Chapter 6
Pretreatment of Lignocellulosic Biomass Using Green Ionic Liquids

Jian Luo, Meiqiang Cai and Tingyue Gu

Abstract Bioenergy is a critical part of renewable energy solution to today's energy crisis that threatens world economic growth. Corn ethanol has been growing rapidly in the past few years. Policy-makers and researchers alike are becoming aware that corn ethanol has some serious drawbacks. It adversely impacts food prices and is harsh on soil fertility. Lignocellulosic ethanol on the other hand uses abundant lignocellulosic biomass. Various types of lignocellulosic biomass are agricultural wastes or can be grown as energy crops on poor lands that are otherwise vacant. However, lignocellulosic biomass is notoriously recalcitrant by nature's design. Enzyme hydrolysis yield for glucose from lignocellulosic is very low without proper pretreatment. Quite a few pretreatment methods have been reported in the literature. For mobile and on-farm biomass processing, a pretreatment method that uses no chemicals or green chemicals without the need for waste treatment is preferred. In recent years, research on using ionic liquids as green solvents for pretreatment of lignocellulosic biomass has exploded. Hundreds of papers have been published in the literature in the past few years alone. Some ionic liquids such as [Amim]Cl and [C_2mim]OAc have been proven highly effective in the dissolution of cellulose, lignin, and hemicellulose in different types of lignocellulosic biomass including corn stover, switchgrass, rice straw, and various hard and softwoods. This simple pretreatment method has been proven highly effective for improving sugar yields in the enzyme hydrolysis of the recovered biomass after pretreatment. Various methods have been developed for ionic liquid recycling after pretreatment. Although costly, ionic liquids hold great potential for green pretreatment of biomass as the technology improves. This chapter investigated the mechanisms and various parameters in ionic liquid pretreatment of various types of lignocellulosic biomass.

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6.1 Introduction

An integrated approach using different forms of renewable energy such as wind, solar, and biomass together with nuclear energy is necessary to supplement the shortfall caused by dwindling fossil fuel (especially petroleum) reserves. Bioethanol has seen a tremendous growth in the last few years. However, this growth cannot be sustained. Due to increased farmland use for corn ethanol, food prices have been increasing. In fact, 25-gallon of corn ethanol filled into the gas tank of a large sports utility vehicle consumes up to 450 pounds of corn. This much corn has sufficient calories to feed one person for a whole year (Runge and Senauer 2007).

Various types of lignocellulosic biomass such as corn stover, rice straw, wood, are abundantly available as agricultural wastes. They may be used as renewable feedstocks for a biorefinery that produces biofuels and chemicals. Some energy crops such as switchgrass may be planted on poor lands that are vacant. Unfortunately, lignocellulosic biomass is very recalcitrant. Without proper pretreatment, it is difficult to release fermentable sugars such as glucose using enzyme hydrolysis. The pretreatment step is often the most expensive part of a lignocellulosic ethanol process. It is critical to improve this step in order to make lignocellulosic ethanol economically competitive.

Chapter 1 in this book discussed cell wall structures and chemical components. Typical lignocellulosic biomass contain lignin (15–25 % w/w), hemicellulose (23–32 %), and cellulose (38–50 %) (Mamman et al. 2008). Cellulose is a glucan biopolymer containing glucopyranose subunits with a molecular formula of $(C_6H_{10}O_5)_n$. Upon hydrolysis, each subunit gains one H_2O molecule. Thus, the maximum theoretical glucose yield for 100 g pure cellulose is 111 g. The glucopyranose subunits in the cellulose are linked by β-1,4-glycosidic bonds that are highly resistant to hydrolysis. Apart from this, enzyme hydrolysis is greatly hindered by the crystallinity of cellulose and the protective sheath of lignin and hemicellulose that wrap around cellulose (Laureano-Perez et al. 2005). An effective pretreatment method can weaken all these hindrances and exposes cellulose to cellulase enzymes for effective hydrolysis. Alizadeh et al. (2005) reported that only less than 20 % glucose is released from lignocellulosic biomass without pretreatment while the yield can be as high as 90 % with proper pretreatment. However, pretreatment is often expensive. It constitutes 20 % of the overall process cost for lignocellulosic ethanol (Yang and Wyman 2008). Thus, it is imperative to improve pretreatment methods.

Many types of lignocellulosic biomass such as corn stover and switchgrass are bulky and costly to transport on a mass basis to a central processing facility. Thus, it is desirable in some situations to use mobile (tactical) or on-farm processing to eliminate the need for biomass transportation. It is possible to integrate pretreatment, enzyme hydrolysis, fermentation, and ethanol fermentation and separation to produce fuel ethanol on farms where certain types of lignocellulosic biomass are abundant.

It can be economical even at relatively small scales to supply such fuels when the local supplies are unusually expensive, such as in some military forward operating bases.

Many pretreatment methods have been proposed for lignocellulosic biomass. They include mechanical pretreatment, biological pretreatment, acid and alkaline pretreatment, steam explosion pretreatment, (supercritical) hot water pretreatment, ammonia pretreatment, supercritical CO_2 explosion pretreatment and ionic liquid pretreatment (Zheng et al. 1995; Teymouri et al. 2004; Alizadeh et al. 2005; Lloyd and Wyman 2005; Mosier et al. 2005; Kim and Lee 2007; Hendriks and Zeeman 2009; Wan and Li 2010; Karunanithy and Muthukumarappan 2011; Narayanaswamy et al. 2011; Wang et al. 2012). Among the chemical pretreatment methods, CO_2 and ionic liquids are considered green treatment methods because CO_2 and ionic liquids are green solvents. Chapter 5 in this book discussed CO_2 pretreatment in depth already.

The three major components in lignocellulosic biomass (lignin, hemicellulose, and cellulose) are biopolymers in an organized network that are considered insoluble because they cannot be dissolved in common solvents. If a special solvent that is able to dissolve any of the three components, it would weaken the biomass structure and makes the biomass less recalcitrant for enzyme hydrolysis. Ionic liquids are such solvents that can be used in the pretreatment step to achieve some or all of the following objectives that help to reduce the biomass recalcitrance: (1) Amorphization of cellulose, (2) delignification, and (3) deacetylation of hemicellulose.

Ionic liquids are a special group of organic salts that can exist in liquid form at relatively low temperatures (less than 100 °C) and some can even exist as liquids at room temperature (Cull et al. 2000; Marsh et al. 2004; Zhu et al. 2006). They are usually molten salts or oxides (Marsh et al. 2004). Thus, they have much higher viscosities (similar to those for oils) than conventional organic solvents and most of them are heavier than water (Marsh et al. 2004). Ionic liquids are special solvents that can dissolve chemical compounds that are otherwise considered insoluble in conventional solvents. Figure 6.1 shows the complete dissolution of tiny wood chips with the ionic liquid [C_2mim]OAc.

Typically in ionic liquids, the cations are organic while the anions may be inorganic or organic (Marsh et al. 2004; Wang et al. 2012). Some common cations and anions for ionic liquids used for biomass dissolution are listed in Table 6.1. Ionic liquids have found applications in many different areas, such as analytical chemistry (Baker et al. 2005; Han and Armstrong 2007), chemical reactions including biotransformation reactions (Cull et al. 2000; Sun et al. 2011), extractive separations of metal ions, proteins and other organic molecules (Huddleston and Rogers 1998; Han and Armstrong 2007), and lignocellulosic biomass pretreatment and processing (Zhu et al. 2006; Wang et al. 2012). Chemical compounds extracted or dissolved in ionic liquids may be recovered by using an antisolvent such as water, ethanol, acetone, or even supercritical CO_2 (Blanchard and Brennecke 2001; Zhu et al. 2006).

