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# Supercritical $CO_2$ and ionic liquids for the pretreatment of lignocellulosic biomass in bioethanol production

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Owing to high petroleum prices, there has been a major push in recent years to use lignocellulosic biomass as biorefinery feedstocks. Unfortunately, by nature's design, lignocellulosic biomass is notoriously recalcitrant. Cellulose is the most abundant renewable carbon source on the planet and comprises glucan polysaccharides which self-assemble into paracrystalline microfibrils. The extent of cellulose crystallinity largely contributes to biomass recalcitrance. Additionally, cellulose microfibrils are embedded into both hemicellulose and lignin polymeric networks, making cellulose accessibility an additional obstacle. Pretreatment is necessary before enzymatic hydrolysis in order to liberate high yields of glucose and other fermentable sugars from biomass polysaccharides. This work discusses two pretreatment methods, supercritical $CO_2$ and ionic liquids (ILs). Both methods utilize green solvents that do not emit toxic vapours. Mechanisms for destroying or weakening biomass recalcitrance have been explored. Various pretreatment operating parameters such as temperature, pressure, time, dry biomass/solvent ratio, water content, etc. have been investigated for the pretreatment of various biomass types such as corn stover, switchgrass, sugarcane bagasse, soft and hard wood. The two pretreatment methods have their pros and cons. For example, supercritical $CO_2$ explosion pretreatment uses inexpensive $CO_2$, but requires a high pressure. By comparison, while IL pretreatment does not require an elevated pressure, ILs are still too expensive for large-scale uses. Further research and development are needed to make the two green pretreatment methods practical.

**Keywords:** lignocellulosic biomass; cellulose; hemicellulose; lignin; cell wall; pretreatment; $CO_2$; ionic liquid



## 1. Introduction

Earth's fossil fuel supply is a finite, non-renewable resource. At society's current rate of consumption, it is not so much a matter of *if* fossil fuel reserves will be depleted, but rather *when*. In light of the fact that the world's energy consumption will increase by 35% in the next 20 years [1] and the world's population is expected to top 9.2 billion by 2050,[2] it will be important to develop dedicated feedstock crops for biofuel production that will not impact food-market needs. Renewable, plant-based energy alternatives offer the potential to replace a significant portion of fossil fuel usage,[3,4] and the USA is aiming to substitute 20% of its gasoline usage with alternative fuels by 2022, meaning an increase in annual alternative fuel production of up to 35 billion gallons.[1] First-generation liquid biofuels are currently produced via the fermentation of starch-derived sugars from corn grains, the fermentation of sugarcane juice, and via the chemical conversion of plant oils to biodiesel. Unfortunately, these crop-based feedstocks compete with global food demands. Eventually, their use must give way to second-generation feedstocks, such as plant lignocellulosic biomass derived from grasses (i.e. switchgrass and *miscanthus*), woody plants (i.e. hybrid poplar and eucalyptus), and crop residues (i.e. corn stover and wheat straw).[5] Another challenge is how to achieve the volume of lignocellulosic-based biofuels mandated by the Renewable Fuel Standard (RFS2) adopted in 2010 within the Energy Independence and Security Act of 2007. A possible alternative would be to develop local biorefineries close to farmers that can process wastes, residues and non-food lignocellulosic biomass, which would help reduce greenhouse gas (GHG) emissions. In this regard, sugar cane seems to have the lowest GHG emission (50% of that of fossil fuel), while the highest GHG emission comes from soy (110% of that of fossil fuel).[6]

Plant biomass is composed primarily of plant cell wall materials consisting of 80–90% carbohydrates and 10–20% lignin and proteins that interact to form a structurally complex network. A detailed knowledge of plant cell wall biosynthesis and architecture will be invaluable to help understand the basis of lignocellulosic biomass recalcitrance, and optimize both pretreatment and enzymatic breakdown strategies accordingly. Pretreatment is typically the most costly step in biofuel production from

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biomass, with costs that can reach up to 30¢/gallon ethanol produced.[7] However, pretreatment costs vary depending upon the goals of downstream processing steps, and many variables must be considered (i.e. catalyst cost and recycling, generation of higher value lignin co-product, formation of degradation products that inhibit fermentation, energy demands, etc.). A review of the structure and composition of plant cell wall polymers found in plant biomass is given below to illustrate the complexity of biomass feedstocks and points to consider for designing pretreatment strategies.

