

Catalytic Role of Ionic Liquids for Dissolution and Degradation of Biomacromolecules

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Natural biomacromolecules constitute a diverse feedstock, including carbohydrate-based polysaccharides (cellulose, hemicellulose, starch, agarose, and *Konjac* glucomannan) together with lignin — extracted mainly from biomass — and other protein based polymers, namely keratin, chitin, chitosan, and silk fibroin. The complex and heterogeneous chemical structure of biomacromolecules makes them difficult to dissolve and disintegrate into simpler molecules for further applications. In this regard, ionic liquids are potential solvents for the dissolution and modification of long chain biopolymers. This provides a promising pretreatment technology and is known to allow adequate extraction of biopolymers from natural sources. This paper highlights the properties of ionic liquids for their use as versatile solvents. This review provides a critical outlook regarding the influence of several process parameters that govern the fractionation of biomacromolecules into their constituent elements and further pretreatment processes. The performance of different types of ionic liquids for processing of biomacromolecules, focusing on their pertinent capability as catalysts to enhance the rate of hydrolysis, also is discussed in this article.

Keywords: Biopolymers; Cellulose; Chitosan; Keratin; Polysaccharides; Lignin; Biomass

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INTRODUCTION

The forthcoming inadequate supply of fossil fuels has necessitated the search for alternatives sources for chemicals and energy. To date, huge efforts have been made to maximize the utilization of biopolymers and identify new species of biomass resources to fulfill the future demand for materials and energy. Biomass – such as hard wood, soft wood, and agricultural residues – is considered one of the most renewable feed stocks that is produced by living things (Chowdhury *et al.* 2013). The transformation of biomass can yield value-added products with little or zero emission of toxic chemicals (Arami-Niya *et al.* 2012; Doherty *et al.* 2010). In this context, it can be considered as a greener alternative to fossil fuels. Green plants trap solar energy and produce complex macromolecules of lignin, carbohydrates, proteins, and others (Doherty *et al.* 2010).

Cellulose, a fibrous homo-polysaccharide, is the major fraction of biomass. It contains many hydrophilic –OH groups in its structure (Hubbe *et al.* 2013). It is almost insoluble in all types of organic solvents and water. The long polymeric chain of this biopolymer does not disintegrate easily to yield glucose. However, this biopolymer is

nontoxic, biodegradable, and inexpensive. Furthermore, it can be chemically treated to yield compounds with specific functional groups. Hemicellulose is amorphous and distinctly hydrophilic due to the presence of carboxyl groups in its structure (Hubbe *et al.* 2013). It is the second most abundant polymer, with a lower molecular weight than cellulose. It consists of amorphous branched, heterogeneous polymers of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and acetylated sugars. It also contains xylose sugars bonded by β -(1, 4)-glycosidic bonds and branched α -(1, 2) - glycosidic bonds containing 4-methyl glucuronic acid groups (Saha 2003). It can be easily hydrolyzed and made soluble in alkaline solutions (Chowdhury *et al.* 2013). The rigid texture of plant biomass is contributed by lignin, which acts as a strong adhesive to hold cellulose and hemicellulose by ester linkages and hydrogen bonding. It is an amorphous and resin-like substance. Lignocellulosic biomass, such as coir, has approximately 45% of lignin, whereas softwood contains 25 to 31%, and hardwood contains 16 to 24% of lignin (Suhas *et al.* 2007). In the case of hardwood, lignin is covalently attached with xylans, and in softwood it is bonded with galactoglucomannans. Lignin is a more hydrophobic macromolecule than the two polysaccharides (cellulose and hemicellulose) present in wood (Hubbe *et al.* 2013).

Compared to lignocellulosic derivatives, less research has been reported on the dissolution of starch, keratin, and chitin biopolymers (Qin *et al.* 2010; Zakrzewska *et al.* 2010). The polysaccharide starch is abundantly available and biodegradable. It is mainly extracted from plant residues. When starch is dissolved, it forms unstable pastes and gels (Wang and Xie 2010). Amylopectin is soluble, while amylose may crystallize from aqueous solution to form fine particles dispersed in water. Keratin, a protein macromolecule, contains 15% serine and cysteine with hydroxyl amino acids (Arai *et al.* 1983). It has di-sulfide covalent bonds and hydrogen bonds. It is insoluble in water, weak acids, and bases. Thus a large amount of conventional reagent (acid) is required to extract keratin from poultry feather biomass (Wang and Cao 2012; Barone and Schmidt 2006). Chitosan is obtained after deacetylation of chitin, which consist of β - (1-4)-2-amino-D-glucose and β -(1-4)-2-acetamido- D-glucose linked through 1,4- β -glucosidic bonds (Chen *et al.* 2012). Its high molecular weight makes it sparingly soluble.

To overcome problems related to low solubility of such biomacromolecules, a new type of solvent, referred to as an ionic liquid, has been used extensively by several researchers. Ionic liquids are salts containing organic cations such as imidazolium, pyridinium, pyrrolidinium, or ammonium derivatives (Tokuda *et al.* 2006). These cations can be combined with organic or inorganic anions such as Cl^- , Br^- , I^- , BF_4^- , PF_6^- , CF_3SO_3^- , and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ (Hirao *et al.* 2006). Ionic liquids have an elaborate network of asymmetric ions that are bonded by electrostatic charges and hydrogen bonding. They melt at approximately room temperature or below 100 °C. They are nonvolatile. They are thermally and chemically stable over wide ranges of temperatures. More specifically, ionic liquids have negligible vapor pressure and high ionic conductivity under ambient conditions, which enables them to be used in different types of synthesis processes, especially where loss of the vapor phase limits the overall extraction process (Olivier-Bourbigou *et al.* 2010). Application of ionic liquids can make it possible to minimize the use of hazardous organic solvents. Presently, ionic liquids are extensively used for catalyzing chemical processes associated with hydrolysis of biomass or its constituent biopolymers. The more recent studies based on dissolution of lignocellulosic materials in ionic liquids, with partial extraction and degradation of the major constituent

biopolymers, leads towards further opportunities to obtain sustainable chemicals (Sun *et al.* 2011). However, questions remain about the large-scale application of ionic liquids. Careful measures should be taken to prevent them from entering the process stream. It has been reported that a kilogram of ionic liquid costs about 30,000 times more than the common organic solvent acetone (Keskin *et al.* 2007). However, the cost can be reduced significantly by optimizing the composition of ionic liquids with large-scale production. Another problem associated with ionic liquid applications is the use of volatile compounds during the synthesis process. Furthermore, incomplete data is available regarding the physio-chemical properties that determine the toxicity of ionic liquids.

This review focuses on efforts of researchers to show a different perspective on the utilization of ionic liquids (ILs) for the dissolution and extraction of biomacromolecules, irrespective of source. It also highlights the process parameters influencing the dissolution mechanisms of ionic liquids. It is well known that the dissolution and thereby functionalization of different types of biopolymers in ILs continues to be an enormous field of scientific endeavor; yet functionalization is not the major focus of this review. Instead, a more rigorous literature survey has been conducted concerning the utilization of ionic liquids (ILs) and their sometimes catalytic roles in the dissolution of natural polysaccharides and lignin, mainly derived from biomass residues.

DEGRADATION AND EXTRACTION OF POLYSACCHARIDES USING IONIC LIQUIDS (ILs)

The recalcitrance of lignocellulosic biomaterials originates from the cellulosic structure embedded in the biomass core by complex interactions with hemicellulose and lignin macromolecules. Thus, to make the biomass or the extracted cellulose more susceptible to transformation, disruption of the crystalline structure of cellulose or reduction of lignin content inside the biomass matrix is necessary. The solubility of macromolecules is profoundly influenced by the presence of ionic liquids in the reaction medium.

Cellulose

The macromolecule of cellulose is composed of β -D-glucopyranose units that are linked via β -(1, 4) glycoside bonds (Swatloski *et al.* 2002; Zhu *et al.* 2006). The repeating unit of the linear chain of cellulose is known as cellobiose, a disaccharide. The strong intra- and intermolecular hydrogen bonds present in cellulose can result in a crystalline or amorphous texture of cellulose (Laureano-Perez *et al.* 2005). The percentage solubility of cellulose is dependent on its degree of polymerization (DP), temperature, time, concentration of cellulose in ILs, and finally the presence of a co-solvent and anti-solvent in the reaction medium. Table 1 summarizes the most widely used ILs/solvent systems to dissolve cellulose.

The negative anions of ILs interact with the -OH groups of cellulose (Olivier-Bourbigou *et al.* 2010). Consequently, the network of H- bonds between the cellulosic chains is disrupted. Literature studies revealed that it is possible to design more effective ILs through a comprehensive understanding of cellulose-ILs interaction mechanisms. It was observed that the bond strength between cellulose and the ionic liquids of 1-ethyl-3-methyl imidazolium acetate ([Emim][OAc]) was stronger (3 times) than conventional solvents like water or methanol (Remsing *et al.* 2008).