Graenacher (1934) was the first to file a patent on the use of an ionic liquid for cellulose dissolution. He claimed to have used molten N-ethylpyridinium chloride (an ionic liquid) in the presence of nitrogen-containing bases to dissolve cellulose without derivation. Not enough attention was paid to this kind of application because there was no great push for cellulosic ethanol and green chemistry at the time. Although some of the claims in the patent were found to be inaccurate by Sun et al. (2011), Graenacher was

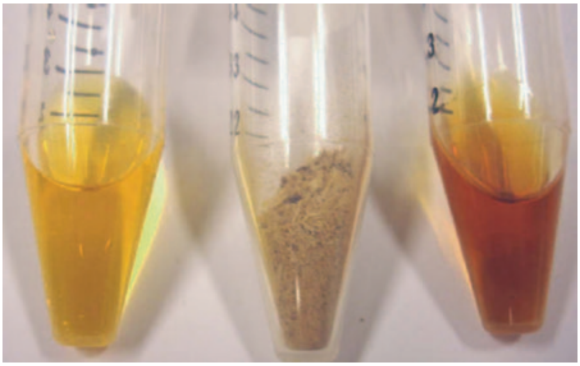


Fig. 6.1 Dissolution of tiny wood chips from common beech in an ionic liquid (*left*: blank [C_2mim]OAc; *middle*: wood chips from common beech; *right*: a homogeneous ionic liquid solution after dissolution) (Reprinted from Bioresource Technology, 100/9, High-throughput screening for ionic liquids dissolving (ligno-)cellulose, Michael Zavrel, Daniela Bross, Matthias Funke, Jochen Büchs, Antje C. Spiess, 8, Copyright 2009, with permission from Elsevier)

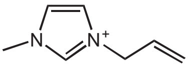
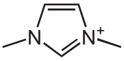
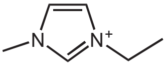
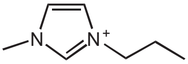
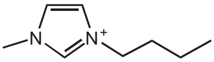
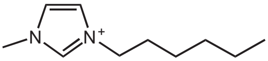
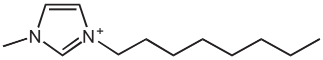
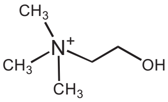
still considered the first person who brought up the use of ionic liquids for cellulose dissolution. It was Swatloski et al. (2002) who ignited this research area by publishing a widely cited study in 2002 on the use of ionic liquids for dissolution of pulp cellulose. They also showed that cellulose dissolved in ionic liquids could be precipitated using water. There has been an explosion in the number of publications dealing with ionic liquid pretreatment in the past few years. Dozens of ionic liquids are found to dissolve cellulose (Shill et al. 2011; Wang et al. 2012). The dissolved cellulose can be recovered and hydrolyzed using enzymes with much higher glucose yields. Research in this area was also expanded to raw biomass containing lignin and hemicellulose in addition to cellulose that was used as a model biomass for early investigations in its essentially pure form (e.g., Avicel, microcrystalline cellulose, and pulp cellulose). Many ionic liquids are found to dissolve lignin and hemicellulose as well (Lee et al. 2009; Zavrel et al. 2009; Fu et al. 2010; Casas et al. 2012; Lynam et al. 2012; Xin et al. 2012). By removing lignin and hemicellulose, enzyme hydrolysis of cellulose can also be improved greatly.

This chapter investigated the mechanisms for ionic liquid pretreatment and discusses various key operating parameters involved in the ionic liquid pretreatment of different types of lignocellulosic biomass. An emphasis is placed on how ionic liquid could be used for green mobile or on-farm pretreatment.

6.2 Mechanisms for Ionic Liquid Dissolution of Biomass

Swatloski et al. (2002) proposed that the high Cl^- concentration and activity in an ionic liquid such as [C_4mim]Cl can effectively break the extensive network of intra- and intermolecular hydrogen bonds in cellulose, thus allowing cellulose

Table 6.1 Some common cations and anions in ionic liquids used in biomass dissolution

Type	Formula	Structure	Full name
Cations	$[Amim]^+$		1-allyl-3-methylimidazolium
	$[C_1mim]^+$, $[Mmim]^+$		1,3-dimethylimidazolium
	$[C_2mim]^+$, $[Emim]^+$		1-ethyl-3-methylimidazolium
	$[C_3mim]^+$,		1-propyl-3-methylimidazolium
	$[C_4mim]^+$, $[Bmim]^+$		1-butyl-3-methylimidazolium
	$[C_6mim]^+$, $[Hmim]^+$		1-hexyl-3-methylimidazolium
	$[C_8mim]^+$		1-octyl-3-methylimidazolium
	$[Cholinium]^+$		2-hydroxy-N,N,N-trimethylethanaminium
Anions	Cl^-		Chloride
	CH_3COO^- (OAc^-, Ac^-)		Acetate
	$HCOO^-$		Formate
	$(C_2H_5O)_2(PO_2)^-$ (DEP)		Diethyl phosphate
	Gly^-		Glycine
	Lys^-		Lysine

dissolution in the ionic liquid. For example, decreased Cl^- concentrations (e.g., when using $[C_6mim]Cl$ and $[C_8mim]Cl$ instead of using $[C_4mim]Cl$) led to lower cellulose solubility in the ionic liquids. They also observed a significant impairment of cellulose solubility by adding as little as 1 wt% water in the ionic liquid, suggesting that competitive hydrogen bonding of water with cellulose was likely to blame for the impairment. This effect also means that water can be used to precipitate cellulose from ionic liquids. The NMR data presented by Remsing et al. (2006)

confirmed that the solvation of cellulose by [C_4mim]Cl had a 1:1 molar ratio for hydrogen-bonding between Cl^- anions in the ionic liquid and the hydroxyl hydrogen atoms in cellulose polymer. Figure 6.2 shows a schematic presentation of solvation mechanism of cellulose using [C_4mim]Cl as an example.

Some other anions that are good hydrogen bond acceptors such as OAc^-, $HCOO^-$ and $(C_2H_5O)_2(PO_2)^-$ have also been found effective for cellulose dissolution in ionic liquids. Acetate anion (OAc^-) is considered more effective than chloride anion (Wang et al. 2012). Zhang et al. (2010) presented NMR data that suggested that acetate anions in [C_2mim]OAc formed hydrogen bonds with the hydroxyl hydrogen atoms in cellobiose that is the repeating subunit in cellulose. They found that acetylation of the hydroxyl groups in cellobiose led to weakened solvation of cellobiose by [C_2mim]OAc. NMR and solvatochromic studies of microcrystalline cellulose dissolution in ionic liquids containing [C_4mim]$^+$ cation paired with Brønsted basic anions $[CH_3COO]^-$, $[HSCH_2COO]^-$, $[HCOO]^-$, $[(C_6H_5]COO]^-$, $[H_2NCH_2COO]^-$, $[HOCH_2COO]^-$, $[CH_3CHOHCOO]^-$ and $[N(CN)_2]^-$ carried out by Xu et al. (2010) showed that cellulose solubility increased nearly linearly with the anion's hydrogen-bonding accepting ability. They also found that pretreatment temperature had a major impact on cellulose solubility in the ionic liquids. Molecular dynamics simulation supported the NMR observation of hydrogen bonding between cellobiose's hydroxyl hydrogen atoms with Cl^- anions in [C_4mim]Cl (Novoselov et al. 2007), and between cellulose's hydroxyl hydrogen atoms and OAc^- anions in [C_2mim]OAc (Liu et al. 2010). Ionic liquids containing anions that are low basicity anions such as BF_4^- or PF_6^- were found ineffective for cellulose dissolution (Swatloski et al. 2002). It should be pointed out that some ionic liquids such as those containing [PF_6] and [BF_4] anions also have a tendency to decompose (Marsh et al. 2004).

Experimental results (Wang et al. 2012) and molecular dynamics simulation (Liu et al. 2010) seem to suggest that cations in ionic liquids also play a role in solvation of cellulose. It was found that [C_2mim]Cl, [C_4mim]Cl and [C_6mim]Cl had good solubility for cellulose while [C_3mim]Cl and [C_5mim]Cl had almost no solubility and a low solubility, respectively. Wang et al. (2012) speculated that such disparities in cellulose solubility might be because cations played a role in solvating and dispersing the anionic hydrogen bonded cellulose•Cl_n moieties. Based on molecular dynamics simulation results, Liu et al. (2010) suggested that hydrophobic interactions between imidazolium cations in ionic liquids and glucopyranose subunits in the cellulose polymer play an important role in cellulose dissolution. The roles of cations are still somewhat controversial. More investigative work is needed (Sun et al. 2011; Wang et al. 2012).