## 2. Cell wall architecture in lignocellulosic biomass

In general, the cell walls of plant biomass consist of crosslinked networks of cellulose and hemicellulose, which are embedded into a hydrophobic and complex lignin network. During biomass accumulation, plant cells produce first a thin, elastic primary cell wall, which is assembled during cell growth and elongation. Primary cell walls contain 25–35% cellulose, 25–35% hemicellulose, 20–35% pectin, 5–10% glycoproteins, and are generally not lignified.[8] In most cell types, a thick secondary cell wall is deposited interior to the primary wall, after cell growth has ceased,[8,9] Secondary walls comprise around 90% of plant lignocellulosic biomass and are generally composed of 30–60% cellulose, 10–30% hemicellulose, and 20–30% lignin.[7,10,11] For the purpose of understanding biomass deconstruction, it is important to know the structure and composition of the main components of secondary cell walls in lignocellulosic materials.

### *2.1. Cellulose*

Cellulose is the most abundant, renewable carbon source on the planet, yet it is extremely recalcitrant to degradation. Cellulose can comprise as much as 50 wt% of plant biomass [12] and is composed of $\beta$-1,4 linked glucan chains that self-assemble via hydrogen bonding into paracrystalline microfibrils, each containing ~36 glucan chains (Figure 1a). Plant microfibril diameters range from about 2.4–3.6 nm and up to 5 μm in length.[13–15] The extent of crystallinity is mediated by the hydrogen bonding of the glucan chains and can vary both within and along the length of each microfibril. Cellulose synthase (CESAs) proteins of land plants and closely related algae are uniquely arranged into subunit complexes made up of six CESAs, which are further organized into a larger, circular multi-subunit complex (containing 18–36 CESA proteins) called cellulose synthase complexes (CSCs) or 'rosettes'.[16] Rosette organization influences glucan chain assembly, whereby interior glucans of cellulose microfibrils more tightly packaged and more crystalline than the exterior chains (more amorphous) [17,18] (Figure 1a). Bacterial CSCs, on the other hand, are linear and produce cellulose microfibrils with different physical structures.[19] Thus, the recalcitrance of plant cellulose is imparted not only by its crystallinity, but also by its accessibility. In addition, cellulose microfibrils are thought to be coated with hemicellulose and lignin (Figure 1b). These aspects must be considered when developing a pretreatment procedure for plant biomass. The enzymatic digestibility of the cellulose in native plant biomass is ~20% and a very large excess of enzyme (cellulase) is needed to achieve higher yields. For example, 72 units of Genencor Cytolase cellulase per gram of Avicel, a pure cellulose, released 80% glucose after six days of treatment.[20] Cellulose can be dissolved using chemical additives and can result in 90% glucose yield, but these chemicals are too expensive when considering the value of the glucose (approximately 5¢/lb).[7]

### *2.2. Hemicellulose*

Hemicellulose (also called crosslinking glycans) comes in a variety of polymers depending upon plant species and tissue type. Hemicellulosic polymers are non-crystalline, $\beta$-(1,4)-linked D-glycans that are thought to coat and crosslink cellulose microfibrils to assist and mediate cell growth and development.[9] The biosynthesis of hemicellulosic polysaccharides occurs in the plant Golgi apparatus where nascent polymers are packaged into secretory vesicles and trafficked to the plasma membrane for deposition to the plant cell wall.[21,22] It has been accepted that hemicelluloses associate with cellulose microfibrils at the cell surface and become deposited into the wall, though this process is not well understood.[20,23] Most relevant to plant lignocellulosic biomass are xylan, xyloglucan and mannan hemicellulosic polysaccharides.

Xylan is the most abundant hemicellulosic polysaccharide found in plant lignocellulosic biomass.[10] Xylan is a set of polysaccharides which are characterized by having a $\beta$-(1,4)-linked D-xylopyranosyl (Xyl*p*) backbone that is variably substituted depending on plant species and tissue type. There are three major types of xylan in plants: glucuronoarabinoxylan (GAX), glucuronoxylan (GX), and arabinoxylan (AX).[24,25] GAX is the major crosslinking glycan component of cell walls from commelinoid monocot plants, which includes most major crop species and bioenergy grasses. GAX is an important polymer that must be considered during biomass deconstruction, as GAX can make-up 40–50 wt% of walls in grass lignocellulosic biomass. The $\beta$-(1,4)-linked xylan backbone of GAX can be variably monosubstituted or disubstituted with $\alpha$-(1,2) and/or $\alpha$-(1,3)-linked arabinofuranosyl (Ara*f*) units in addition to $\alpha$-(1,2)-linked glucuronic acid (GlcA) residues that are often 4-*O*-methylesterified. While lignocellulosic biomass from dicot plants contains a small amount of GAX,[26] the major xylan is GX, which makes up ~20–30 wt% of their secondary walls. Unlike GAX, the xylan backbone of GX is substituted only with $\alpha$-(1,2) 4-*O*-Me-GlcA and $\alpha$-(1,2) 4-*O*-GlcA [27] (Figure 1). The Ara*f*