Table 1. Summary of Salt/Solvent System to Dissolve Cellulose

Ionic liquids/solvent system	Acronyms
Dimethyl sulfoxide/Tetrabutylammonium fluoride	DMSO/TBAF
Dinitrogen tetraoxide/Dimethyl formamide	N ₂ O ₄ /DMF
Dimethyl sulfoxide/paraformaldehyde	DMSO/CH ₂ O
Lithium chloride/dimethylacetamide	LiCl/DMAc
Lithium chloride/dimethylimidazolidinone	LiCl/DMI
Lithium chloride/N-methyl pyrrolidine	LiCl/NMP

The results indicated that the (1,4)-glycosidic linkage of cellulose was disintegrated when the cellulose was dissolved in [Emim][OAc]. This change was irreversible even after the regeneration process. It was concluded that the structural change of cellulose by ILs made them more accessible for enzymatic hydrolysis (Liu *et al.* 2010). After that, several types of ionic liquids have been synthesized for dissolution of cellulose and lignocellulosic materials (Fukaya *et al.* 2006; Kilpelainen *et al.* 2007; Zavrel *et al.* 2009; Zakrzewska *et al.* 2010). Some imidazolium-based ILs containing phosphate, formate, and acetate anions have shown a high ability for dissolving cellulose (Liu *et al.* 2010; Remsing *et al.* 2008). It was observed that imidazolium-based ionic liquids in the presence of anti-solvents such as water and ethanol can dissolve up to 25 wt% of cellulose, resulting in amorphous-phase cellulose (Swatloski *et al.* 2002). Even non-imidazolium-based ionic liquids also acted as good solvents for cellulose (Zakrzewsk *et al.* 2010). Table 2 summarizes some recent works done for degradation of cellulosic biomaterials using ionic liquids.

Starch

Starch has been dissolved in ILs to improve its functionality for different industrial applications (Wang and Xie 2010). ILs containing Cl⁻ destroy the semi-crystalline structure of starch granules (Xie *et al.* 2010). Starch granules were dissolved successfully in 1-methoxymethyl-3-methylimidazolium bromide or 1-methoxyethyl-3-methylimidazolium bromide to produce a 30 mg/L solution after heating (Kimizuka and Nakashima 2001).

Wheat, barley, potato, rice, corn, and waxy cornstarch were dissolved in [Bmim][Cl] under controlled microwave conditions in an oil bath (Karkkainen *et al.* 2011). It was found that temperature, time, and experimental method had a significant effect on the molecular weight of extracted amylose and amylopectin. The time for dissolution varied with the origin of starch sample. Waxy corn and potato starch granules were comparatively resistant to ILs. On the contrary, rice, wheat, and barley starch were fully gelatinized under identical reaction conditions. Increased temperature and time facilitated the dissolution process, resulting in a lower molecular weight of starch. After a certain limit, increasing temperature accelerated the degradation of amylose and amylopectin. Another investigation was carried out for corn, rice, wheat, and potato starch in [Bmim][Cl] (Stevenson *et al.* 2007). Among all the substrates, the molecular weight for amylopectin derived from potato starch was the highest. This was attributed to the interactions between negatively charged phosphorous monoesters of the potato starch and positively charged imidazolium ring of the ionic liquid (Stevenson *et al.* 2007).

Table 2. Application of Ionic liquids (ILs) for Dissolution of Cellulose

Ionic liquids (ILs)	Abbreviation	Substrate Cellulose	Reaction Condition		Solubility	References
			Temperature (°C)	Time	wt %	
1-allyl-2,3-dimethylimidazolium Bromide	[Ammim][Br]	Pulp (DP= 286)	80	-	12	Mosier <i>et al.</i> 2005
		Avicel	90	-	5	Zavrel <i>et al.</i> 2009
1-allyl-3-methylimidazolium chloride	[Amim][Cl]	Cellulose pulp	80	-	14.5	Zhang <i>et al.</i> 2007
		Cotton Pulp	100-130	40-240 min	5-14.5	Zhang <i>et al.</i> 2005
		Avicel	100	1	20	Zavrel <i>et al.</i> 2009
1-butyl-3-methylimidazolium chloride	[Bmim][Cl]	Avicel	90	-	5	Vitz <i>et al.</i> 2009
		Cellulose Avicel	100	-	20	Erdmenzer <i>et al.</i> 2009
		Cellulose	85	-	13.6	Kosan <i>et al.</i> 2008
		Cellulose	83	12	18	Heinze <i>et al.</i> 2005
		Pulp Cellulose DP= 1000	100	-	10	Swatloski <i>et al.</i> 2002
		Cellulose	85	-	12.8	Kosan <i>et al.</i> 2008
1-benzyl-3-methylimidazolium chloride	[Bnmim][Cl]	Cellulose	85	-	12.8	Kosan <i>et al.</i> 2008
1-butyl-3-methylimidazolium Bromide	[Bmim][Br]	Cellulose	Microwave	-	5-7	Swatloski <i>et al.</i> 2002
		Avicel	100	1	2-3	Vitz <i>et al.</i> 2009
		Avicel	50	-	Fractionally soluble	Zavrel <i>et al.</i> 2009
1-butyl-3-methylimidazolium Iodide	[Bmim][I]	Avicel	50	-	5	Zavrel <i>et al.</i> 2009
		Avicel	100	1	1-2	Vitz <i>et al.</i> 2009

Table 2. Application of Ionic liquids (ILs) for Dissolution of Cellulose (Continued)

Ionic liquids (ILs)	Abbreviation	Substrate Cellulose	Reaction Condition		Solubility	References
			Temperature (°C)	Time	wt %	
1-butyl-3-methylimidazolium acetate	[Bmim][OAc]	Avicel	100	1	12	Vitz <i>et al.</i> 2009
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	Pulp Cellulose	Microwave	-	Insoluble	Swatloski <i>et al.</i> 2002
1-butyl-2,3-dimethylimidazolium dicyanamide	[Bmim][DCA]	Avicel	110	-	1	Zhao <i>et al.</i> 2009
1-butyl-3-methylimidazolium bis [(trifluoromethane) sulfonyl]imide	[Bmim][NTf ₂]	Avicel	110	-	0.5	Zhao <i>et al.</i> 2009
1-butyl-3-methylimidazolium thiocyanate	[Bmim][SCN]	Avicel	100	1	20	Zavrel <i>et al.</i> 2009
Tetrabutylphosphonium formate	[Bu ₄ P][HCOO]	Avicel (DP=225)	110	-	6	Mosier <i>et al.</i> 2005
1-butyl-3-methylpyridinium chloride	[BMPy][Cl]	Pulp (DP= 593)	105	-	37	Mosier <i>et al.</i> 2005
1-butyl-3-methylpyrrolidinium chloride	[3MBPy][Cl]	Cellulose (DP=286)	105	12	39	Kosan <i>et al.</i> 2008
1-decyl-3-methylpyridinium chloride	[Dmim][Cl]	Avicel	100	-	>1	Erdmenzer <i>et al.</i> 2009
1-ethyl-3-methylimidazolium chloride	[Emim][Cl]	Cellulose	85	-	15.8	Kosan <i>et al.</i> 2008
		Avicel	100	1	10-14	Vitz <i>et al.</i> 2009
		Avicel	90	-	5	
1-ethyl-3-methylimidazolium Fluoride	[Emim][F]	Avicel	100	1	2	Vitz <i>et al.</i> 2009
1-ethyl-3-methylimidazolium Bromide	[Emim][Br]	Avicel	100	1	1-2	Vitz <i>et al.</i> 2009
1-ethyl-3-methylimidazolium acetate	[Emim][OAc]	Cellulose	85	-	13.5	Kosan <i>et al.</i> 2008
		Avicel	110	-	15	Zhao <i>et al.</i> 2009
		Avicel	100	35 min	10	Fukaya <i>et al.</i> 2008

Table 2. Application of Ionic liquids (ILs) for Dissolution of Cellulose (Continued)

Ionic liquids (ILs)	Abbreviation	Substrate Cellulose	Reaction Condition		Solubility wt %	References
			Temperature (°C)	Time		
1-ethyl-3-methylimidazolium bis [(trifluoromethane) sulfonyl]imide	[Emim][NTf ₂]	Avicel	110	-	Very low	Zhao <i>et al.</i> 2009
1-ethyl-3-methylimidazolium dimethylphosphonate	[Emim][MePO ₃ Me]	Microcrystalline cellulose	45	30 min	10	Fukaya <i>et al.</i> 2008
1-ethyl-3-methylimidazolium dimethylphosphate	[Emim][(MeO) ₂ PO ₂]	Microcrystalline cellulose	65	30 min	10	Fukaya <i>et al.</i> 2008
1-hexyl-3-methylimidazolium bromide	[Hexmim][Br]	Avicel	100	1	1-2	Vitz <i>et al.</i> 2009
1-heptyl-3-methylimidazolium bromide	[Hepmim][Br]	Avicel	100	1	>1	Vitz <i>et al.</i> 2009
1-hexyl-3-methylimidazolium chloride	[Hexmim][Cl]	Pulp Cellulose	100	-	5	Swatloski <i>et al.</i> 2002
		Avicel	100	-	7	Erdmenzer <i>et al.</i>
		Avicel	100	1	6	Vitz <i>et al.</i> 2009
1-heptyl-3-methylimidazolium chloride	[Hepmim][Cl]	Pulp Cellulose	100	-	Sparingly soluble	Swatloski <i>et al.</i> 2002
		Avicel	100	-	5	Erdmenzer <i>et al.</i>
		Avicel	100	1	5	Vitz <i>et al.</i> 2009
1,3-dimethylimidazolium dimethylphosphate	[Mmim][(MeO) ₂ PO ₂]	Avicel	100	1	10	Vitz <i>et al.</i> 2009
		Avicel	90	-	5	Zavrel <i>et al.</i> 2005
1-nonyl-3-methylimidazolium chloride	[Nmim][Cl]	Avicel	100	-	2	Erdmenzer <i>et al.</i> 2009
1-nonyl-3-methylimidazolium bromide	[Nmim][Br]	Avicel	100	1	1	Vitz <i>et al.</i> 2009

Table 2. Application of Ionic liquids (ILs) for Dissolution of Cellulose (Continued)