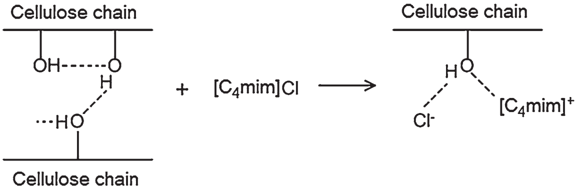


Fig. 6.2 Possible mechanism for cellulose dissolution in [C_4mim]Cl (Adapted from Feng and Chen 2008)

When any of the three components in lignocellulosic biomass (cellulose, hemicellulose, and lignin) is dissolved in an ionic liquid, the extensive network within plant cell wall is disrupted. This reduces recalcitrance of the biomass. The cellulose regenerated after the pretreatment tends to be more amorphous in its macrostructure and thus is easier for enzyme hydrolysis (Wang et al. 2012). Cheng et al. (2011) studied the cellulose crystallinity transition and surface morphology of Avicel, switchgrass, pine wood, and eucalyptus wood after $[C_2mim]OAc$ pretreatment at 120 and 160 °C for 1–12 h. The pretreatment resulted in the loss of native cellulose crystalline I structure. Avicel was easier to transform into the cellulose II structure than switchgrass and eucalyptus, while the cellulose II structure was not detected for pine after 12 h at 160 °C. Singh et al. (2009) visualized switchgrass dissolution in $[C_2mim]OAc$ through confocal fluorescence images and found that in 2 h the ionic liquid completely broke down the organized cell wall structure (Fig. 6.3). Their analysis of SEM images of switchgrass before and after the pretreatment indicated that there was no lignin accumulation in pretreated and regenerated cellulose (Fig. 6.4).

Ionic liquid pretreatment of biomass has gone far beyond the initial intention of just dissolving cellulose. Lignin and hemicellulose can also be selectively dissolved in some ionic liquids, thus providing more options for pretreatment of lignocellulosic biomass. Liu et al. (2012) synthesized a series of ionic liquids containing cholinium cation paired with different amino acids as the anion. They found that [Cholinium]Gly pretreatment of rice straw improved enzyme hydrolysis yield of glucose by several folds due to lignin removal by the ionic liquid, which was found to have a high lignin solubility of 220 mg/g and a low cellulose solubility of less than 5 mg/g at 90 °C. Lee et al. (2009) found that when 40 % of the lignin in wood flour was dissolved in $[C_2mim]OAc$, the crystallinity of the cellulose component was much reduced without cellulose dissolution in the ionic liquid. This led to greater than 90 % cellulose hydrolysis by *Trichoderma viride* cellulase. They noticed that when a type of lignin had a similar Hildebrand solubility parameter as that for the ionic liquid used for its dissolution, the lignin solubility was high because solubility of polymers in solvents could be predicted by the Hildebrand solubility parameter. For $[C_1mim][MeSO_4]$ and $[C_4mim][CF_3SO_3]$, lignin solubility greater than 0.5 kg/kg ionic liquid were observed by Lee et al. (2009). These ionic liquids have low solubility for cellulose and hemicellulose and the regenerated lignin after dissolution was chemically unaltered. Apart from using cellulose to yield glucose for bioethanol production, lignin can be used as a renewable chemical feedstock for many other applications (Lee et al. 2009). Tan et al. (2009) successfully extracted lignin from bagasse using an ionic liquid consisting of $[C_2mim]^+$ cation and a mixture of alkylbenzenesulfonates and xylenesulfonate anions. The dissolved lignin was subsequently separated from dissolved cellulose using aqueous sodium hydroxide. Fort et al. (2007) demonstrated that $[C_4mim]Cl$ could dissolve woods with different hardness for further processing. Lignin extraction from biomass using an ionic liquid containing chloride anion requires a virtual absence of water moisture in biomass and the ionic liquid, and an inert atmosphere (Tan and MacFarlane 2010; Shill et al. 2011). It was suggested that lignin dissolution was facilitated by the π–π interactions between the cation and the lignin (Shill et al. 2011).

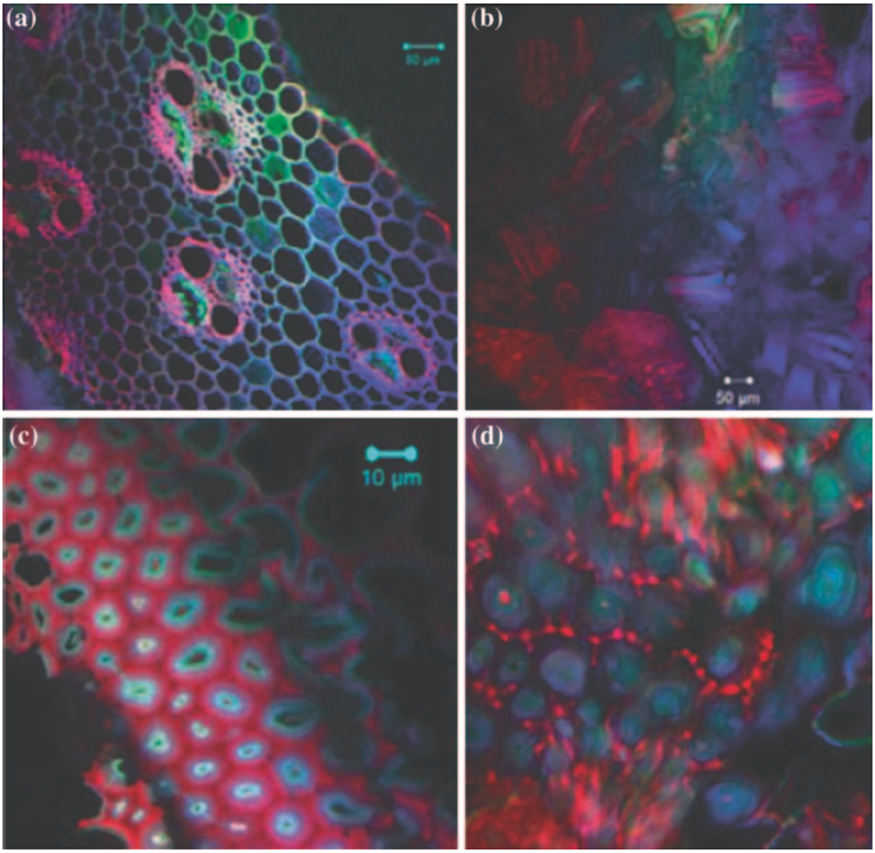


Fig. 6.3 Confocal fluorescence images of switchgrass stem section before and after [C$_2$mim]OAc pretreatment: **a** before pretreatment, **b** after 20 min pretreatment, **c** after 50 min pretreatment, and **d** after 2 h pretreatment. (Reprinted from Biotechnology and Bioengineering, Visualization of biomass solubilization and cellulose regeneration during ionic liquid pretreatment of switchgrass, Seema Singh, Blake A. Simmons, Kenneth P. Vogel,104:68–75, Copyright 2009, with permission from John Wiley and Sons)

Lynam et al. (2012) found that pretreatment of rice hulls at 110 °C for 8 h in [C$_2$mim]OAc dissolved 100 % of lignin and up to 29 % hemicellulose, but it was ineffective in dissolving cellulose. However, [Amim]Cl under the same conditions dissolved 33 % cellulose and 75 % hemicellulose. For [C$_6$mim]Cl, the numbers were 23 and 70 %, respectively. Both [Amim]Cl and [C$_6$mim]Cl were ineffective in dissolving lignin. The impact of ionic liquid pretreatment on hemicellulose was studied using NMR by Çetinkol et al. (2010), who observed deacetylation of hemicellulose when *Eucalyptus globules* biomass was dissolved in [C$_2$mim]OAc, leading to enhanced release of xylose during saccharification. They also found that the syringyl to guaiacyl ratio in lignin increased after the pretreatment and there was possible acetylation of β-aryl ether linkages in lignin.

