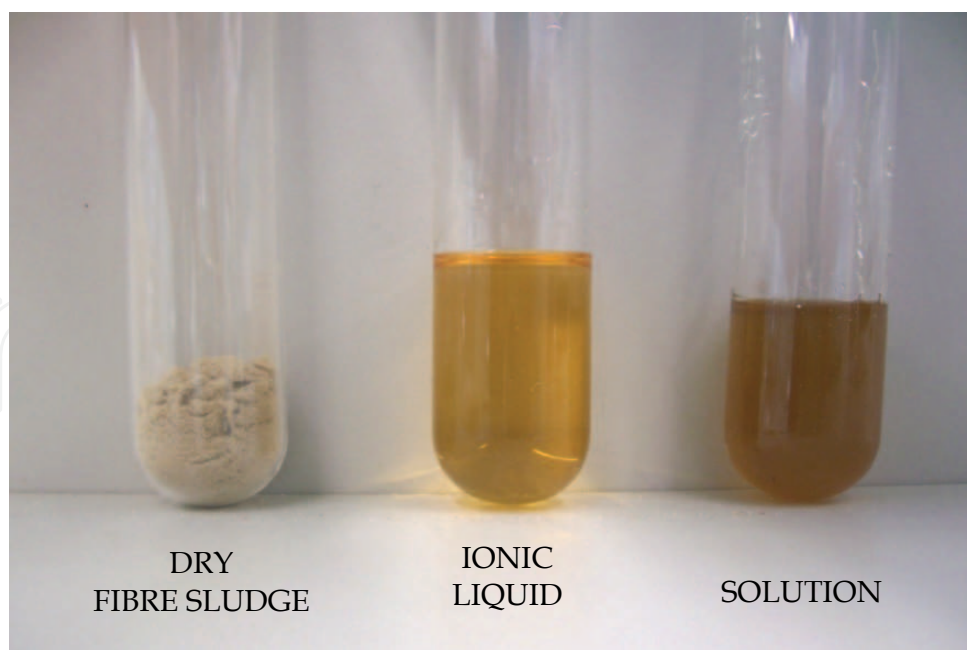


Fig. 5. Dissolution of dry fibre sludge in [BMIM][Cl].

centrifugation while the ionic liquid can be recovered through distillation of the anti-solvent. The recovery of ionic liquids still requires much more research, although studies on biphasic systems in regards to the recovery have already been performed.

The regenerated cellulose can differ from the native cellulose in both the macro- and micro-structure while the degree of crystallinity can be changed due to the changes in the regeneration conditions. The regenerated cellulose can have the same degree of polymerisation and polydispersity as the native cellulose but this depends on the operating conditions in the treatment (Olivier-Bourdigou et al., 2010). The regenerated cellulose demonstrated improved enzymatic hydrolysis kinetics (Dadi et al., 2006).

During the cellulose regeneration, careful attention should be taken when removing ionic liquid residues as their presence has detrimental effect on the cellulase activity depending on the amount of ionic liquid remaining. Such an inactivation may affect the final concentration levels of the total sugars reduction and glucose after the completion of hydrolysis (Zhao et al., 2009).

5. Hydrolysis of biomass

Much research is being undertaken in the conversion of lignocellulosic biomass into valuable products through a sugarplatform which includes two processes, namely the hydrolysis of lignocellulosic materials to monosaccharides and transforming the gained sugars to bio-based products. The lignocellulosic material, provided by nature, is resistant to hydrolysis due to their structure.

Until now, hydrolysis of lignocelluloses to monosaccharides is usually catalysed either by enzymes or acid catalysts under heterogeneous conditions. Concentrated acids such as H_2SO_4 and HCl have been the preferred choice to treat lignocellulosic materials. They are powerful agents for cellulose hydrolysis but they are also toxic, hazardous and corrosive. The concentrated acid needs to be recovered after hydrolysis.