Ionic liquids (ILs)	Abbreviation	Substrate Cellulose	Reaction Condition		Solubility	References
			Temperature (°C)	Time	wt %	
1-octyl-3-methylimidazoliumbromide	[Omim][Br]	Avicel	100	1	>1	Vitz <i>et al.</i> 2009
1-octyl-3-methylimidazolium Chloride	[Omim][Cl]	Avicel	100	-	4.5	Erdmenzer <i>et al.</i> 2009
		Avicel	100	1	4	Vitz <i>et al.</i> 2009
		Avicel	80	-	Very low	Zavrel <i>et al.</i> 2009
1-pentyl-3-methylimidazolium chloride	[Pemim][Cl]	Avicel	100	-	1.5	Erdmenzer <i>et al.</i> 2009
1-pentyl-3-methylimidazolium bromide	[Pemim][Br]	Avicel	100	1	1-2	Vitz <i>et al.</i> 2009
1-propyl-3-methylimidazolium chloride	[Prmim][Cl]	Avicel	100	-	>1	Erdmenzer <i>et al.</i> 2009
1-propyl-3-methylimidazolium bromide	[Prmim][Br]	Avicel	100	1	1-2	Vitz <i>et al.</i> 2009
1-butyl-3-methylimidazolium hexafluorophosphate	[Bmim][PF ₆]	Pulp Cellulose	Microwave	-	Insoluble	Swatloski <i>et al.</i> 2002
1-ethyl-3-methylimidazolium tosylate	[Emim][Tos]	Avicel	100	1	1	Vitz <i>et al.</i> 2009

- Not available

Agarose

Agarose is an algal polysaccharide comprised of alternating D-galactose and 3,6-anhydro-L-galactose repeating units (Singh *et al.* 2012). It is insoluble in cold water and many common organic solvents, as it contains a large number of hydroxyl groups. At high temperature, dissolution of agarose in water is difficult. In this regard, some nitrogen-based ionic liquids that have good potential for dissolving cellulose are used as alternative dissolution media for agarose (Trivedi *et al.* 2012). Recently some studies have investigated the dissolution properties of agarose in single and binary mixtures of ILs (Trivedi *et al.* 2012). The solubility obtained was higher, and the IL was regenerated by using methanol as an anti-solvent. Slight degradation was observed for agarose regenerated from a solution of N-butyl-3-methylpyridinium chloride [BmPy][Cl]. Table 3 summarizes the results for dissolution of agarose in different types of ionic liquids

Table 3. Dissolution of Agarose in a Single Solute System of Ionic Liquid

Ionic Liquid	Abbreviation	Solubility (wt%)	References
Water	H ₂ O	8	Singh <i>et al.</i> 2012
1-butyl-3-methylimidazolium chloride	[Bmim][Cl]	16	Singh <i>et al.</i> 2012
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	Insoluble	Singh <i>et al.</i> 2012
1-butyl-3-methylimidazolium hexafluorophosphate	[Bmim][PF ₆]	Insoluble	Singh <i>et al.</i> 2012
1-butyl-3-methylimidazolium methylsulfate	[Bmim][MeOSO ₃]	5	Singh <i>et al.</i> 2012
1-butyl-3-methylimidazolium octylsulfate	[Bmim][OctOSO ₃]	Insoluble	Singh <i>et al.</i> 2012
1-octyl-3-methylimidazolium Chloride	[Omim][Cl]	4.5	Singh <i>et al.</i> 2012
1-octyl-3-methylimidazolium tetrafluoroborate	[Omim][BF ₄]	insoluble	Singh <i>et al.</i> 2012
N-butyl-3-methylpyridinium chloride	[BmPy][Cl]	13	Singh <i>et al.</i> 2012
N-(2-hydroxyethyl) ammonium formate	[HEA][HCOO]	5	Trivedi <i>et al.</i> 2012
Methyl ammonium formate	[MA][HCOO]	14	Trivedi <i>et al.</i> 2012
Ethyl ammonium formate	[EA][HCOO]	20	Trivedi <i>et al.</i> 2012

From the table, it can be seen that ILs having the same length of cationic chains containing chloride anions are better solvents for agarose as compared to the methyl sulfate anion. The non-coordinating groups of tetrafluoroborate or hexafluorophosphate anions along with the β amphiphilic octyl sulfate anion failed to dissolve agarose. This is due to the strong interaction of chloride ions with the hydroxyl groups of agarose (Singh *et al.* 2012). Agarose has very good solubility in [MA][HCOO] and [EA][HCOO] compared to [HEA][HCOO], which was a poorer solvent than water also (Trivedi *et al.* 2012).

The researchers further analyzed the dissolution behavior of agarose in binary ionic liquid solvents, as summarized in Table 4. It can be inferred from Table 4 that binary ionic liquid mixtures are comparatively better than single ionic liquids (Trivedi *et al.* 2012).

Table 4. Dissolution of Agarose in a Binary Solute System of Ionic Liquid

Ionic Liquid	Solubility (wt %)	References
[HEA][HCOO] + [Bmim][Cl]	8	Trivedi <i>et al.</i> 2012
[MA][HCOO] + [Bmim][Cl]	18	Trivedi <i>et al.</i> 2012
[EA][HCOO] + [Bmim][Cl]	7	Trivedi <i>et al.</i> 2012
[HEA][HCOO] + [Bmpy][Cl]	7	Trivedi <i>et al.</i> 2012
[MA][HCOO] + [Bmpy][Cl]	21	Trivedi <i>et al.</i> 2012
[EA][HCOO] + [Bmpy][Cl]	25	Trivedi <i>et al.</i> 2012
[HEA][HCOO] + [Bmim][MeOSO ₃]	14	Trivedi <i>et al.</i> 2012
[MA][HCOO] + [Bmim][MeOSO ₃]	23	Trivedi <i>et al.</i> 2012
[EA][HCOO] + [Bmim][MeOSO ₃]	26	Trivedi <i>et al.</i> 2012

Konjac glucomannan (KGM)

KGM is a natural polysaccharide obtained from the tubers of *Amorphophallus konjac* plants. It contains β -1,4-linked D-glucose and D-mannose units (Shen *et al.* 2011). Recently [Amim][Cl] and [Bmim][Cl] were used for the dissolution of *konjac glucomannan* (KGM). Regeneration was carried out with anhydrous alcohol. Better dissolution properties were exhibited by [Amim][Cl] (Shen *et al.* 2011). Acylation of *konjac glucomannan* (KGM) was carried out with vinyl acetate and lipase enzyme in five types of ionic liquids (ILs). For comparison, the same reaction was carried out in the presence of *tert*-butanol instead of ILs (Chen *et al.* 2006). In the presence of ionic liquid, the activity of enzyme was better than in *tert*-butanol.

DISSOLUTION AND EXTRACTION OF CONSTITUENT BIOPOLYMERS FROM LIGNOCELLULOSIC BIOMASS

The difficulties that need to be dealt with carefully for biomass conversion processes that yield biomacromolecules are divided into the following three steps (1) disintegration of the lignocellulosic chain present in biomass, (2) diminishing the oxygen content of the parent biomass or the intermediates, and (3) enhancing the formation of C-C bonds between biomass-derived intermediates that will subsequently increase the molecular weights of the end products (Alonso *et al.* 2010).

Several reports have shown that partial delignification of the lignocellulosic biomass is possible in the presence of ionic liquids. External reagents, catalysts, or enzymes can easily penetrate through initially pretreated biomass with ionic liquids (Xie *et al.* 2009; Xie *et al.* 2007). However, the exact mechanisms by which an ionic liquid

solubilizes the biomass substrate and induces significant changes within the structure of the plant cell walls are not fully understood.

Dissolution of Wood Biomass in Ionic Liquids (ILs)

The relative proportion of constituent biopolymers in wood varies depending on the wood source. Typically wood consists of 40 to 50% cellulose by dry weight, 20 to 40% hemicellulose, and 18 to 25% of lignin in hardwood and 25 to 35% of lignin in softwood (Ververis *et al.* 2004). 1-ethyl-3-methylimidazolium acetate ([Emim][OAc] in the presence of dilute sulfuric acid was used to pretreat aspen wood (*Populus tremula*) at 120 °C for 1, 3, and 5 h followed by regeneration using water as an anti-solvent. The treated wood sample showed more than 95% enzymatic digestibility. The yield from the untreated wood was only 5.3% (Goshadroura *et al.* 2013). Cellulose-rich material and pure lignin can be extracted separately from woody biomass by using aqueous acetone as a solvent. A schematic representation of the procedure is shown by Fig. 1 (Viell and Marquardt 2011).

In another work, cellulose fibers (CFs) were extracted from woody biomass by treatment with the ionic liquid (IL), [Emim][OAc] at 80 °C for 1 h (Moniruzzaman and Ono 2013). Approximately 73.1% cellulose and 9.8% of lignin were obtained. On the contrary, an untreated wood sample contained 29.3% of lignin. Another ionic liquid [Bmim][Cl] dissolved in DMSO solvent was used to dissolve wood chips partially (Fort *et al.* 2007). Meanwhile, the dissolution behavior of Norway spruce and southern pine wood samples were observed by using both [Bmim][Cl] and [Amim][Cl] ILs, in the temperature range from 80 to 130 °C for 8 h (Li *et al.* 2010; Sun *et al.* 2009). The researchers concluded that smaller particle size favors better dissolution of wood in water. Softwood of southern yellow pine and hardwood of red oak were dissolved by [Emim][CH₃COO], and the findings showed that biomass can be effectively dissolved in [Emim][CH₃COO] rather than [Bmim][Cl] and [Amim][Cl] (Sun *et al.* 2009). These results were not in agreement with the findings proposed by previous researchers, who observed very low solubility of wood flour (< 5 g/kg) and a high solubility of micro-crystalline cellulose (> 100 g/kg) in [Emim][CH₃COO] (Lee *et al.* 2009). Beech and spruce wood were dissolved at 115 °C in [Emim][CH₃COO] for 72 h. Even after this long contact period, none of the wood samples were dissolved completely (Viell and Marquardt 2011). Similar results were found for pinewood dissolved in this IL at 120 °C and 155 °C for 3 h (Torr *et al.* 2012). Another investigation was carried out under identical conditions for different types of ILs using spruce, silver fir, common beech, and chestnut wood chips (Yang *et al.* 2010). The researchers concluded that [Emim][Cl], [Bmim][Cl], and [Emim][Et₂PO₄] were only able to partially dissolve different samples of wood. The ionic liquid, [Amim][Cl] was found to be the most suitable solvent for dissolving all tested wood. However, silver fir was incompletely dissolved in [Emim][CH₃COO]. The major components of wood can be recovered, after ionic liquid treatment. It was found that water significantly reduces the solubility of wood in ILs (Swatloski *et al.* 2002). Thus it can be concluded that proper selection of co-solvent and anti-solvent agents along with the ionic liquid is required for separation of extracted biopolymers from the reaction medium. Table 5 summarizes recent literature reviews regarding applications of ionic liquids to treat different types of woody biomass.