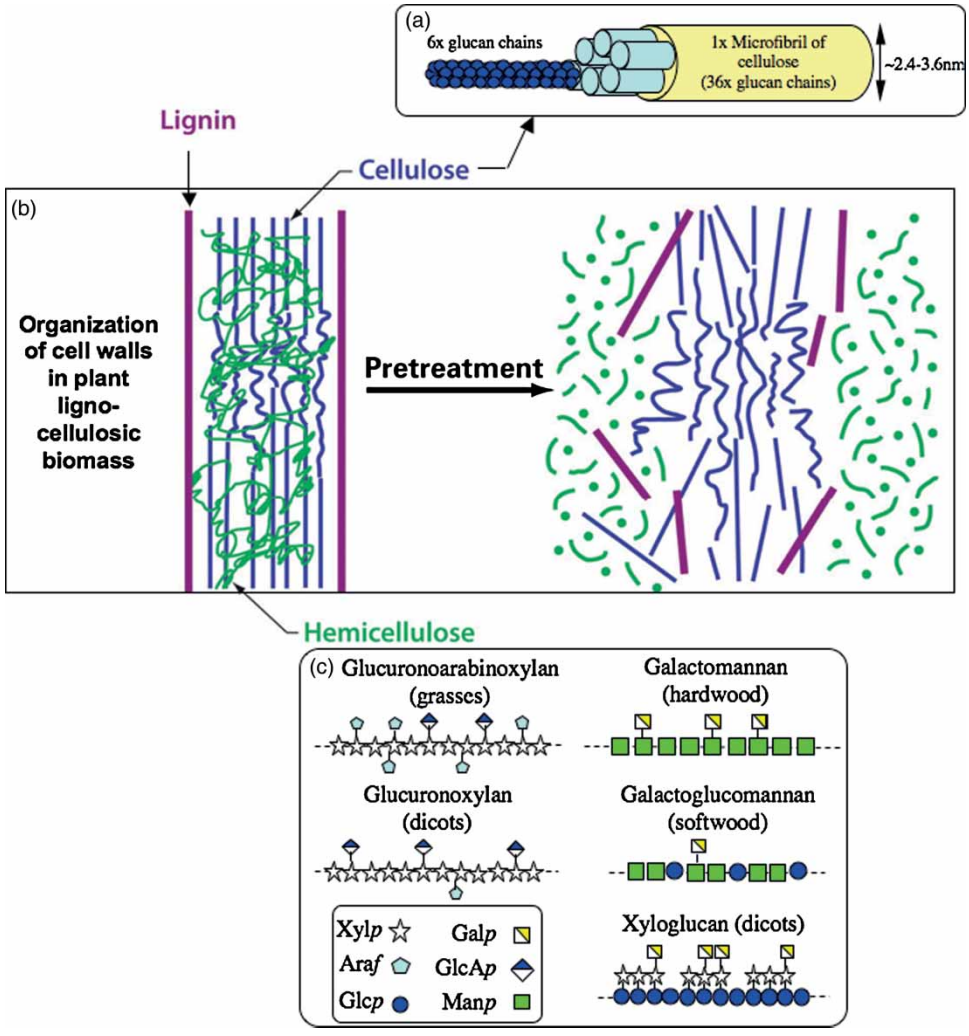


Figure 1. Schematic representation of cell wall structure in plant lignocellulosic biomass. Panel (a) shows the general organization of a cellulose microfibril. Panel (b) illustrates that biomass pretreatment dissociates plant cell wall polymers, thus facilitating enzyme accessibility. Panel (c) details the general structures of hemicelluloses most relevant to plant biomass deconstruction. Panel (a) was reprinted from US DOE. May 2007. *Biofuels Primer Placemat: From Biomass to Cellulosic Ethanol and Understanding Biomass: Plant Cell Walls*, US Department of Energy Office of Science. Panels (b) and (c) were modified after.[11]



and GlcA side chains in GAX can be esterified to ferulic, acetic, or *p*-coumaric acid groups, which can connect GAX polymers to themselves or to lignin polymers,[24,28–31] and contribute to cell wall recalcitrance. Since GX does not appear to contain ferulate esters, the linkage between GX polymers and GX-lignin involves Me-GlcA and GlcA residues instead of Ara*f*. In addition, the hydrolysis of these side chains during the pretreatment process releases inhibitory compounds that affect downstream fermentation yields.[32–34] Also, the breakdown of GAX and GX results in the liberation of pentose sugars that are not easily fermented by most yeast strains.[11] Therefore, when dealing with a lignocellulosic biomass that is rich in GAX/GX, these chemical characteristics must be taken in consideration. Finally, AX polymers are found in the specialized cell walls of cereal grain endosperm and do not significantly impact second-generation and later biofuel production.