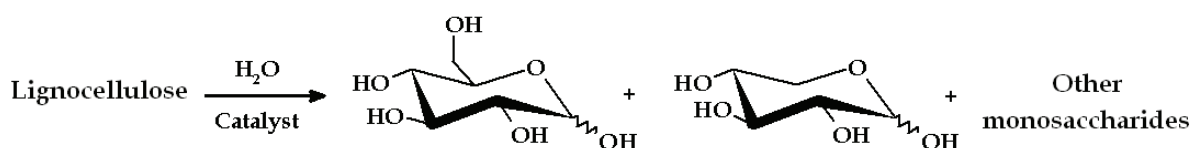


Fig. 6. Hydrolysis of lignocellulosic material adopted from Li et al., 2008.

The main factors that affect the enzymatic hydrolysis of lignocellulosic material can be divided in two groups, namely enzyme-related and substrate-related factors, though many of them are interrelated in the hydrolysis process.

Enzymatic hydrolysis is considered as the most promising method in breaking down cellulosic biomass to fermentable sugars. However, one of the main obstacles to this is the poor enzymatic hydrolysis of cellulose which cannot be explained due to a combination of many factors. There are many reasons behind the poor hydrolysis of cellulose (Zhao et al., 2008). Enzyme factors such as synergism, adsorption, thermal stability and product inhibition influence the cellulose hydrolysis while the degree of polymerisation, crystallinity, accessible surface area, hemicellulose and lignin content, distribution and specific surface area are all substrate related factors that limit the hydrolysis too. Enzyme related factors also include the inhibition of by-products such as cellobiose and D-glucose (Zhao et al., 2009).

Hydrochloric acid/[BMIM][Cl] has been found to be an efficient system for the hydrolysis of lignocellulosic biomass but the reason for this is still unclear. The consensus is that lignocellulosic materials dissolved in [BMIM][Cl] promote the dispersion of the majority of cellulose and hemicelluloses molecules, leading to the substrates being more exposed to H⁺ in the homogeneous solution. This in turn should be an advantage when compared to conventional enzymatic or dilute acid hydrolysis under heterogeneous conditions. The result of this is that the physical barrier for hydrolysis has been successfully extinguished through the formation of a solution. The dissociated Cl⁻ and [BMIM]⁺ may also weaken the glycosidic linkage contained in the substrates (Swatloski et al., 2002).

Dadi et al., 2006 reported that the cellulose structure and hydrolysis rates were neither affected by the extended cellulose incubation period in [BMIM][Cl], nor by the selection of antisolvents (water, methanol or ethanol). After being regenerated from IL solutions, celluloses exhibited lower crystallinity and higher cellulose adsorption compared with untreated substrates. These regenerated celluloses were hydrolysed by cellulase much faster than untreated substrates (Zhao et al., 2009).

Maleic acid effectively accelerated the hydrolysis of cellulose in [BMIM][Cl]. The catalytic activity on hydrolysis of lignocelluloses in [BMIM][Cl] for studied acids roughly followed the following sequence: hydrochloric acid > nitric acid > sulphuric acid > maleic acid > phosphoric acid. (Li et al., 2008)

6. Conventional methods for pretreatment

Pretreatment is a significant tool for practical cellulose conversion processes. Pretreatment methods are either chemical or physical but in some cases both can be used. Physical pretreatment methods include comminution (mechanical reduction in a particular biomass size), steam explosion and hydrothermolysis. Chemically, acids or bases are used to promote hydrolysis. The most commonly used acid and base is sulphuric acid and sodium

hydroxide respectively (Mosier et al., 2005) while cellulose solvents are another type of chemical additive. Solvents such as alkaline peroxide, ozone, organosolv, glycerol, dioxane, and phenol are known to disrupt the cellulose structure and promote hydrolysis. Concentrated mineral acids, ammonia-based solvents, aprotic solvents, metal complexes and wet oxidation are known to reduce cellulose crystallinity, dissolve hemicelluloses and disrupt the linkage between lignin and cellulose. Sulphuric acid has initially been applied to remove hemicelluloses in combination with the breakdown of cellulose to glucose before acid hydrolysis. However, before starting any fermentation process the acid needs to be neutralized. Following from dilute acid pretreatment condensed lignin remains on the surface of crystalline cellulose, which can block the enzyme access to the substrate in sugar production.