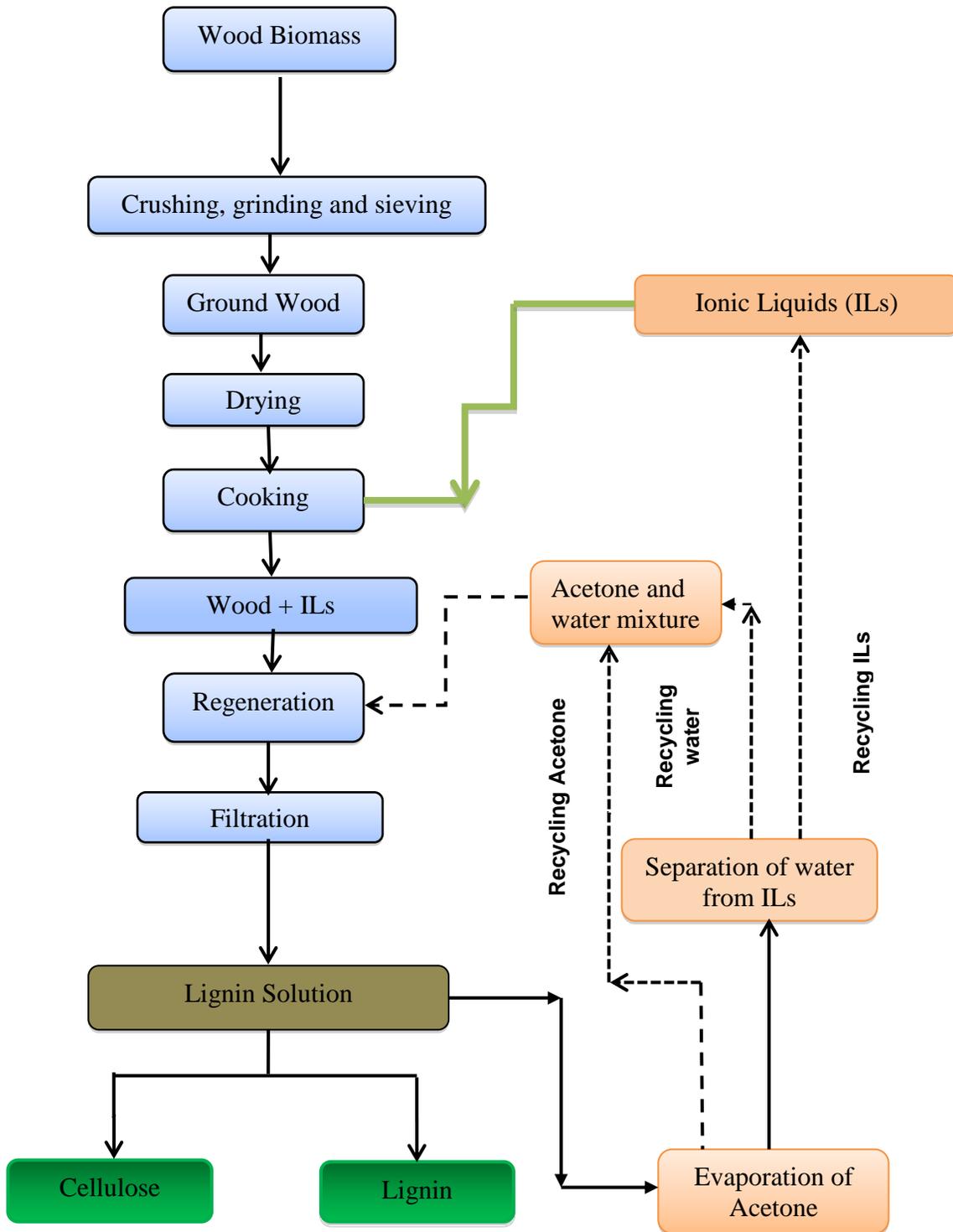


Fig. 1. Extraction of biomacromolecules from wood by using ILs

Table 5. Application of Ionic liquids (ILs) for Extraction of Biopolymers from Wood

Ionic liquids (ILs)	Abbreviation	Substrate wood	Reaction Condition				References
			Temperature (°C)	Time (h)	Co-solvent	Anti-solvent	
1-allyl-3-methylimidazolium chloride	[Amim][Cl]	Spruce Chips	90	24	-	-	Kilpelainen <i>et al.</i> 2007
		Norway Spruce	130	8	-	-	Zavrel <i>et al.</i> 2009
		Southern pine	120	5	-	H ₂ O or MeOH	Li <i>et al.</i> 2010
		Norway Spruce	120	5	-	H ₂ O or MeOH	Li <i>et al.</i> 2010
		Spruce sawdust	80	8	-	-	
		Maple wood	90	24	-	-	Lee <i>et al.</i> 2009
		Pine	100	3	DMSO	H ₂ O	Wang <i>et al.</i> 2011
		Pine	100	2	DMSO	Aceton-H ₂ O	Wang <i>et al.</i> 2011
		Catalpa	100	3	DMSO	H ₂ O	Wang <i>et al.</i> 2011
1-butyl-3-methylimidazolium chloride	[Bmim][Cl]	Maple wood	90	24	-	-	Lee <i>et al.</i> 2009
		Pine	100	24	DMSO	-	Fort <i>et al.</i> 2007
		Southern yellow pine	110	16	-	-	Sun <i>et al.</i> 2009
		Poplar	100	24	DMSO	-	Fort <i>et al.</i> 2007
		Wood chips	130	15	-	-	Kilpelainen <i>et al.</i> 2007
		Spruce chips	90	-	-	-	Zavrel <i>et al.</i> 2009
		Eucalyptus	100	24	DMSO	-	Fort <i>et al.</i> 2007
		Oak	100	24	DMSO	-	Fort <i>et al.</i> 2007
		Norway Spruce chips	130	8	-	-	Kilpelainen <i>et al.</i> 2007

Table 5. Application of Ionic liquids (ILs) for Extraction of Biopolymers from Wood (Continued)

Ionic liquids (ILs)	Abbreviation	Substrate wood	Reaction Condition				References
			Temperature (°C)	Time (h)	Co-solvent	Anti-solvent	
1-butyl-3-methylimidazolium acetate	[Bmim][CH ₃ OO]	Spruce wood	120	1,3,15	-	H ₂ O	Shafiei <i>et al.</i> 2012
		Maple wood	90	12	-	-	Doherty <i>et al.</i> 2010
		Willow	22	120	H ₂ O	MeOH	Brandt <i>et al.</i> 2011
		Poplar	12	130	H ₂ O	Acetone	Vo <i>et al.</i> 2011
1-butyl-3-methylimidazolium hydrogen sulfate	[Bmim][HSO ₄]	Willow	22	120	H ₂ O	MeOH	Brandt <i>et al.</i> 2011
1-butyl-3-methylimidazolium methane sulfonate	[Bmim][MeOSO]	Maple wood	12	90	-	-	Doherty <i>et al.</i> 2010
1-butyl-3-methylimidazolium trifluoromethane sulfonate	[Bmim][OTf]	Maple wood	90	24	-	-	Lee <i>et al.</i> 2009
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	Maple wood	90	24	-	-	Lee <i>et al.</i> 2009
1-butyl-3-methylimidazolium hexafluorophosphate	[Bmim][PF ₆]	Maple wood	90	24	-	-	Lee <i>et al.</i> 2009
1-ethyl-3-methylimidazolium acetate	[Emim][OAc]	Southern yellow pine	110	16	-	1:1 Acetone and water	Sun <i>et al.</i> 2009
		Spruce	120	1,3,15	-	H ₂ O	Shafiei <i>et al.</i> 2012
		Pine	120	3	-	H ₂ O	Torr <i>et al.</i> 2012
		Red Oak	110	16	-	Acetone	Sun <i>et al.</i> 2009
		Maple wood	90	6	-	-	Doherty <i>et al.</i> 2010
Poplar	125	1	-	H ₂ O	Wu <i>et al.</i> 2011		

Table 5. Application of Ionic liquids (ILs) for Extraction of Biopolymers from Wood (Continued)

Ionic liquids (ILs)	Abbreviation	Substrate wood	Reaction Condition				References
			Temperature (°C)	Time (h)	Co-solvent	Anti-solvent	
1-butyl-3-methylimidazolium Chloride	[Bmim][Cl]	Eucalyptus	150	1	-	H ₂ O	Pezoa <i>et al.</i> 2010 Zavrel <i>et al.</i> 2009
			90	-	-	-	
1,3-dimethylimidazolium methylsulfate	[Mmim][MeSO ₄]	Maple wood	80	24	-	-	Lee <i>et al.</i> 2009
1,3-dimethylimidazolium dimethylphosphate	[Mmim][((MeO) ₂ P O ₂]	Spruce	90	-	-	-	Zavrel <i>et al.</i> 2009
1-benzyl-3-methylimidazolium dicyanamide	[Bnmim][DCA]	Aspen wood	150	24	-	-	Kilpelainen <i>et al.</i> 2007
1-benzyl-3-methylimidazolium chloride	[Bnmim][Cl]	Southern pine	130	8	-	-	Kilpelainen <i>et al.</i> 2007

- Not Available

Dissolution of Agricultural Biomass in Ionic Liquids

Partial dissolution of the lignocellulosic matrix is the first step for processing of agricultural residues. Generally, at the initial stage, the biomass is added with an IL. At this stage, temperature, time, co-solvent, solid to liquid ratio, and water content in biomass is carefully optimized. The subsequent step of regeneration is most important with the addition of a precipitating solvent, which is usually referred to as the anti-solvent. Examples include water, acetone, dichloromethane, and acetonitrile. Figure 2 shows the schematic representation for the pre-treatment, regeneration, and fractionation into cellulose, hemicellulose, and lignin content of the biomass using ILs.