Xyloglucan (XyG) is the major crosslinking glycan (20–25% wt) of both non-grass monocot and dicot primary walls, though it is a minor component in grasses.[9,10] XyG consists of a $\beta$-(1,4)-linked D-glucan backbone that is regularly substituted with $\alpha$-(1,6) Xyl*p* [35–38] (Figure 1c). Xyl*p* residues can be unsubstituted or further decorated with either galactosyl,[39] or galactosyl-fucosyl additions [40] (Figure 1c). XyG is often esterified with *O*-acetyl groups.[41] The release of these acetyl groups during pretreatment affects lignocellulosic biomass conversion to biofuel.[32–34]

Mannan is an important hemicellulose of woody biomass and comes in several variants: galactomannan (GM) and galacto(gluco)mannan (GGM). While GM consists of a $\beta$-(1,4)-linked D-mannopyranosyl (Man*p*) backbone substituted with $\alpha$-(1,6)-linked galatcopyranosyl (Gal*p*) residues, GGM has alternating $\beta$-(1,4) Man*p*,

$\beta$-(1,4) Glc*p* residues in its backbone with $\alpha$-(1,6)-Gal*p* side chains. GM is abundant in the secondary cell walls of hardwoods,[27,42] while GGM is particularly abundant in the secondary cell walls of gymnosperm wood (softwood).[43]

### 2.3. Lignin

Lignin is a hydrophobic, heterogeneous, polyphenolic network deposited around the 'cellulose-hemicellulose' complex during secondary cell wall deposition (Figure 1b). Lignin evolved in plants to help protect cells from pathogen degradation, to provide mechanical strength and maintain plant stature, and to waterproof vascular tissues for conducting water and mineral nutrients. The basic monomers of lignin (called monolignols) are produced by the stepwise conversion of phenylalanine to coniferyl, sinapyl, or *p*-coumaryl alcohol before secretion to the cell wall, where they are assembled by peroxidase/laccase catalyzed oxidative coupling reactions.[44–46] The monolignol composition of the lignin polymer is dependent upon cell type, environmental conditions and plant species. Upon incorporation into the lignin polymer, coniferyl, sinapyl and *p*-coumaryl alcohols give rise to guaiacyl (G-lignin), syringyl (S-lignin), and *p*-hydroxyphenyl subunits (H-lignin), respectively.[47] Softwoods are rich in G-lignin, whereas hardwoods contain both G- and S-lignin, in roughly equal proportions. The lignin of grasses contains all three subunits, G, S, and H-lignin.[47–49] The composition of G, S, and H-lignin significantly affects the recalcitrance of the cell wall, most notably a high S to G ratio correlates to increased digestibility.[50,51] Attempts to modify lignin content,[52, 53] lignin composition,[54–58] and lignin biosynthesis [59] are currently underway and have met some success. Any pretreatment that enhances the release of cellulose and hemicellulose from lignin would tremendously impact the cost of bioethanol production.

## 3. Pretreatment methods

The conversion efficiency of plant lignocellulosic biomass to biofuel depends largely upon the cost of energy spent on cell wall deconstruction and/or the solvent cost.[7] Each biomass pretreatment method has its pros and cons. Currently, no single method is suitable for all types of lignocellulosic biomass. Conventional pretreatment strategies are aimed at breaking lignin and polysaccharide crosslinks and reducing cellulose crystallinity to allow polysaccharide accessibility to degrading enzymes. The end product is a mixture of monosaccharides ready for fermentation by yeast and some other microorganisms. Mechanical pretreament methods such as milling, steam explosion (autohydrolysis), and hot water offer chemical-free options and are some of the most cost-effective methods for biomass deconstruction. More expensive chemical pretreatment methods include acids ($H_2SO_4$) and alkalis (ammonia, KOH), and offer better conversion yields, but at the cost of having a higher carbon footprint and producing inhibitory compounds and chemical wastes. A key step in biofuel production from lignocellulosic biomass is to optimize the processes (pretreatment, saccharification and fermentation) to increase monosaccharide yield and fermentation of both six-carbon as well as five-carbon monosaccharides. This work discusses two pretreatment methods using two different types of green solvents, namely $CO_2$ and ILs. The use of these green solvents that do not emit organic vapours can be particularly attractive for mobile/tactical biomass processing.