Li et al., 2010 investigated the difference between dilute acid and ionic liquid pretreatment of Switch grass, and came to the conclusion that the ionic liquid [C2mim][OAc] and dilute sulphuric acid both remove lignin and hemicelluloses successfully, whilst producing higher glucan content compared with untreated materials. Furthermore, ionic liquid pretreatment removes much more lignin and less hemicellulose than dilute acid pretreatment. Li et al., 2010 results show that the ionic liquid pretreatment resulted in a significant level of delignification. The results also confirm that the dilute acid process removes the majority of hemicelluloses present and small amounts of amorphous cellulose.

7. Conclusion

Lignocellulosic materials which include wood, grass, forestry waste, agricultural residues and municipal solid waste are sustainable energy sources of the future; however, utilizing the unique properties of these materials is a challenge. Due to the different physio-chemical characteristics of lignocellulosic materials a suitable pretreatment technology should be chosen. The implementation of a pretreatment step is necessary to release the components of lignocellulosic materials for usage. The effectiveness of lignocelluloses pretreatment is one of the key factors to a successful conversion of the originally low-cost material into a sugar platform and from there, into biofuels or biofuel intermediates. Cellulose crystallinity, the protective lignin shield and the sheathing of hemicelluloses makes it resistant to enzymatic and chemical hydrolysis.

The dissolution of cellulose using ionic liquids has provided a platform for the utilization of green cellulose in addition to providing a comprehensive application of lignocellulosic materials in a green way. The excellent chemical and physical properties of task-specific ionic liquids make them effective and rapid cellulose solvents. This allows optimal ionic liquids to be designed for a specific application. Compared with traditional solvents ionic liquids express properties such as broad liquid regions, high thermal stabilities and negligible vapour pressure. The viscosity of the ionic liquid is at a disadvantage because it negatively affects the mass transfer. Finally, further research should be preformed on the toxicity of ionic liquids.

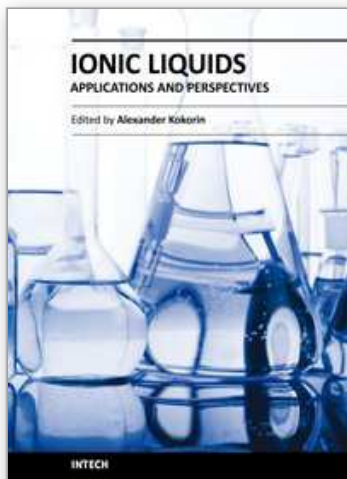
8. References

- Alvira, P.; Tomás-Pejó, M.; Ballesteros, M. & Negro, M.J. (2010). Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology*, Vol. 101, 4851-4861.