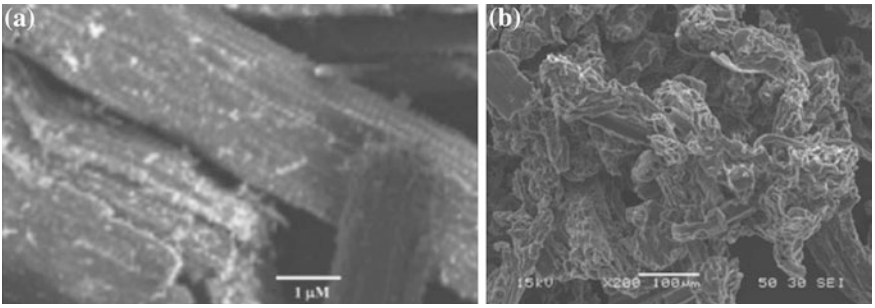


Fig. 6.4 SEM images of untreated (**a**), and ionic liquid treated and recovered switchgrass fibers (**b**). (Reprinted from Biotechnology and Bioengineering, Visualization of biomass solubilization and cellulose regeneration during ionic liquid pretreatment of switchgrass, Seema Singh, Blake A. Simmons, Kenneth P. Vogel, 104:68–75, Copyright 2009, with permission from John Wiley and Sons)

Ionic liquid pretreatment is comparable to other mainstream pretreatment methods in sugar yields, but it requires no harsh operating conditions such as high temperature and high pressure. The maximum sugar conversion could reach 90.0 % (w/w) based on regenerated biomass from cassava pulp residue treated with [C_2mim]OAc at 120 °C for 24 h (Weerachanchai et al. 2012). Xu et al. (2012) reported that after [C_2mim]OAc pretreatment of corn stover at a relatively low pretreatment temperature of 70 °C for 24 h, they achieved glucose, xylose and total sugar yields of 84.9, 64.8, and 78.0 %, respectively, which are comparable to the yields of 82.0, 72.2, and 78.4 % obtained using the Ammonia Fiber Expansion (AFEX) pretreatment method by Li et al. (2011a, b) as shown in Fig. 6.5. These were achieved when corn stover was not completely dissolved in the ionic liquid. Another group of researchers compared dilute acid pretreatment with ionic liquid pretreatment of switchgrass experimentally (Li et al. 2010). For ionic liquid pretreatment, they used [C_2mim][OAc] at 160 °C for 3 h. For dilute acid pretreatment, the switchgrass sample was presoaked at room temperature in 1.2 % (w/w) sulfuric acid for at least 4 h before the reactor temperature was raised to 160 °C for 20 min. Figure 6.6 shows that yields of different sugars including glucose and xylose after enzymatic saccharification were slightly lower for ionic liquid pretreatment.

Many factors impact ionic liquid pretreatment of biomass. They include ionic liquid type, ionic liquid to biomass mass ratio, pretreatment time and temperature, and water content, etc. These factors are discussed in the sections below.

6.3 Selection of Ionic Liquids

Clearly, there are several possible basic strategies for ionic liquid pretreatment of lignocellulosic biomass: (1) Dissolve cellulose in processed cellulose material such as pulp cellulose in an ionic liquid, (2) remove lignin (and hemicellulose) by

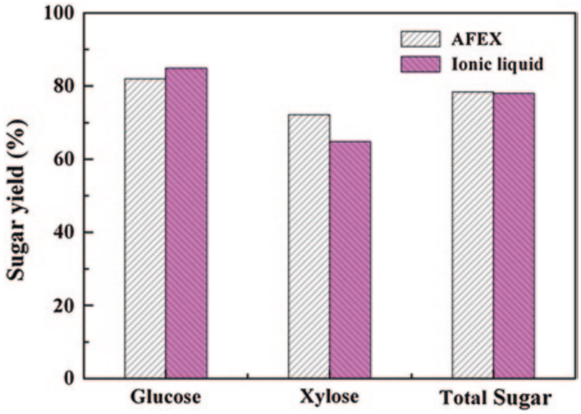


Fig. 6.5 Enzyme hydrolysis sugar yields from corn stover with pretreatment using [C_2mim]OAc at 70 °C for 24 h compared with those with pretreatment using AFEX (Figure plotted with data from Xu et al. 2012)

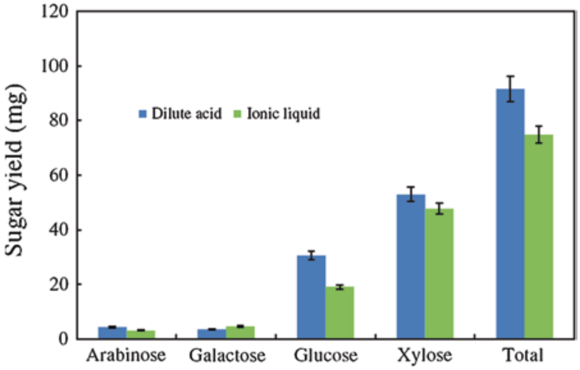


Fig. 6.6 Various enzyme hydrolysis sugar yields from switchgrass pretreated in an ionic liquid compared with those with pretreatment using dilute acid. (Reprinted from Bioresource Technology, 101/13, Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification, and enzymatic saccharification, Chenlin Li, Bernhard Knierim, Chithra Manisseri, Rohit Arora, Henrik V. Scheller, Manfred Auer, Kenneth P. Vogel, Blake A. Simmons, Seema Singh, 4900–4906, Copyright 2010, with permission from Elsevier)

dissolving the lignocellulosic biomass in an ionic liquid while leaving cellulose behind, and (3) dissolve all the biomass components and then selectively recover the needed component(s). Table 6.2 shows some ionic liquids that have been used for lignocellulosic biomass pretreatment in the literature.

An effective ionic liquid for cellulose dissolution in biomass pretreatment should satisfy the following three criteria: (1) Its anion is a good hydrogen bond acceptor; (2) its cation should be a moderate hydrogen bond donator, and (3) its cation should not be too bulky (Fukaya et al. 2008; Mäki-Arvela et al. 2010; Feng and Chen 2008).

From the perspective of process engineering, a good ionic liquid for cellulose dissolution should have high cellulose solubility, low melting point, low viscosity, good stability, and low toxicity (Sun et al. 2011). Experimental data suggest that with the same cation, the decreasing order for cellulose solubility for different anions is: $(CH_3CH_2O)_2PO_2^- \approx OAc^- > SHCH_2COO^- > HCOO^- > Cl^- > Br^- \approx SCN^-$ (Swatloski et al. 2002, Klemm et al. 2005). The most effective cations for cellulose dissolution are found to be those based on the methylimidazolium and methylpyridinium cores, and contain allyl-, methyl-, ethyl-, or butyl- side chains (Wang et al. 2012). Some ionic liquids can be used to remove lignin from biomass while leaving behind cellulose. For example, [C_2mim]OAc removes lignin from triticale (a hybrid of wheat and rye) straw efficiently at 70–150 °C in 1.5 h with some hemicellulose removal, but little removal of cellulose (Fu et al. 2010).

The cost of ionic liquid is another important factor in the selection of an ionic liquid for pretreatment. Table 6.3 shows published research chemical prices at www.sigmaaldrich.com in August 2012. The prices may only be used to compare relative prices because large-scale prices will be much lower. Some ionic liquids are about

Table 6.2 Some ionic liquids used in lignocellulosic biomass pretreatment

Ionic Liquid	Biomass	Dissolved components	References
[Amim]Cl	Southern pine TMP	All[a]	Kilpeläinen et al. (2007)
	Avicel cellulose	All	Zhao et al. (2009)
	Corn stalk	All	Li et al. (2008)
	Rice hull	Hemicellulose and some cellulose	Lynam et al. (2012)
[C_2mim]Cl	Avicel	Cellulose	Erdmenger et al. (2007)
[C_4mim]Cl	Pine, poplar, oak, and eucalyptus	All	Fort et al. (2007)
	Pulp cellulose	Cellulose	Swatloski et al. (2002)
	Bagasse	All	Lan et al. (2011)
	Corn stalk and rice straw	All	Li et al. (2008)
[C_6mim]Cl	Corn stalk	All	Li et al. (2008)
	Rice hull	Hemicellulose and some cellulose	Lynam et al. (2012)
[C_2mim]OAc	Softwood and hardwood	All	Sun et al. (2009)
	Triticale straw	Lignin (and a little hemicellulose)	Fu et al. (2010)
	Bagasse and southern yellow pine	All	Li et al. (2011b)
[C_4mim]OAc	Microcrystalline cellulose	Cellulose	Zhao et al. (2008)
	Poplar sawdust	All	Vo et al. (2011)
[C_4mim]HCOO	Avicel cellulose	Cellulose	Zhao et al. (2008)
[C_2mim]DEP	Cassava pulp residue, rice straw	All	Weerachanchai et al. (2012)
[Cholinium]Gly	Rice straw	All	Hou et al. (2012)
[Cholinium]Lys	Rice straw	All	Hou et al. (2012)

[a] Cellulose, hemicellulose, and lignin can all be dissolved

Table 6.3 Prices for some ionic liquids used in lignocellulosic biomass pretreatment

Ionic Liquid	Prices (US$/g)	Comment
[Amim]Cl	19.14	Based on 5 g purchase
[Amim]Br	25.60	Based on 5 g purchase
[C_2mim]Cl	31.80	Based on 5 g purchase
[C_4mim]Cl	11.86	Based on 5 g purchase
[C_2mim]OAc	7.04	Based on 5 g purchase
[C_4mim]OAc	2.70	Based on 100 g purchase
[Cholinium]Cl	18.58	Based on 5 g purchase

5–20 times more expensive than conventional solvents for laboratory applications (Plechkova and Seddon 2008). This is because their synthesis and purification costs are much higher. As ionic liquid applications are expanding, their costs will certainly be more affordable in the future. This may shift biomass loading that is also a key parameter in the selection of ionic fluids for pretreatment (Sect. 6.4).