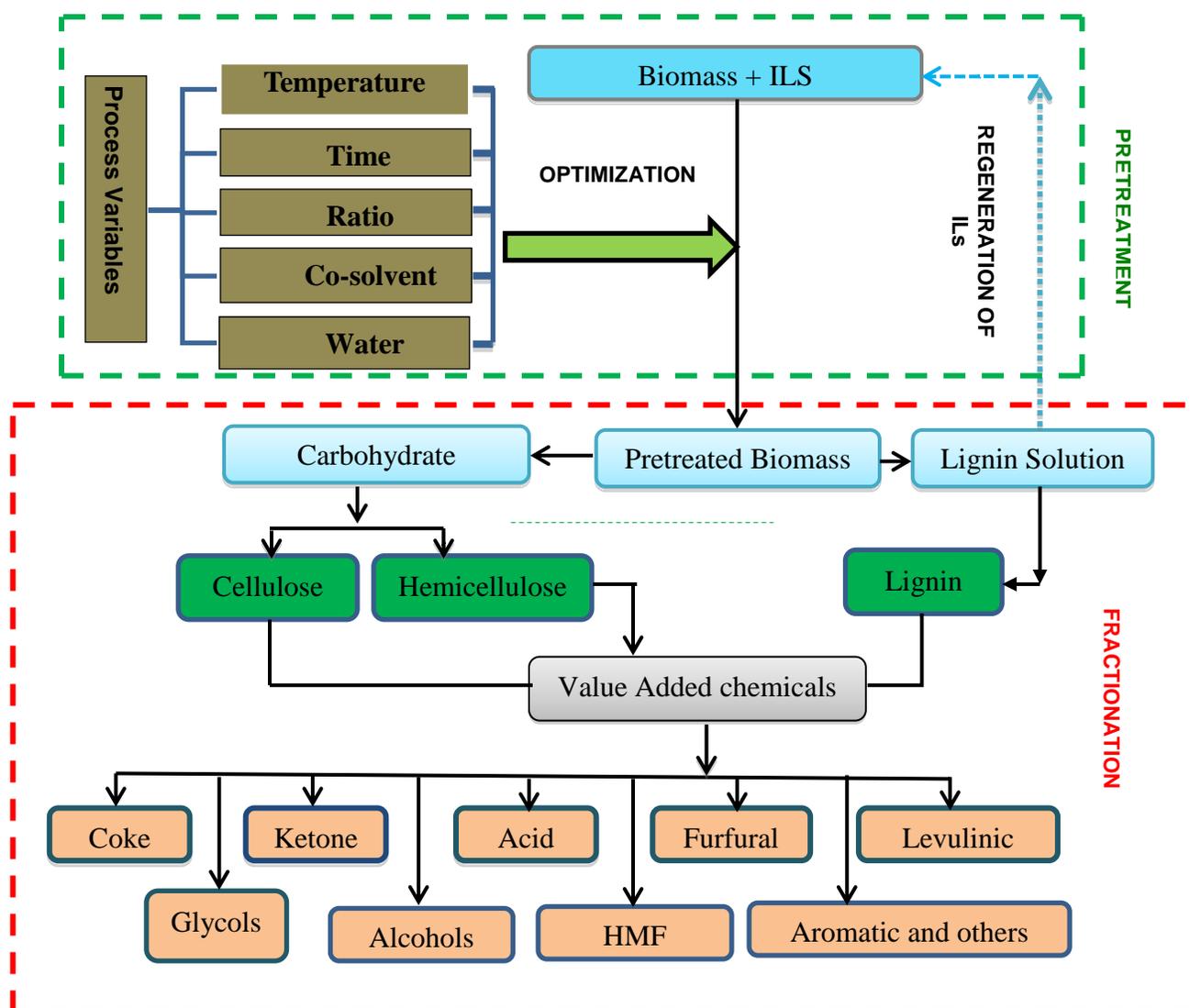


Fig. 2. Pretreatment, regeneration, and fractionation of biomass in ILs

During the regeneration process, ions of the ILs are extracted into the liquid phase through hydrogen bonding, dipolar, and columbic forces (Zavrel *et al.* 2009). In fact, water molecules form hydrodynamic shells around ions of the ILs. This consequently

disrupts the direct interactions of cations and anions of ILs with cellulose. As the intra- and inter-molecular hydrogen bonds start to rebuild, cellulose starts to precipitate (Zavrel *et al.* 2009). Bamboo (*Phyllostachys praecox* f. *preveynalis*) shoot shell (BSS) was hydrolyzed by [Bmim] [HSO₄] to obtain levulinic acid (Cunshan *et al.* 2013). Partial degradation of corn stover was carried out in IL with enhanced glucose and xylose yield. IL-pretreated sample showed a sugar yield of 78.0% at 70 °C for 24 h (Xu *et al.* 2012). Cassava pulp residue and rice straw were successfully pretreated with an ionic liquid of 1-ethyl-3-methylimidazolium acetate at 120 °C for 24 h (Weerachanchai *et al.* 2012). The effectiveness of ionic liquids for both types of samples were: 1-ethyl-3-methylimidazolium acetate > 1-ethyl-3-methylimidazolium diethyl phosphate > 1,3-dimethylimidazolium methyl sulfate. The increase of temperature from 25 to 120 °C and decrease of particle size were favorable for the overall extraction process, leading to higher sugar and lignin yield with reduced crystallinity index (Weerachanchai *et al.* 2012). Wheat straw was pretreated with the aqueous ionic liquid, 1-ethyl-3-methylimidazolium acetate, and the investigated variables were temperature (130 to 170 °C), time (0.5 to 5.5 h), and ionic liquid concentration (0 to 100%). The maximum yield was observed at optimum pretreatment conditions of 158 °C, an ionic liquid concentration of 49.5% (w/w), and time of 3.6 h (Fu and Mazza 2011). However, pretreatment of wheat straw and pinewood at 100 °C for 24 h in [Emim][CH₃COO] demonstrated incomplete dissolution properties of the solvent (Van Spronsen *et al.* 2010). At the same conditions, [Bmim][Cl] showed best results for the dissolution of straw and [Emim][Cl] was most efficient solvent for both types of biomass. Similar results were reported for dissolution of switch grass by [Emim] [CH₃COO] (Torr *et al.* 2012). Finding ILs that are good solvents, another study involved pretreatment of wheat straw with 1-ethyl-3-methylimidazolium acetate ([Emim][CH₃COO]). Significant amounts of pure carbohydrate (cellulose and hemicellulose) and lignin were obtained. Moreover, it was recovered efficiently from the reaction mixture (da Costa Lopes *et al.* 2013). Table 6 summarizes recent literature reviews regarding applications of ILs to treat different types of agricultural residues.

PHYSIOCHEMICAL PROPERTIES OF IONIC LIQUIDS (ILs)

Viscosities of Ionic Liquids

The viscosities of ILs play a vital role for dissolution of biomacromolecules (Abe *et al.* 2010). The performance of ionic liquids having low viscosities was better for extracting pure carbohydrate from bran (Abe *et al.* 2010). The researchers interpreted that in low viscosity ILs, bran dispersed easily and the polysaccharides were fractionated in a shorter period of time. Another study reported poor solubility of wood in [Bnmim][Cl] (Kilpelainen *et al.* 2007). Basically, alkylimidazolium chloride based ionic liquids have high viscosities, whereas the corresponding carboxylates, formates, and phosphonates have relatively lower viscosities. Thus microcrystalline cellulose was dissolved in 1-ethyl-3-methyl imidazolium methylphosphonate at a lower temperature as compared to 1-ethyl-3-methyl imidazolium dimethylphosphosphate (Fukaya *et al.* 2006). Despite the π - π interaction between the benzyl group of ionic liquid and phenolic group of lignin, it could not exhibit adequate solvent capacity for wood. This was attributed to its high viscosities (Kilpelainen *et al.* 2007).

Table 6. Application of Ionic liquids (ILs) for Dissolution of Agricultural Biomass

Ionic liquids (ILs)	Abbreviation	Substrate Biomass	Reaction Condition				References
			Temperature (°C)	Time (h)	Co-solvent	Anti-solvent	
1-allyl-3-methylimidazolium chloride	[Amim][Cl]	Bamboo	100	12	-	H ₂ O	Yang <i>et al.</i> 2013
		Rice hulls	90	4	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	90	8	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	110	4	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	110	8	-	H ₂ O	Lynam <i>et al.</i> 2012
1-benzyl-3-methylimidazolium chloride	[Bnmim][Cl]	Bagasse	110	4	-	Acetone/ H ₂ O (9:1 v/v)	Lan <i>et al.</i> 2011
1-butyl-3-methylimidazolium acetate	[Bmim][CH ₃ COO]	Corn Stover	140	3	-	EtOH/IL (mol/mol)	Dibble <i>et al.</i> 2011
		Rice hulls	90	4	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	90	8	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	110	4	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	110	8	-	H ₂ O	Lynam <i>et al.</i> 2012
1-hexyl-3-methylimidazolium chloride	[Hexmim][Cl]	Rice hulls	90	4	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	90	8	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	110	4	-	H ₂ O	Lynam <i>et al.</i> 2012
		Rice hulls	110	8	-	H ₂ O	Lynam <i>et al.</i> 2012

- Not available

Melting Point of Ionic Liquids

Melting points are correlated with the viscosities of ionic liquids. These two parameters are directly proportional (Mizumo *et al.* 2004). [Emim][OAc] showed better dissolution properties than [Emim]Cl and [Bmim][Cl] (Sun *et al.* 2009). At room temperature [Emim][Cl] and [Bmim][Cl] are in a solid state whereas [Emim][OAc] is in a liquid state. Therefore a higher temperature was required to melt these two aforementioned ILs in the first phase and subsequently dissolve the substrate biomass in the second phase of the reaction (Abe *et al.* 2010).