- Anderson, J.L.; Ding, J.; Welton, T. & Armstrong, D.W. (2002). Characterizing ionic liquids on the basis of multiple salvation interactions. *Journal of the American Chemical Society*, Vol. 124, 14253-14254.
- Barthel, S. & Heinze, T. (2006). Acylation and carbanilation of cellulose in ionic liquids. *Green Chemistry*, Vol. 8, 301-306.
- Bhat, M.K. & Bhat, S. (1997) Cellulose degrading enzymes and their potential industrial applications. *Biotechnology Advances*, Vol. 15, No. 3-4, 583-620.
- Brennecke, J.F. & Maginn, E.J.(2001) Ionic liquids: Innovative fluids for chemical processing. *AIChE Journal*, Vol. 47, No. 11, 2384-2389.
- Cara, C.; Ruiz, E.; Ballesteros, M.; Manzanares, P.; Negro, M.J. & Castro, E. (2008) Production of fuel ethanol from steam-explosion pretreated olive tree pruning. *Fuel* Vol. 87, No. 6, 692-700.
- Chandra, R.P.; Bura, R.; Mabee, W.E.; Berlin, A.; Pan, X. & Saddler, J.N. (2007) Substrate pretreatment: The key to effective enzymatic hydrolysis of lignocellulosics? *Biofuels* Vol. 108, 67-93.
- da Costa Sousa, L.; Chundawat, S.; Balan, V. & Dale, B. (2009). 'Cradle-to-grave' assessment of existing lignocellulose pretreatment technologies. *Current Opinion in Biotechnology*, Vol. 20, 339-347.
- Dadi, A.; Varanasi, S & Schall, C. (2006). Enhancement of Cellulose Saccharification Kinetics Using an Ionic Liquid Pretreatment Step. *Biotechnology and Bioengineering*, Vol. 95, No. 5, 904-910.
- El Seoud, O.A.; Koschella, A.; Fidale, L.C.; Dorn, S. & Heinze, T. (2007). Applications of ionic liquids in carbohydrate chemistry: a window of opportunities. *Biomacromolecules*, Vol. 8, 2629-2647.
- Feng, L. & Chen, Z-I. (2008). Research progress on dissolution and functional modification of cellulose in ionic liquids. *Journal of Molecular Liquids*, Vol. 142, 1-5.
- Fort, D.A.; Remsing, R.C; Swatloski, R.P; Moyna, P; Moyna, G. & Rogers, R.D. (2006). Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-*n*-butyl-3-methylimidazolium chloride. *Green Chemistry*, Vol.9, 63-69.
- Fukaya, Y.; Hayashi, K.; Wada, M. & Ohno, H. (2008). Cellulose dissolution with polar ionic liquids under mild conditions: required factors for anions. *Green Chemistry*, Vol.10, 44-46.
- Fukaya, Y.; Sugimoto, A. & Ohno, H. (2006). Superior Solubility of Polysaccharides in Low Viscosity, Polar and Halogen-Free 1,3-Dialkylimidazolium Formates. *Biomacromolecules*, Vol. 7, No. 12, 3295-3297.
- Graenacher, C. (1934). Cellulose Solution. US patent 1,943,176.
- Heinze, T.; Schwikal, K. & Barthel, S. (2005). Ionic liquids as reaction medium in cellulose functionalization. *Macromolecular Bioscience*, Vol. 5, 520-525.
- Holm, J.; Asikkala, J. & Lassi, U. (2009). Cellulose fractionation from real sludge samples through ionic liquid [BMIM][Cl]. *Chemical Engineering Transactions* Vol. 17, 1645-1650.
- Holm, J. (2010) Unpublished data.
- Huber, G.W.; Iborra, S. & Corma, A. (2006) Synthesis of transportation fuels from biomass: chemistry, catalysts and engineering. *Chemical Reviews* Vol. 106, No. 9, 4044-4098.
- Huddleston, J.G.; Visser, A.E.; Reichert, W.M.; Willauer, H.D.; Broker, G.A. & Rogers, R.D. (2001). Characterization and comparison of hydrophilic and hydrophobic room

- temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry*, Vol. 3, 156-164.
- IPCC (2007). The Fourth Assessment Report of the Intergovernmental Panel on Climate Change. IPCC, Geneva, Switzerland.
- Kaar, W.E. & Holtzapple, M.T. (2000). Using lime pretreatment to facilitate the enzymic hydrolysis of corn stover. *Biomass Bioenergy*, Vol. 18, No. 3, 189-199.
- Kamm, B. & Kamm, M. (2004). Principles of biorefineries. *Applied Microbiology and Biotechnology*, Vol. 64, 137-145.
- Kilpeläinen, I.; Xie, H.; King, A.; Granström, M.; Heikkinen, S. & Argyropoulos, D.S. (2007). Dissolution of wood in ionic liquids. *Journal of Agricultural and Food Chemistry*, Vol. 55, No. 22, 9142-9148.
- Kosan, B.; Michels, C. & Meister, F. (2008). Dissolution and forming of cellulose with ionic liquids. *Cellulose*, Vol. 15, 59-66.
- Kuo, C-H. & Lee, C-K. (2009). Enhancement of enzymatic saccharification of cellulose by cellulose dissolution pretreatments. *Carbohydrate Polymers*, Vol. 77, 41-46.
- Larsson, S.; Palmqvist, E.; Hahn-Hägerdal, B.; Tengborg, C.; Stenberg, K.; Zacchi, G. & Nilvebrant, N-O. (1999). The generation of fermentation inhibitors during dilute acid hydrolysis of softwood. *Enzyme and Microbial Technology*, Vol. 24, 151-159.
- Li, C.; Wang, Q. & Zhao Z.K. (2008). Acid in ionic liquid: An efficient system for hydrolysis of lignocellulose. *Green Chemistry*, Vol. 10, 177-182.
- Li, C.; Knierim, B.; Manisseri, C.; Arora, R.; Scheller H.V.; Auer, M.; Vogel, K.P.; Simmons, B.A. and Singh, S. (2010). Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. *Bioresource Technology*, Vol. 101, 4900-4906.
- Liebert, T. & Heinze, T. (2008). Interaction of ionic liquids with polysaccharides 5. solvents and reaction media for modification of cellulose. *Bioresources*, Vol. 3, No. 2, 576-601.
- Lloyd, T.A. & Wyman, C.E. (2005). Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. *Bioresource Technology*, Vol. 96, No. 18, 1967-1977.
- Lynd, L.R.; Weimer, P.J.; van Zyl, W.H. & Pretorius, I.S. (2002) Microbial cellulose utilization: fundamentals and biotechnology. *Microbiology and Molecular Biology Reviews*, Vol. 66., No. 3, 506-577.
- Lynd, L.R.; Wyman, C.E. & Gerngross, T.U. (1999) Biocommodity engineering. *Biotechnology progress*, Vol. 15, No. 5, 777-793.
- March, K.N.; Boxall, J.A. & Lichtenthaler, R. (2004). Room temperature ionic liquids and their mixtures – a review. *Fluid Phase Equilibria*, Vol. 219, 93-98.
- Mosier, N.; Wyman C.; Dale, B.; Elander, R.; Lee, Y.Y.; Holtzapple, M. & Ladisch, M. (2005) Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource Technology*, Vol. 96, 673-686.
- Moulthorp, J.S.; Swatloski, R.P.; Moyna, G. & Rogers, R.D. (2005). High-resolution ¹³C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions. *Chemical Communications*, 1557-1559.
- Myllymäki, V. & Aksela, R. (2008). Dissolution method. US patent 2008/0023162 A1.
- Mäki-Arvela, P.; Anugwom, I; Virtanen, P.; Sjöholm, R. & Mikkola, J.P. (2010). Dissolution of lignocellulosic materials and its constituents using ionic liquids-A review. *Industrial Crops and Products*, Article in press.