6.4 Biomass Loading

Biomass loading largely depends on the biomass solubility in the particular ionic liquid at the operating temperature and the biomass dissolution rate that influences pretreatment time. Because the time requirement can be excessively long, thermodynamic solubility limit may not be reached during the given pretreatment time. Thus, the ionic liquid to biomass mass ratio should be substantially higher than the solubility limit. A smaller biomass particle size typically means faster biomass dissolution rate. Microwave and ultrasound can also be used to accelerate biomass dissolution (Ha et al. 2011; Wang et al. 2012).

Table 6.4 shows that researchers typically use a nominal biomass loading ratio of 20/1–30/1 (g ionic liquid/g biomass) in ionic liquids pretreatment of various types of biomass under different temperature and time conditions. In comparison, a ratio of 10/1 (g liquid/g biomass) is common for aqueous ammonia, acid hydrolysis, supercritical CO_2, and hydrothermal pretreatment methods (Narayanaswamy 2010; Garrote et al. 1999). It should be noted that if the biomass concentration reaches 10 % (w/w), the ionic liquid solution is almost always very viscous, which makes it difficult to process (Laus et al. 2005). Thus, viscosity could be a limiting factor rather than biomass solubility in a practical pretreatment process.

6.5 Pretreatment Temperature

Apart from selecting a suitable ionic liquid for desired biomass pretreatment outcome, pretreatment temperature is the most important operating parameter (Schultz et al. 1983; Yu et al. 2010). A higher temperature typically achieves higher biomass solubility and shortens the pretreatment time. It reduces the biomass recalcitrance better. However, it also means higher energy input. Compared with steam explosion

Table 6.4 Selected data on ionic liquid (IL) pretreatment conditions and biomass dissolution

Biomass	IL	T(°C)	t(h)	IL/ biomass (g/g)	Biomass dissolved (wt%)	References
Southern pine powder	[Amim]Cl	80	8	NM[a]	8	Kilpeläinen et al. (2007)
Wood flour	$[C_2mim]OAc$	90	1.5	20/1	17	Lee et al. (2009)
Rice straw	[Cholinium]Gly	90	24	20/1	48.4	Hou et al. (2012)
Triticale straw	$[C_4mim]Cl$	90	24	20/1	23.1	Fu et al. (2010)
Southern yellow pine	$[C_2mim]OAc$	110	16	20/1	98.2	Sun et al. (2009)
Southern yellow pine	$[C_4mim]Cl$	110	16	20/1	52.6	Sun et al. (2009)
Norway spruce sawdust	$[C_4mim]Cl$	110	8	NM[a]	8	Kilpeläinen et al. (2007)
Southern pine TMP	[Amim]Cl	130	8	NM[a]	5	Kilpeläinen et al. (2007)
Sugarcane bagasse	[Amim]Cl	140	1	32/1	40.4	Zhu et al. (2012)
Triticale straw	$[C_2mim]OAc$	150	1.5	20/1	48.8	Fu et al. (2010)
Corn stover	$[C_2mim]OAc$	160	3	32/1	53.3	Li et al. (2011a, b)
Switchgrass	$[C_2mim]OAc$	160	3	32/1	49.3	Li et al. (2010)
Wheat straw	$[C_2mim]OAc$	162	4.5	20/1	57.6	Fu and Mazza (2011)
Cassava pulp	$[C_2mim]DEP$	180	24	20/1[b]	88	Weerachanchai et al. (2012)

[a] NM: not mentioned

[b] This special case used 20 ml ionic liquid/1 g biomass

and hot water pretreatment methods, the required pretreatment temperature for ionic liquid pretreatment is relatively mild with a typical temperature range of 80–180 °C (Table 6.4). This is comparable to the typical temperature range used in supercritical CO_2 explosion pretreatment discussed in Chap. 5, but ionic liquid pretreatment does not require pressurization, which is needed by supercritical CO_2. Compared with the typical 140–250 °C temperature range used in steam explosion pretreatment and hot water pretreatment (Schultz et al. 1983; Kaar et al. 1998; Kim and Hong 2001; Yu et al. 2010), ionic liquid has a major advantage. Typically, the upper-end temperature in the temperature ranges is required for the desired pretreatment outcome. Thus, ionic liquid pretreatment enjoys a much lower optimal temperature. This also means that pyrolysis side reaction is easier to avoid when using ionic liquid pretreatment compared with steam or hot water pretreatment.

Fu et al. (2010) treated triticale straw for 1.5 h in [C_2mim]OAc at temperatures ranging from 70–150 °C, and then conducted enzyme hydrolysis of residual biomass using *Trichoderma reesei* cellulase at 50 °C. They found that [C_2mim]OAc removed little cellulose, but removed lignin efficiently from triticale straw and this reduced the recalcitrance of the remaining cellulose. Figure 6.7 shows that the pretreatment improved cellulose hydrolysis sugar yield greatly and the pretreatment temperature had a strong effect. Higher temperature resulted in better lignin removal and cellulose hydrolysis yield. Complete cellulose hydrolysis (with a hydrolysis time of 11 h) required a pretreatment temperature of 150 °C with a pretreatment time of 1.5 h.

Li et al. (2009) pretreated wheat straw with 1-ethyl-3-methylimidazolium diethyl phosphate ([C_2mim]DEP) for 1 h at various temperatures from 25 to 150 °C. Cellulose was precipitated by adding water to the ionic liquid after biomass dissolution. The regenerated cellulose was then hydrolyzed using cellulase. Their data in Fig. 6.8 suggest that 70 °C pretreatment temperature showed no improvement over 25 °C, while 100 °C had a big improvement in reducing sugar yield. Further increasing the pretreatment temperature until 130 °C continued to improve the yield, but increasing the pretreatment temperature from 130 to 150 °C had only a small improvement, indicating that 130 °C could be used as the optimal pretreatment temperature. For lignin removal from rice straw using [Cholinium]Lys, Hou et al. (2012) found that 90 °C pretreatment for 24 h provided the highest glucose yield of 87.7 % after hydrolysis, while 110 and 130 °C actually reduced the yield to 77.1 and 77.2 %, respectively, due to prolonged exposure to the high temperatures. Their data also indicated that 70 °C provided the highest xylose yield of 38.7 %. These relatively low optimal temperatures were partially the result of a rather long pretreatment time of 24 h.

Pezoa et al. (2010) pretreated corn stover with [C_2mim]Cl at different temperatures for 60 min. The ionic liquid weakened the biomass by removing lignin while dissolving less than 10 % cellulose. They measured the various sugars released

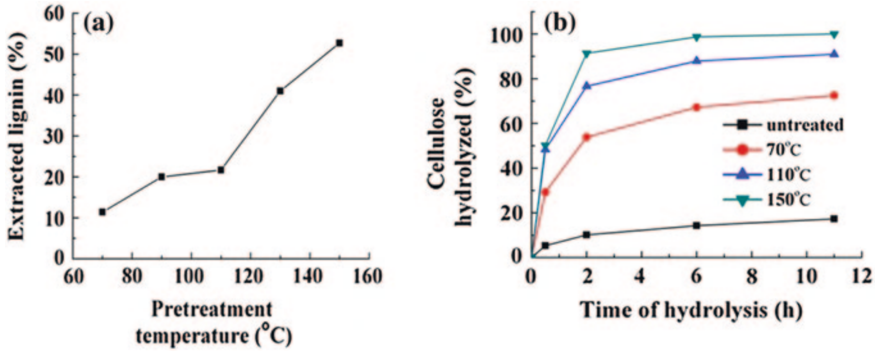
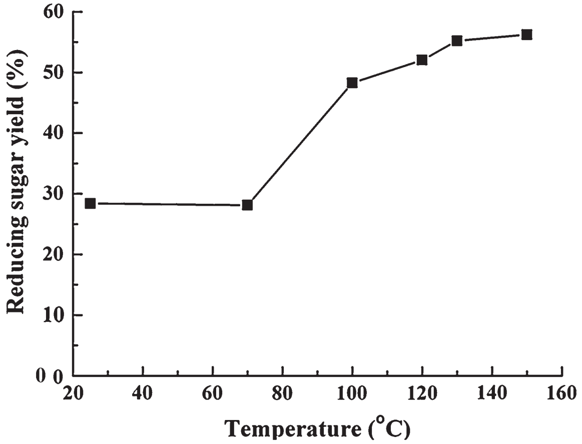