Cationic Chain Length and Type of Ionic Liquids

It was observed that a short cationic chain favors the dissolution of biopolymers. It was concluded by the researchers that a combination of bulky cations with halide ions inhibits the dissolution of both cellulose and lignin. The large size of cations lowers the tendency to form hydrogen bonds with the cellulosic matrix (Zhao *et al.* 2009). It was found that an odd number of carbons in the chain such as 1-heptyl-3-methylimidazolium chloride were quite efficient for dissolution of cellulose at 100 °C (Heinze *et al.* 2005). The presence of a branched alkyl chain in cations such as 1-butyl-3-(3,6,9-trioxadecyl)imidazolium acetate, 1-ethyl-3-(4,8,12-trioxatridecyl)imidazolium acetate, and 1-(3,6-dioxaheptyl)-3-(3,6,9-trioxadecyl)imidazolium acetate, were least efficient due to the bulkier size of the cation (Zhao *et al.* 2009).

Types of Anions

The chloride anion is a small anion with potential for cellulose dissolution. However, large, non-coordinating anions, such as PF_6^- and BF_4^- , together with Br^- and SCN^- have relatively less dissolution capacities (Abe *et al.* 2010). Br^- and I^- anions containing ionic liquid such as [Bmim][Br] and [Bmim][I] were not good solvents for cellulose (Zavrel *et al.* 2009). It was found that by using the same cations, the activity of the anions follow in the order:



Even a chloride-containing ionic liquid such as [Pmim][Cl] was found to be a poor solvent for cellulose (Erdmenger *et al.* 2007). This implies that not only anions but also the structure of cations affects the dissolution process significantly. Thus ionic liquids containing small polarizing cation with chloride anion are better choices for cellulose dissolution. The radii of different anions increase in the following order: $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{PF}_6^-$, which follows the trend of cellulose dissolution demonstrated by the ionic liquids: [Bmim][Cl] > [Bmim][I] and [Bmim][Br] (partial solubility) (Rooney and Seddon 2001). Moreover, [Bmim][PF_6] and [Bmim][BF_4] were incapable of dissolving cellulose.

Hydrogen Bond Basicity

The ILs with strong hydrogen bond basicity are more efficient for disrupting the biopolymer chains. The increased basicity of the $[\text{CH}_3\text{COO}]^-$ anions allows it to disrupt inter- and intramolecular hydrogen bonding in biopolymers (Sun *et al.* 2009). The Kamlet-Taft parameter β is an important tool to predict the efficiency of a specific IL in disrupting lignocelluloses (Brandt *et al.* 2011). $[\text{CH}_3\text{COO}]^-$ -based ILs having $\beta = 1.20$ demonstrated better efficiency than chloride based ILs having $\beta = 0.83$ for degradation of pine wood chips (Brandt *et al.* 2011). The ILs with $\beta \geq 1.0$ support higher yields of

fermentable sugars (Wu *et al.* 2011). ILs containing anions such as [Bmim][MeSO₄], [Bmim][HSO₄], and [Bmim][MeSO₃] are unable to perform complete dissolution of the biomass due to low hydrogen bond basicity (Brandt *et al.* 2011).

Functional Groups in Cations

Functional groups in the cations exhibit a key role for dissolution of biopolymers. If the cationic chain contains a hydroxyl end-group, it reduces the solubility of cellulose to a greater extent. Lower solubility of cellulose was exhibited by 1-(3,6-dioxahexyl)-3-methylimidazolium chloride and 1-(3,6,9-trioxanonyl)-3-methylimidazolium acetate than 1-(3,6-dioxaheptyl)-3-methyl-imidazolium chloride and 1-ethyl-3-(3,6,9-trioxadecyl)imidazolium acetate containing a hydroxyl-end group. A hydroxyl group in the cation can interact with acetate or chloride anions, which prevents the cellulose from forming hydrogen bonds with them (Zhao *et al.* 2009). ILs containing imidazolium groups form an extended hydrogen-bonded network where the main contribution comes from C-2 hydrogen of the imidazolium ring (Dupont and Suarez 2006, Tang *et al.* 2012). The strength of these H-bonds is more dependent on the type of anions present inside the structure. The bond strength is less influenced by the oxygen-functionalization of the side chain (Tang *et al.* 2012).

PROCESS PARAMETERS AFFECTING THE DISSOLUTION OF BIOMACROMOLECULES

Percentage Composition of Biomass and Type

Different types of biopolymers derived from lignocellulosic biomass such as grass, softwood, and hardwood possess different physiochemical properties including percentage composition of cellulose, hemicellulose, and lignin; degree of polymerization; effective surface area; and others (Wu *et al.* 2011). It was found that softwood having less density could be more easily dissolved in ionic liquids than hardwood (Kilpelainen *et al.* 2007). *Eucalyptus grandis* showed less dissolution properties in [Amim][Cl] than southern pine and Norway spruce due to its high density (Li *et al.* 2010). The treatment of pine wood chips with [Amim][Cl] gave a higher recovery percentage of cellulose than other types of wood chips such as poplar, Chinese parasol, and catalpa (Li *et al.* 2010). The above findings clearly show that for high density biomass, pretreatment with ILs need relative harsh reaction conditions such as high temperature with prolonged reaction time. Another study using oak hardwood in [Emim][CH₃COO] showed better dissolution properties than yellow pine softwood (Sun *et al.* 2009). It was inferred that the high proportion of lignin in hardwood yielded better dissolution efficiencies.

Biopolymers to Ionic Liquids Ratio

The ratio between biopolymers and ionic liquids has a strong influence on dissolution reaction, regeneration efficiency, and overall conditions required for the dissolution process. This was investigated by changing the ratio of wood chips from 4 to 10% (w/w) in [Emim][CH₃COO] at 110 °C for 16 h (Sun *et al.* 2009). The optimum ratio found was 5% (w/w). An increasing ratio of wood in [Amim][Cl] from 1 to 5% decreased the dissolution amount from 35 to 26% (Wang *et al.* 2011). When the ratio was relatively lower, the dispersion of substrate biopolymer was facilitated, leading to a higher diffusion

rate of ionic liquids. An opposite trend was observed by other researchers (Tan and Lee 2012). This might be due to an increased number of effective collisions between biomass and ionic liquid molecules. From the literature it can be concluded that optimizing the concentration of the biopolymers in ionic liquids is a challenging task, as there has to be a compromise between the opposing factors of energy demand as well as better dissolution properties with higher regeneration efficiencies.

Temperature

Increasing temperature promotes swelling and disintegration of biopolymer matrices. Higher temperature enhances the dissolution rates of lignocellulose in ILs (Sun *et al.* 2009; Wang *et al.* 2011). At high temperatures, the strong network of hydrogen bonds present in three-dimensional cellulose a structure becomes destabilized (Zavrel *et al.* 2009). However, at a relatively lower temperature, longer contact time is required for dissolution (Xie and Shi 2010). As discussed earlier, the viscosity and melting point of ionic liquids have a strong influence on the dissolution of biomass. Both of these physiochemical properties of ionic liquids are concurrently related with the temperature of the process stream. Increasing temperature decreases the viscosity of the ionic liquid, leading to enhanced swelling of the lignocellulosic particles (Tan and Lee 2012; Yoon *et al.* 2012). The ILs with short alkyl chains such as [Amim][Cl] have lower viscosity than ILs with aromatic side chains such as [Bnmim][Cl]. Literature studies reveal that ILs containing aromatic chains require a comparatively higher temperature to initiate as well as to complete the dissolution of biomass (Kilpelainen *et al.* 2007; Zavrel *et al.* 2009). Analogous phenomena have been reported for wood chips dissolution using [Amim][Cl] (Wang *et al.* 2011). It was observed that at 50 °C, the wood chips retained their original fibrous structure but swelling was observed at 70 °C, and finally at 100 °C, dissolution started in the presence of the ionic liquid solution. At 120 °C within 10 min, the fibrous structure disappeared resulting in a dark color solution. After 30 min at the same temperature, no significant change was observed. The researchers concluded that partial dissolution of wood chips could be possible after 4 h at 120 °C.

Temperature also has a significant effect on the regeneration of the biomass. It has been shown that higher temperature facilitates higher yield in regeneration (Yoon *et al.* 2012). An opposite trend also was observed in some studies of the degradation of extracted chemicals with a lower yield for regeneration of the biomass (Wang *et al.* 2011; Wu *et al.* 2011). The highest regeneration rate was observed for pine wood treated at a temperature of 120 °C with [Amim][Cl], whereas no regeneration products were isolated for catalpa treated with the same reaction conditions (Wang *et al.* 2011). A similar feature was noticed for pinewood at 140 °C, indicating complete degradation of the substrate biomass. Sugarcane bagasse was treated with [Bmim][Cl] at various temperatures (110 to 160 °C). It was observed that a temperature above 150 °C was needed to decrystallize the cellulosic matrix and increase the scarification rate to a larger extent (Kimon *et al.* 2011). It was observed that the sugar yield was increased with an increase of temperature from 110 °C to 160 °C for switch grass in the presence of ionic liquid (Arora *et al.* 2010). The sugar yield was 12 times higher than that observed at 110 °C. At higher temperatures, [Emim][CH₃COO] can disrupt the covalent linkage of acetyl groups inside the hemicellulose content of yellow poplar (Labbe *et al.* 2012). These results demonstrate that at higher temperature, ILs can effectively disintegrate the carbohydrate–lignin linkages, releasing hemicellulose.