- Olivier-Bourbigou, H.; Magna, L. & Morvan, D. (2010). Ionic liquids and catalysis: Recent progress from knowledge to applications. *Applied Catalysis A: General*, Vol. 373, 1-56.
- Rogalinski, T.; Ingram, T & Brunner, G. (2008). Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. *The Journal of Supercritical Fluids*, Vol. 47, 54-63.
- Sánchez, Ó.J. & Cardona, C.A. (2008). Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresource Technology*, Vol.99, 5270-5295.
- Swatloski, R.P.; Spear, S.K.; Holbrey, J.D. & Rogers, R.D. (2002). Dissolution of Cellulose with Ionic Liquids. *Journal of the American Chemical Society*, Vol. 124, 4974-4975.
- Vitz, J.; Erdmenger, T.; Haensch, C. & Schubert, U.S. (2009). Extended dissolution studies of cellulose in imidazolium based ionic liquids. *Green Chemistry*. Vol. 11, 417-424.
- Wagner, M. & Hilgers, C. (2008). *Ionic liquids in synthesis*, Wiley-VCH, ISBN 978-3-527-31239-9, Weinheim
- Weil, J.; Westgate, P.; Kohlmann, K. & Ladisch, M.R. (1994). Cellulose pretreatments of lignocellulosic substrates. *Enzyme and Microbial Technology*, Vol. 16, No. 11, 1002-1004.
- Wu, B.; Liu, W.W.; Zhang, Y.M.; & Wang, H.P. (2009). Do We Understand the Recyclability of Ionic Liquids? *Chemistry A European Journal*. Vol. 15, 1804-1810.
- Wyman, C.E.; Dale, B.E.; Elander, R.T.; Holtzapple, M.; Landisch, M.R. & Lee, Y.Y. (2005). Coordinated development of leading biomass pretreatment technologies. *Bioresource Technology*, Vol. 96, 1959-1966.
- Zavrel, M.; Bross, D; Funke, M.; Büchs, J. & Spiess, A.C. (2009). High-throughput screening for ionic liquids dissolving (ligno-)cellulose. *Bioresource Technology*, Vol. 100, 2580-2587.
- Zhang, H.; Wu, J.; Zhang, J. & He, J. (2005). 1-Allyl-3-methylimidazolium Chloride Room Temperature Ionic Liquid: A New and Powerful Nonderivatizing Solvent for Cellulose. *Macromolecules*, Vol. 38, 8272-8277.
- Zhang, J.; Zhang, H.; Wu, J.; Zhang, J.; He, J. & Xiang, J. (2010). NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids. *Physical Chemistry Chemical Physics*, Vol. 12, 1941-1947.
- Zhang, Z. & Zhao, Z.K. (2010). Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. *Bioresource Technology*, Vol. 101, 1111-1114.
- Zhao, H.; Baker, G.A.; Song, Z.; Olubajo, O.; Crittle, T. & Peters, D. (2008). Designing enzyme-compatible ionic liquids that can dissolve carbohydrates. *Green Chemistry*, Vol. 10, 696-705.
- Zhao, H.; Jones, C.L.; Baker, G.A.; Xia, S.; Olubajo, O. & Person, V.N. (2009). Regenerating cellulose from ionic liquids for an accelerated enzymatic hydrolysis. *Journal of Biotechnology*, Vol. 139, 47-54.
- Zhbankov, R.G. (1992). Hydrogen bonds and structure of carbohydrates. *Journal of Molecular Structure*, Vol. 270, 523-539.
- Zheng, Y.Z.; Lin, H.M. & Tsao, G.T. (1998). Pretreatment for cellulose hydrolysis by carbon dioxide explosion. *Biotechnology Progress*, Vol. 14, No. 6, 890-896.
- Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Ding, Y. & Wu, G. (2006). Dissolution of cellulose with ionic liquids and its application: a mini-review. *Green Chemistry*, Vol. 8, 325-327.
- Zhu, S.D. (2008). Use of ionic liquids for the efficient utilization of lignocellulosic materials. *Journal of Chemical Technology and Biotechnology*, Vol. 83, No. 6, 777-779.



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This book is the second in the series of publications in this field by this publisher, and contains a number of latest research developments on ionic liquids (ILs). This promising new area has received a lot of attention during the last 20 years. Readers will find 30 chapters collected in 6 sections on recent applications of ILs in polymer sciences, material chemistry, catalysis, nanotechnology, biotechnology and electrochemical applications. The authors of each chapter are scientists and technologists from different countries with strong expertise in their respective fields. You will be able to perceive a trend analysis and examine recent developments in different areas of ILs chemistry and technologies. The book should help in systematization of knowledges in ILs science, creation of new approaches in this field and further promotion of ILs technologies for the future.

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