Fig. 6.7 Effect of pretreatment temperature on lignin extract rate from triticale straw by [C_2mim]OAc with a fixed pretreatment time of 1.5 h (**a**), and effect of pretreatment temperature on the hydrolysis of cellulose recovered from triticale straw after lignin removal by the ionic liquid (**b**) (Figure plotted with data from Fu et al. 2010)

Fig. 6.8 Effect of pretreatment temperature on reducing sugar yield after enzyme hydrolysis using cellulase for wheat straw pretreated with [C_2mim]DEP 1 h (Figure plotted with data from Li et al. 2009)



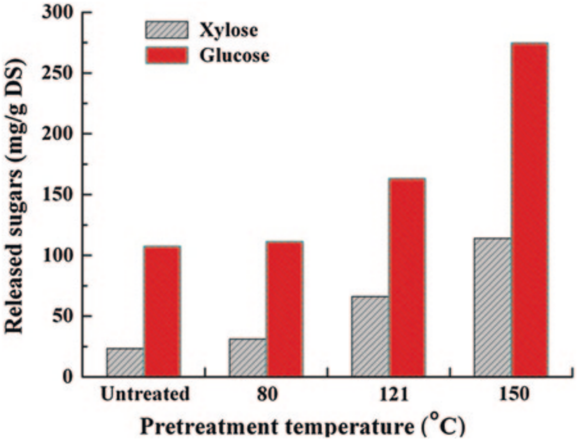
after enzyme hydrolysis of undissolved solid residue by a mixture of cellulase and β-glucosidase for 72 h at 47 °C. Figure 6.9 shows that 80 °C pretreatment temperature had almost no improvement over untreated sample, while 121 °C and 150 °C improved glucose and xylose yields considerably. For wheat straw, they found that 80 °C was ineffective and 121 °C showed only slight improvement, while 150 °C more than doubled glucose and xylose yields.

Instead of conventional conductive heating to raise the temperature for enhanced biomass dissolution in ionic liquids, microwave irradiation can be used. Ha et al. (2011) found that microwave heating not only increased cotton cellulose solubility in ionic liquids, but also reduced the degree of polymerization in the regenerated cellulose obtained after the pretreatment compared with pretreatment at 110 °C without microwave. They suggested that internal heating by microwave irradiation was more effective for polar solvents such as ionic liquids. Casas et al. (2012) used microwave successfully as a thermal source to reduce dissolution time required for *Pinus radiata* and *Eucalyptus globulus* woods in the following ionic liquids: [C_2mim]OAc, [C_4mim]OAc, [C_2mim]Cl, [C_4mim]Cl, and [Amim]Cl. Despite its advantages, microwave heating also has significant drawbacks. Apart from increased equipment cost and scale-up difficulties, another drawback for microwave heating is that uneven heating may cause pyrolysis of cellulose due to high local temperatures (Feng and Chen 2008). Sonication was also used to enhance cellulose dissolution in ionic liquids by some researchers (Swatloski et al. 2002; El Seoud et al. 2007; Mikkola et al. 2007; Wang et al. 2012), but it is costly and difficult to scale up.

6.6 Pretreatment Time

Lignocellulosic biomass dissolution in an ionic liquid is far from instantaneous. Typically, several hours are required for biomass dissolution as shown in Table 6.4. Biomass solubility limit in a particular ionic liquid may not be reached within the

Fig. 6.9 Effect of pretreatment temperature on glucose and xylose yields after [C_2mim]Cl pretreated corn stover was enzyme hydrolyzed (Figure plotted with data from Pezoa et al. 2010)



given pretreatment time frame. The solubility of dissolving pulp cellulose in different ionic liquids was investigated by Swatloski et al. (2002). The highest solubility was obtained using [C_4mim]Cl. Various types of biomass were pretreated with [C_2mim]Cl at 150 °C by Pezoa et al. (2010) to study how lignin removal made the residual biomass easier to hydrolyze. Apart from lignin dissolution, some cellulose and hemicellulose were also dissolved. Thus, it was important to control pretreatment time. They found that for corn stover, wheat straw, and eucalyptus, 1 h pretreatment time led to significantly higher glucose and xylose yields compared with 0.5 h. However, the opposite trend was observed for Lenga (*Nothofagus pumilio*). They argued that the Lenga biomass pieces were smaller in size and thus faster for ionic liquid pretreatment. More cellulose and hemicellulose were lost due to dissolution in [C_2mim]Cl when the pretreatment time was excessive.

Xu et al. (2012) studied the effect of [C_2mim]OAc pretreatment time by dissolving corn stover at a relatively low temperature of 70 °C. Longer pretreatment time continuously improved sugar yield (Fig. 6.10). After 24 h of pretreatment, they achieved very good glucose and xylose yields of 84.9 % and 64.8 %, respectively. They observed that even after 24 h of pretreatment, undissolved residual corn stover was still found.

The effect of pretreatment time using triticale straw pretreatment in [C_2mim]OAc for lignin removal at 90 °C was investigated by Fu et al. (2010). Figure 6.11 shows that longer pretreatment time increased cellulose hydrolysis yield. A pretreatment time of 24 h was sufficient for complete cellulose hydrolysis. Obviously, pretreatment time and temperature are closely related. Higher temperature requires less time.

Comparing Figs. 6.7 and 6.11, at 150 °C pretreatment temperature only 1.5 h pretreatment time was required to achieve complete cellulose hydrolysis after pretreatment, while 90 °C required 24 h. In comparison with rice straw treated with [Cholinium]Lys at 90 °C for lignin removal, 5 h was considered the optimal pretreatment time as seen in Fig. 6.12 according to Hou et al. (2012). Lignin removal by [Cholinium]Lys greatly reduced the recalcitrance of rice straw. Without the pretreatment, the glucose and xylose yields from enzyme hydrolysis were only 20.4 and 6.8 %, respectively.

When a temperature of 130 °C was used in the pretreatment of wheat straw in [C_2mim]DEP, pretreatment times greater than 30 min showed very little improvements as shown in Fig. 6.13 (Li et al. 2009). This was because 130 °C was a sufficiently high pretreatment temperature as indicated earlier in Fig. 6.8.

6.7 Water Content

Ionic liquids tend to be highly hygroscopic (Brandt et al. 2012), which can bring water into the pretreatment process. Water can also be introduced by moist biomass. Mazza et al. (2009) investigated the effect of water on cellulose dissolution in [C_4mim]Cl and 1,3-dimethylimidazolium dimethylphosphate ([C_1mim]DMP).

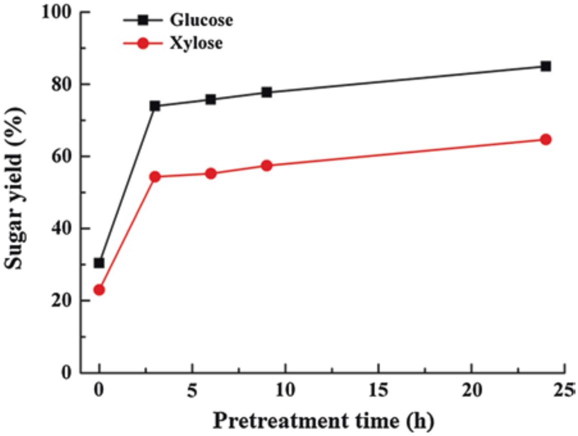


Fig. 6.10 Effect of pretreatment time on sugar yields after enzyme hydrolysis using cellulase for corn stover after pretreatment with [C_2mim]OAc at 70 °C (Figure plotted with data from Xu et al. 2012)