At high temperature, lignin undergoes self-condensation reactions, resulting in precipitation of high molecular weight compounds. If the temperature is high enough, the condensed lignin starts to decompose and consequently dissolve [Baptista *et al.* 2006; El Hage *et al.* 2010]. The delignification process of sugarcane bagasse was favored by using alkyl benzene sulphonate IL ([Emim][ABS]) at temperatures from 170 °C to 190 °C (Tan *et al.* 2009). A similar trend was followed by wood flour and triticale straw using an [Emim][CH₃COO] ionic liquid (Fu *et al.* 2010). A study suggested that delignification of biomass can be carried out at average glass transition temperature of 165 °C (Shigematsu *et al.* 1994). This implies that temperature applied for the process should be adjusted to an optimum by considering the type of ionic liquids as well as the biomass type and composition. Nevertheless, application of higher temperatures than required is a major drawback for sustainable process development and is not desirable.

Time

Extended contact time facilitates extraction of lignin (Tan *et al.* 2009; Hou *et al.* 2012). A longer contact period enhances the diffusion of ILs into the pores of the biomass matrix, resulting in improved dissolution and extraction of lignin (Tan and Lee 2012). 40% of lignin was extracted from [Emim][CH₃COO]-pretreated wood flour within 5 h and more than 85% was extracted after 70 h at 90 °C. The regenerated products contained 3.2% of lignin with a cellulose-rich substrate (Lee *et al.* 2009). Similar reaction conditions were used to pretreat straw, which resulted in a recovery of 21.1% lignin within 5 h. After 24 h, 30.3% lignin was obtained (Fu *et al.* 2010). The effect of longer dissolution time was more pronounced for beech wood with higher lignin recovery percentage than for spruce wood pretreated with [Emim][CH₃COO] under identical conditions (Viell and Marquardt 2011). However, cellulose degradation is more pronounced at higher temperatures (Tan *et al.* 2011). In this context, a shorter reaction time is recommended for the process using a higher temperature. For preselecting the temperature, the stability of ionic liquids with expected side reactions should be carefully considered (Brandt *et al.* 2011). The dissolution of red oak and southern yellow pine in [Emim][CH₃COO] at 110 °C was observed for 25 and 46 h, respectively (Sun *et al.* 2009). Improved dissolution capacity was observed for a longer pretreatment time accompanied by some degradation of either the dissolved biopolymers along with platform chemicals or the IL itself (Sun *et al.* 2009; Arora *et al.* 2010). Oil palm frond was pretreated with [Bmim][Cl] at 60 to 100 °C for a shorter reaction time (Tan *et al.* 2011). The glucose recovery percentage was increased almost linearly from 26.2% to 96.7% with the increase of temperature. Another study showed that [Emim][CH₃COO] was capable of disrupting the lignocellulosic materials in a shorter period of time, resulting in a higher yield of monosaccharides (Bahcegul *et al.* 2012). The degree of crystallization (DP) of cellulose-rich materials after regeneration was also found to decrease with the increasing pre-treatment time (Sant'Ana Da Silva *et al.* 2011). The solubility of rice straw in [Emim][CH₃COO] gave a higher cellulose recovery after 24 h (Nguyen *et al.* 2010). However, after 48 h of pre-treatment, the cellulose of the rice straw converted into soluble oligosaccharides. Thus, cellulose recovery percentage was decreased (Nguyen *et al.* 2010).

Particle Size

The particle size of the biomass sample is one of the most important parameters affecting the dissolution. Smaller particle size enhances the surface area and diffusion of chemicals into the lignocellulosic materials. However, the ideal particle size of a certain biomass might vary depending on the type of the IL used (Bahcegul *et al.* 2012). For pre-treatment of cotton stalks with [Emim][CH₃COO] and [Emim][Cl], four different particle sizes (< 0.15 mm, 0.15 to 0.5 mm, 0.5 to 1.0 mm, and 1.0 to 2.0 mm) were used. It was observed that the smallest particle size (< 0.15 mm) gave the least glucose yield in [Emim][CH₃COO] solution. This might be due to extensive depolymerization reactions leading to soluble oligosaccharides. The trend was opposite for [Emim][Cl] solution, where the highest yield was achieved for larger size particles (Bahcegul *et al.* 2012). The transformation from cellulose I to cellulose II was only observed by using [Emim][CH₃COO] for the smallest particle size studied (< 0.15 mm). Another research group investigated the influence of particle size using the same IL for rice straw (Nguyen *et al.* 2010). The study was carried out with three size ranges: smaller than 2 mm, 2 to 5 mm, and larger than 10 mm. The finest particle size provided products with considerable loss of cellulose content. The glucose recovery percentage from 2- to 5-mm particle-size samples was significantly higher than that of > 10-mm particle-size samples.

The disintegration and dissolution kinetics of different particle sizes of beech and spruce wood was investigated in [Emim][CH₃COO] (Torr *et al.* 2012). The authors concluded that the dissolution process of wood is size-independent. They discovered that [Emim][CH₃COO] provided a quick disintegration of wood tissue and in that larger wood chips were better. The dissolution of wood chips (size in excess of 5 mm × 5 mm × 1 mm) in [Bmim][Cl] and [Amim][Cl] was observed and the researchers concluded that smaller particles were more suitable to be used for IL pre-treatment process (Kilpelainen *et al.* 2007).

Presence of Water

The presence of water at more than 1 wt% in ionic liquids reduces the solubility of cellulose (Swatloski *et al.* 2002). A higher percentage of water provides more water molecules that would compete with the anions of ionic liquids and inhibit the formation of chemical bonds with cellulose (Swatloski *et al.* 2002). Water in acetate- and chloride-based ionic liquids also has a negative impact on the dissolution of lignocelluloses (Doherty *et al.* 2010; Shill *et al.* 2011). However, a certain amount of water is necessary for dissolution of lignin in a [Bmim][Cl] ionic liquid (Brandt *et al.* 2011).

Role of Ionic Liquids for Degradation and Extraction of Biopolymers

Hydrolysis of biomass is an essential step to extract biopolymers from lignocellulosic residues. Some chemical processes including acid hydrolysis, enzymatic hydrolysis, and catalytic hydrolysis are frequently used for this (Huber *et al.* 2006; Chheda *et al.* 2007). To facilitate the hydrolysis mechanisms, a pretreatment process with ionic liquids can be incorporated within the overall hydrolysis process. Compared to other organic solvents, lime, mineral acids, or oxidants, ionic liquids are considered as green catalysts or an inert medium for accelerating the hydrolysis of biomass (Stephanopoulos 2007).

Acid Hydrolysis

The transformation of biomass as well as cellulose can be conducted by using mineral acid. The disposal of acidic liquids is a limitation of the process. In some cases, the super-molecular crystalline structure of cellulose prevents itself from dissolving easily in acids, resulting in slower kinetics of the process. However, application of too high a temperature and pressure in the presence of acid is detrimental to synthesis because it degrades the end products. Pretreatment of sugarcane bagasse was carried out at 130 °C for 30 min with 1-butyl-3-methylimidazolium chloride [Bmim][Cl] solution containing 1.2% HCl (Zhang *et al.* 2012). The presence of HCl with the ionic liquid was found to be more effective than H₂SO₄ or FeCl₃. Corn stalk, rice straw, pine wood, and bagasse were hydrolyzed in [Bmim][Cl] in the presence of 7 wt% hydrogen chloride at 100 °C, which resulted in higher product yield (Li *et al.* 2008). The presence of dissociated Cl⁻ and the electron-rich aromatic π system of the ionic liquids weaken the glycosidic linkage and thereby facilitate the exposure of the substrate polysaccharides to H⁺ ions of the acids (Li *et al.* 2008). Li and Zhao (2007) reported that the presence of a small amount of acid in ionic liquids can disrupt the cellulosic chain successfully within a short contact time of 42 min at 100 °C, representing a faster kinetics of the process. It was also reported by the researchers that the presence of excess acid in the ionic liquid system would be deleterious as it could initiate side reactions consuming the hydrolysis products. A recent finding showed that pretreatment of wood species in ionic liquids in the presence of mineral acids degraded a significant amount of lignin together with hydrolysis of cellulose and hemicellulose (Li *et al.* 2010). The results demonstrated that the presence of compounds such as 5-hydroxymethylfurfural, carboxylic acid, catechol, methyl catechol, methyl guaiacol, and acetoguaiacone in the reaction mixture originated from degradation of lignin (Li *et al.* 2010).