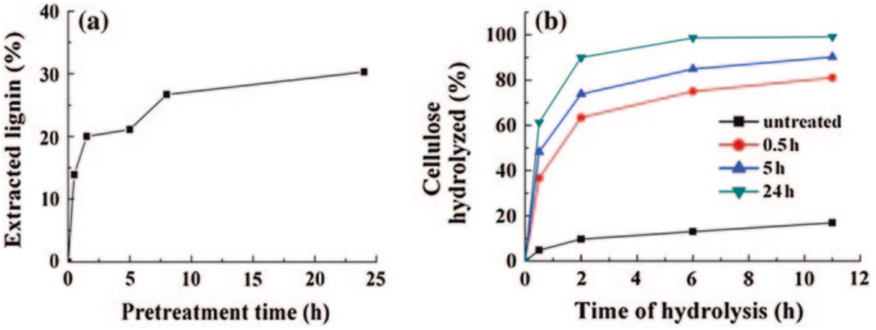


Fig. 6.11 Effect of pretreatment time on lignin extract rate in pretreatment of triticale straw with [C_2mim]OAc at 90 °C (**a**), and effect of pretreatment time on enzyme hydrolysis of the cellulose recovered from triticale straw after lignin removal by the ionic liquid (**b**) (Figure plotted with data from Fu et al. 2010)

Fig. 6.12 Effect of pretreatment time on lignin extraction and sugar yield after enzyme hydrolysis using cellulase for rice straw pretreated with [Cholinium]Lys at 90 °C (Figure plotted with data from Hou et al. 2012)

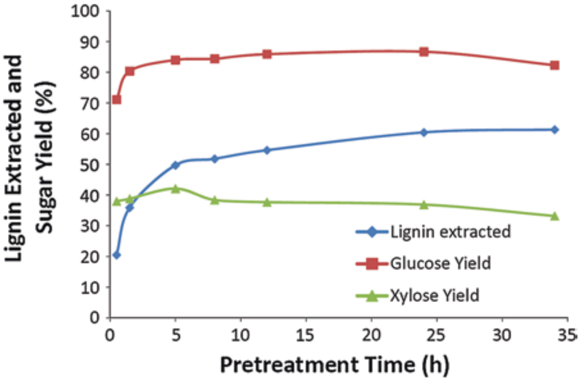
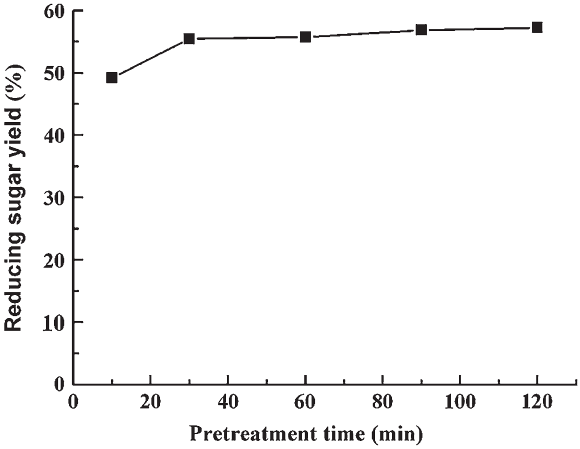


Fig. 6.13 Effect of pretreatment time on reducing sugar yield after enzyme hydrolysis of wheat straw pretreated with [C_2mim]DEP at 130 °C (Figure plotted with data from Li et al. 2009)



They found that increasing water content progressively reduced cellulose solubility. Adding a small amount of water to a cellulose solution in [C_1mim]DMP formed cellulose aggregates. This is consistent with the finding by Swatloski et al. (2002) that cellulose solubility decreased significantly in some ionic liquids when a small amount of water was present. They argued that this probably was a result of competitive hydrogen bonding. Interestingly, Brandt et al. (2010) observed that a small amount of water promoted lignin (in pine) solubilization in [C_4mim]Cl, but not in [C_4mim]OAc. It was likely that the presence of water resulted in the release of HCl acid that was beneficial according to Xie and Shi (2006).

Water can be removed from ionic liquids using vacuum at an elevated temperature (Tan et al. 2009). One traditional method is to dry an ionic liquid over a mixture of Na_2SO_4 and $MgSO_4$ before vacuum drying (Kilpeläinen et al. 2007; Shi et al. 2008). Freeze drying has also been used (Vitz et al. 2009). Furthermore, water can be stripped from an ionic liquid by sparging dry nitrogen gas through the ionic liquid to a mass fraction as low as 0.001 within a few hours (Ren et al. 2010). Biomass drying has been well documented in the literature.

6.8 Ionic Liquid Recycling and Biomass Recovery

Due to the high cost and the potential toxicity of ionic liquids, they must be recycled after biomass pretreatment. Various methods have been used by researchers to recover ionic liquids after biomass pretreatment. Each method has its advantages and limitations (Tan and MacFarlane 2010).

6.8.1 Precipitation Using Antisolvents

Cellulose can be recovered from its ionic liquid solution by adding an antisolvent such as water, which precipitates cellulose from the ionic liquid (Zavrel et al. 2009). Subsequently, the precipitated cellulose can be regenerated using filtration or centrifugation. However, cellulose precipitates typically appear as a gel, making separation difficult. Sometimes, a water/acetone (1:1 v/v) mixture is used instead of water to avoid gel formation (Shill et al. 2011).

6.8.2 Distillation and Evaporation

Distillation or evaporation can be used to remove volatile antisolvents easily because most ionic liquids are practically nonvolatile and they have good thermo-stabilities. However, this is usually an energy-intensive process. Direct removal of ionic liquid without the antisolvent step is also possible. Earle et al. (2006) demonstrated that some ionic liquids are distillable at low pressure without decomposition, but relatively high temperatures (200–300 °C) are needed. Olivier-Bourbigou et al. (2010) described several routes to convert ionic liquids into easily distillable compounds that can be subsequently converted back to ionic liquids by chemical reactions. This obviously could complicate process design.

6.8.3 Phase Separation and Liquid–Liquid Partitioning

Another method for ionic liquid recovery from the pretreatment process is to utilize their ability to form a biphasic system by adding an aqueous solution containing phosphate, carbonate, or sulfate anion, etc. For example, adding potassium phosphate to a water and [C$_4$mim]Cl mixture forms an aqueous biphasic system from which the ionic liquid can be recovered (Shill et al. 2011). Deng et al. (2009) found that the recovery of [Amim]Cl is better using a salt with a higher salting-out strength (e.g., $K_3PO_4 > K_2HPO_4 > K_2CO_3$). Using 46.5 % K_2HPO_4 concentration, they achieved [Amim]Cl recovery as high as 96.8 %. Phase equilibrium data for various ionic liquid/water/salt systems have been presented by several research groups (Deng et al. 2009; Pei et al. 2009; Shill et al. 2011). Alcohols and supercritical CO_2 may also be used for phase partitioning of ionic liquid systems (Aki et al. 2004; Crosthwaite et al. 2004).

6.8.4 Membrane Filtration

Precipitates from ionic liquid pretreatment of biomass can be separated using membrane filtration. For example, nanofiltration membranes have been used to reject ionic liquids while allowing smaller molecules to pass through for ionic liquid recycling (Han et al. 2005; Hazarika et al. 2012). Membrane filtration has the advantage that room temperature operation may be possible. However, high viscosity is often a hurdle.

6.8.5 Chromatography

Ion exclusion chromatography, which is already in use for carbohydrate processing, can also be used for ionic liquid recovery because it can exclude charged species such as ionic liquid species, thus separating them from nonelectrolytes such as sugar molecules (Binder and Raines 2010). For continuous chromatographic separation, Simulated Moving Bed (SMB) chromatography is used. SMB utilizes a series of ion-exchange chromatography columns with synchronized moving ports to simulate resin movement. Although chromatography separation has the advantage of high resolution and more than two separated fractions in the output, it is far more expensive than other separation methods.

6.9 Mobile and On-farm Pretreatment Using Ionic Liquids

Most lignocellulosic biomass tend to be bulky and not cost-effective for transportation from remote agricultural areas to a central processing facility. Mobile and on-farm biomass processing may be an answer to address this problem. Lignocellulosic biomass may be processed using a truck-mounted or on-farm-scale processor to obtain intermediary products such as fermentable sugars that can be shipped to a centralized facility for further processing or fermentation. A self-contained complete mobile or on-farm processor may even be used to produce bioethanol as a fuel cost-effectively in some regions that have abnormally high fuel costs such as a remote military forward operating base in a war zone. Mobile and on-farm processing units favor green pretreatment methods to eliminate the need for on-site waste treatment.

Unlike conventional organic solvents that are volatile, ionic liquids do not give out measurable vapor pressure. This makes them “green” solvents because they do not pollute the atmosphere (Blanchard et al. 1999). Ionic liquids can be recycled easily after pretreatment, thus no waste treatment is needed after the pretreatment process. A pretreatment process that uses ionic liquid typically uses mild temperature and atmosphere pressure without harsh conditions. Thus, ionic liquid pretreatment is particularly suitable for mobile and on-farm lignocellulosic biomass processing.

Figure 6.14 shows a flowchart used by Shill et al. (2011) to process gram quantities of Avicel and *Miscanthus giganteus* (a large perennial grass). The highest temperature used in the process was 140 °C (for biomass dissolution) that is much lower than the 250 °C used in steam pretreatment by Kim and Hong (2001). Figure 6.15 shows a process designed by Sen et al. (2012) for ionic liquid pretreatment of corn stover with ionic liquid recycling using an SMB chromatographic system instead of evaporation of the antisolvent (such as water in the previous flowchart) because evaporation is an energy-intensive process. However, the SMB system overtook the cost of the ionic liquid as the most expensive cost factor in capital investment for the large-scale operation (Sen et al. 2012). SMB may be replaced by a liquid–liquid partitioning process to reduce cost. The process shown in Fig. 6.16 used by Sun et al. (2009) may be scaled up for mobile or on-farm application. It uses water and acetone to selectively precipitate cellulose and lignin from softwood and hardwood after the wood is completely dissolved in $[C_2mim]OAc$. The ionic liquid is recycled in the process. A less volatile solvent may be used to replace acetone for lignin recovery if desired. All these pretreatment processes may be refined and scaled up or scaled down properly for mobile and on-farm applications.

6.10 Conclusion

In recent years, ionic liquid pretreatment of lignocellulosic biomass has drawn considerable attention. They are effective in cellulose dissolution for many types of lignocellulosic biomass. Some ionic liquids can also be used to selectively dissolve lignin and hemicellulose in addition to cellulose, and the components can be selectively recovered for hydrolysis. Separation of cellulose from lignin and hemicellulose greatly enhances cellulose hydrolysis after the pretreatment because the extensive networking consisting of lignin, hemicellulose, and cellulose can be disrupted by the ionic liquid pretreatment. Recovery of dissolved biomass components is relatively easy and ionic liquids can be recycled. Due to their solvation ability and basicity or acidity, ionic liquids are also special solvents that can be used for bioconversion to produce renewable bioproducts as specialty chemicals.

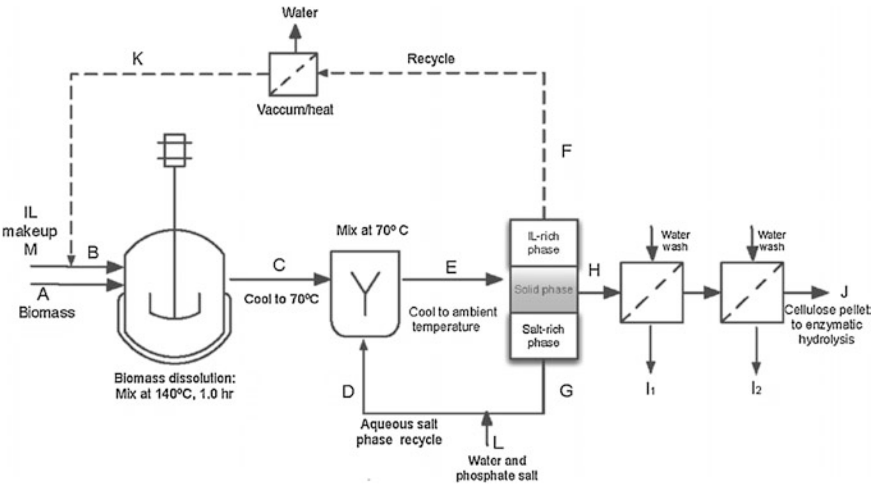


Fig. 6.14 A lignocellulosic biomass pretreatment process using an ionic liquid for cellulose dissolution. (Reprinted from Biotechnology and Bioengineering, Ionic liquid pretreatment of cellulosic biomass: Enzymatic hydrolysis and ionic liquid recycle, Kierston Shill, Sasisanker Padmanabhan, Qin Xin, John M.Prausnitz, Douglas S. Clark, Harvey W. Blanch, 108:511–520, Copyright 2010, with permission from John Wiley and Sons)

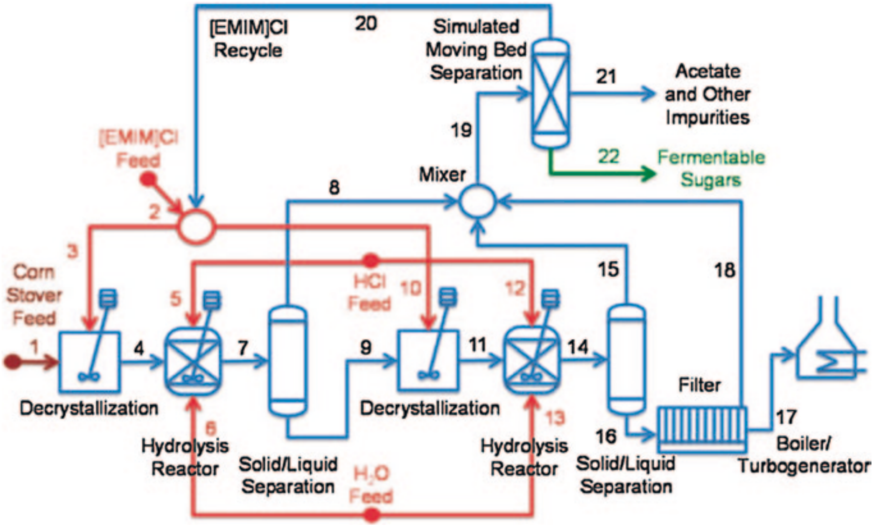


Fig. 6.15 A proposed corn stover pretreatment process using [C$_2$mim]Cl that incorporates SMB for ionic liquid recycling. (Reprinted from Biofuels, Bioproducts and Biorefining, Conversion of biomass to sugars via ionic liquid hydrolysis: process synthesis and economic evaluation, S. Murat Sen, Joseph B. Binder, Ronald T. Raines, Christos T. Maravelias, 6:444–452, Copyright 2010, with permission from John Wiley and Sons)

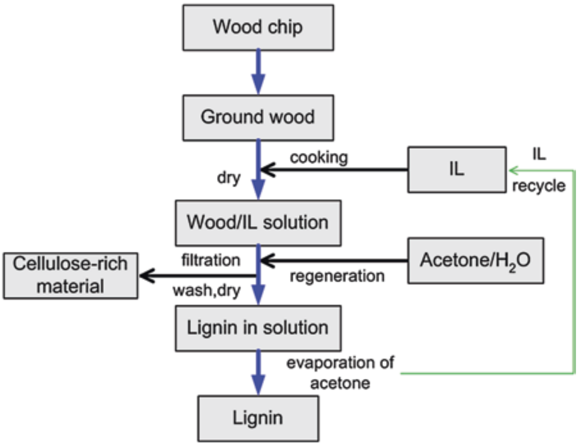


Fig. 6.16 A process with ionic liquid recycle for cellulose and lignin recovery after complete dissolution of softwood or hardwood in [C_2mim]OAc (Adapted from Sun et al. 2009)

Although attractive, ionic liquid pretreatment of lignocellulosic biomass is still not deployed for practical applications because of several drawbacks. No pilot-scale tests have been reported so far. The most noticeable obstacle is the initial high chemical cost. Although research is underway using amino acids to make biodegradable ionic liquids, most ionic liquids for biomass processing are not biodegradable. Toxicity, corrosivity, and hygroscopicity of ionic liquids are also major concerns. Ionic liquids can be recycled easily, but a tiny amount unrecovered ionic liquids may still present a safety concern if the recycling is not complete. Residual ionic liquids in the biomass may cause enzyme inhibition in the hydrolysis step and can be toxic to the microorganisms in the fermentation step (Alvira et al. 2010). Despite these hurdles, ionic liquids have a promising future for biomass pretreatment and processing. It can be envisioned that in the not-too-distant future some low-cost biodegradable ionic liquids with no or low toxicity will be available at reasonable costs. This would make their practical deployment feasible for mobile, on-farm, or even large-scale applications.

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