Enzyme Hydrolysis

Synthesizing an ionic liquid that dissolves cellulose along with retaining the activity of the enzymes and having low viscosity is a challenge (Zhao *et al.* 2008). Anions such as Cl⁻, CH₃COO⁻, and Br⁻ in ionic liquids tend to damage protein linkages in enzymes. High viscosity of ionic liquids inhibits enzymatic functioning. The design and synthesis of ionic liquids capable of dissolving cellulose, as well being compatible with enzymes such as cellulase have been given more priority recently (Zhao 2010). When the concentration of ionic liquid in water was higher, that is the ratio was greater than 3:2, the activity of cellulase decreased substantially. However, when the concentration of ionic liquid was reduced, enzyme activity was enhanced remarkably, resulting in a 70% yield of reducing sugar (composed of 50% glucose + 20% cellulbiose). Within 24 h, when ionic liquid to water ratio was 1:4, the reaction was completed. The glucose formation in the aqueous-ionic liquid mixture was approximately 2-times more by using the enzyme alone (Kamiya *et al.* 2008). This reflects that the structure of anions has a significant impact on the activity of cellulase. Recently the activity and stability of commercial cellulase enzymes were studied with eight ionic liquids (Bose *et al.* 2010). The study showed that the high viscosity of the ionic liquids was a retarding factor for the enzymatic hydrolysis. It slowed the diffusion of the enzyme inside the substrate polymer, resulting in slower kinetics of the process. The hydrolysis rates of wheat straw and steam-exploded wheat straw treated with [Bmim][Cl] were studied. The results demonstrated that the wheat

straw samples pretreated with [Bmim][Cl] gave 70% conversion, while those pretreated with water had only 42% conversion (Liu and Chen 2006).

Transition Metal Catalyzed Hydrolysis

Nanoparticles synthesized from some transition metals exhibit excellent catalytic activities for cellulosic substrates in the presence of ionic liquids. The ILs in the reaction medium stabilize the transition metal nanoparticles. ILs help to maintain the small size of the nanoparticles, which contributes to a large surface area. ILs prevent the nanoparticles from leaching (Zhu *et al.* 2010). The catalyst can be recycled from the ionic liquid, which makes it desirable for cellulose hydrolysis. A recent study reported the reductive depolymerization of cellulose in the presence of ionic liquids of 1-butyl-3-methylimidazolium chloride. The reduction process was carried out by using hydrogen gas and catalyzed by the combination of a heterogeneous metal catalyst and a homogeneous ruthenium catalyst (Ignatyev *et al.* 2010). 68% yield was reported for conversion of glucose to 5-hydroxymethylfurfural (HMF) in the presence of CrCl₂ in [Emim][Cl] (Zhao *et al.* 2007). Another study demonstrated that CrCl₃·6H₂O in ionic liquid was an outstanding system for HMF production from cellulose under microwave irradiation conditions (Li 2008). CuCl₂ was dissolved in 1-(4-sulfonic acid) butyl-3-methylimidazolium methyl sulfate and it was found to be efficient for dissolution of MCC to produce 69.7% HMF (Ding *et al.* 2012). A pair of metal chlorides (CuCl₂ and CrCl₂) was used as the catalysts for direct conversion of cellulose into HMF in [Emim][Cl] under mild conditions (Su *et al.* 2009). Germanium (IV) chloride had been investigated for the direct conversion of carbohydrates into HMF in [Bmim][Cl] (Zhang *et al.* 2011).

EXTRACTION OF MISCELLANEOUS BIOMACROMOLECULES

Lignin

The complex matrix of lignin contains hydroxyl, methoxyl, and carbonyl groups that impart high polarity to the macromolecule. It consists of phenyl propane building units usually having a hydroxyl group in the para position and methoxyl group in the meta position relative to the side chain. It is an environmentally benign macromolecule with unique functionalities. Traditionally, the isolation of lignin has been carried out with alkali, acid, or organic solvents (Ikeda *et al.* 2002; Wu and Argyropoulos 2003). Based on an environmental perspective, these processes are not generally considered green (Pu *et al.* 2007). In that case ionic liquids are the best choice. For the [Bmim]⁺ containing ionic liquids, the order of lignin solubility for different anions is:



This indicates that the solubility of lignin is principally influenced by the properties of the anions (Pu *et al.* 2007). Unlike cellulose, it was found that large, non-coordinating anions of [BF₄], [PF₄], and [PF₆] in ionic liquids were unsuitable as a solvent for lignin. The 1-ethyl-3-methylimidazolium cation coupled with a mixture of alkyl benzene sulfonates with xylene sulfonate was used to extract lignin from bagasse and the extraction efficiency was over 93% (Tan *et al.* 2009). Lignin extraction was efficiently done by 1-butyl-3-methyl imidazolium trifluoromethane sulfonate and 1,3-

dimethylimidazolium methyl sulphate (Lee *et al.* 2009). There are some other equally good solvents, such as 1-butyl-3-methylimidazolium methylsulfate (Pu *et al.* 2007), 1-ethyl-3-methylimidazolium acetate, and 1-allyl-3-methylimidazolium chloride that were used by previous researchers (Lee *et al.* 2009). Table 7 summarizes some recent literature regarding applications of ionic liquids to treat lignin obtained from different sources.

Protein

After successful application of ILs for treating cellulose, few investigations have been carried out for other biomacromolecules. Keratin was extracted from chicken feathers using 1-hydroxyethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) amide (Wyman *et al.* 2005). The extracted keratin was soluble in water and can be easily separated from the reaction system. Previous studies indicated that the dissolution of chitin in ionic liquids was dependent on degree of acetylation (DA), the crystallinity, and the molecular weights of chitin, as well as the nature of the anion of the ionic liquid (Wang *et al.* 2010). Chitin was dissolved in an oil bath at 110 °C in the presence of acetate- and chloride-based ionic liquids (Wang *et al.* 2010; Wu *et al.* 2008). It was reported that by using a much more basic anion in the IL, chitin could be dissolved and even extracted from crustacean shells (Wu *et al.* 2008). The extracted chitin showed high purity and retained its molecular weight (Wu *et al.* 2008). Hydrolysis of chitosan in ionic liquids was carried out under microwave irradiation. Chitosan was successfully dissolved in [Bmim][Cl] or [Bmim][Br] at 100 °C in the presence of different mineral acids. Under mild conditions, total reducing sugar (TRS) yield reached over 60% in the presence of concentrated hydrochloric acid within 7 h (Zhang *et al.* 2009). Table 8 summarizes some recent studies regarding applications of ionic liquids to treat miscellaneous biomacromolecules.

CLOSING STATEMENTS

This work provides an extensive overview of the literature regarding degradation and extraction of some commonly available biomacromolecules. A great number of researchers have concluded that ionic liquids can be synthesized by the appropriate combination of anions and cations for specific applications. Furthermore, appropriate solvent solubility that is co-dissolved with ionic liquids can be chosen to aid the overall pretreatment and extraction process. At present, a critical goal of industrial processing and chemicals procurement is based on the utilization of naturally occurring macromolecules. This can be successfully achieved by using ionic liquids. One of the greatest challenges to applying ionic liquids to large-scale industrial process is their high cost and incomplete chemical and toxicological data. In spite of their high potential for dissolution of biomacromolecules, their recovery and reuse for continuous processes design still remains a difficult task for researchers and potential industrial users. Moreover, the dissolution products must be readily isolated from the process stream; otherwise they can affect the overall performance of the process. Future research and development for macromolecules processing utilizing ionic liquids will rely on careful optimization between the cost and benefits in the industrial sector.

Table 7. Application of Ionic Liquids (ILs) for Dissolution of Lignin

Ionic liquids (ILs)	Abbreviation	Substrate Lignin	Reaction Condition		Solubility	References
			Temperature (°C)	Time		
1-allyl-3-methylimidazolium chloride	[Amim][Cl]	Kraft Lignin	90	24	> 300 g/kg	Lee <i>et al.</i> 2009
1-benzyl-3-methylimidazolium chloride	[Bnmim][Cl]	Kraft Lignin	90	24	> 100 g/kg	Lee <i>et al.</i> 2009
1-butyl-3-methylimidazolium trifluoromethane sulfonate	[Bmim][OTf]	Kraft Lignin	90	24	> 500 g/kg	Lee <i>et al.</i> 2009
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF ₄]	Kraft Lignin	90	24	1 g/kg	Lee <i>et al.</i> 2009
1-butyl-3-methylimidazolium hexafluorophosphate	[Bmim][PF ₆]	Kraft Lignin	90	24	40 g/kg	Lee <i>et al.</i> 2009
1-ethyl-3-methylimidazolium acetate	[Emim][OAc]	Kraft Lignin	90	24	> 300 g/kg	Lee <i>et al.</i> 2009
1-butyl-3-methylimidazolium methylsulfate	[Bmim][MeOSO ₃]	Soft wood lignin	50	-	312 g/L	Pu <i>et al.</i> 2007
1-butyl-2,3-dimethylimidazolium tetrafluoroborate	[Bmmim][BF ₄]	Soft wood lignin	70-100	-	14.5 g/L	Pu <i>et al.</i> 2007
1,3-dimethylimidazolium methylsulfate	[Mmim][MeOSO ₃]	Soft wood lignin	50	-	344 g/L	Pu <i>et al.</i> 2007
		Kraft Lignin	90	24	> 500 g/kg	Lee <i>et al.</i> 2009

Table 8. Application of Ionic Liquids (ILs) for Dissolution of Miscellaneous Bio Macromolecules

Types of Ionic Liquids	Abbreviations	Substrate Biopolymers	Reaction Condition		Solubility	References
			Temperature (°C)	Time (h)		
1-ethyl-3-methylimidazolium acetate	[Emim][OAc]	Chitin	100	19 h	20 wt%	Wu <i>et al.</i> 2008
1-butyl-3-methylimidazolium acetate	[Bmim][OAc]	Chitin	110	-	7 wt%	Wu <i>et al.</i> 2008
		Chitosan	110	5	10 wt%	Xie <i>et al.</i> 2006
		Chitin	110	5	10 wt%	Xie <i>et al.</i> 2006
1-butyl-3-methylimidazolium chloride	[Bmim][Cl]	Zein protein	80	-	15 wt%	Karkkainen <i>et al.</i> 2011
		Keratin	130	10	11 wt%	Xie <i>et al.</i> 2005
		Silk fibroin	100	-	13.2 wt%	Phillips <i>et al.</i> 2004
1-ethyl-3-methylimidazolium chloride	[Emim][Cl]	Silk fibroin	100	-	23.3 wt%	Phillips <i>et al.</i> 2004

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