### 3.1. Supercritical $CO_2$ explosion pretreatment

In glucose fermentation for the production of bioethanol, one mole of $CO_2$ is released stoichiometrically for each mole of ethanol produced. Only a small amount of the $CO_2$ is used to produce dry ice in the bioethanol industry, while the rest is released into the atmosphere without sequestration. This natural chemical is cheap and recyclable through photosynthesis. Thus, $CO_2$ is considered a green solvent. Its $T_c$ (critical temperature) is 31.0°C, much lower than many common chemicals such as water ($T_c = 374.2$°C) and ethanol (243.1°C). Its $P_c$ (critical pressure) is 1071 psi (73.84 bar), higher than that for ethanol ($P_c = 926$ psi), but much lower than that for water (3208 psi). Supercritical $CO_2$ has been used as a green and non-flammable solvent for chemical reactions and separations. It has even been used to modify steric structures of some enzymes to improve their thermostability, organic solvent tolerance and catalytic ability.[60]

Using supercritical $CO_2$ explosion to treat Avicel (a pure cellulose commercial product) for increased glucose yield after enzyme hydrolysis, Zheng et al. [61] were the first researchers who used supercritical $CO_2$ for biomass pretreatment as early as 1995. They subsequently used it to treat sugarcane bagasse and recycled paper with 75% and 22% improvements in glucose yield, respectively.[62] Table 1 shows a list of current literature on lignocellulosic biomass

Table 1. A list of lignocellulosic biomass treated with supercritical $CO_2$ in the literature.

| Biomass | $P$ (psi) | $T$ ($^o$C) | Time (min) | Reference |
|---|---|---|---|---|
| Rice straw | 1450–4350 | 40–110 | 15–45 | [63] |
| Guayule | 2500–4000 | 100–200 | 30–60 | [64] |
| Bagasse | 1100–4000 | 25–80 | 60 | [62] |
| Bagasse | 3626 | 80 | 120 | [65] |
| Switchgrass | 2900 | 160 | 60 | [66] |
| Switchgrass | 2900 | 160–210 | 60 | [67,68] |
| Corn stover | 2900 | 160 | 60 | [66] |
| Corn stover | 3500 | 80–150 | 10–60 | [69] |
| Mixed hardwood | 2900 | 160–210 | 60 | [67,68] |
| Aspen, southern yellow pine | 3100, 4000 | 112–165 | 10–60 | [70] |

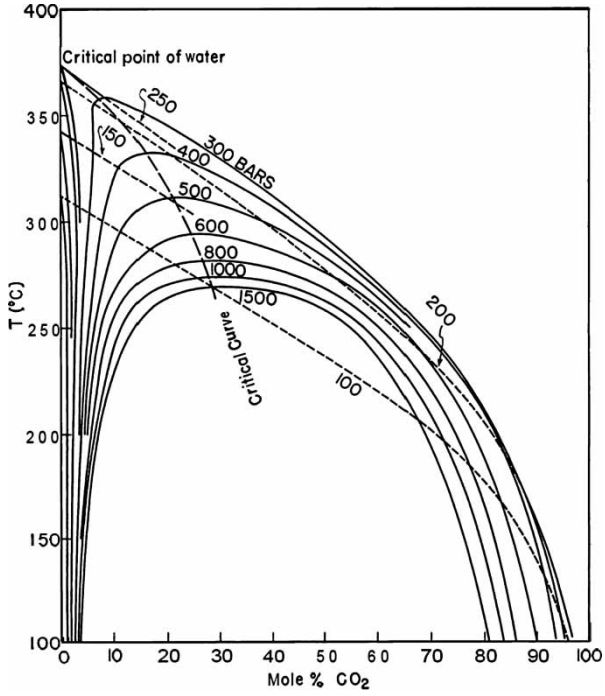


Figure 2. Phase diagram for $CO_2$–$H_2O$ (reprinted with permission of the *American Journal of Science* from [71]).

treated with supercritical $CO_2$ explosion, including corn stover, switchgrass, soft wood and hard wood. For many of the biomass in Table 1, glucose yields greater than 70% or even 85% of the theoretical maximum were achieved. The table also shows that the typical pretreatment temperature and pressure used are considerably higher than the $T_c$ and $P_c$ of pure $CO_2$. The lower temperature and pressure values listed in Table 1 were used for parametric studies by the authors rather than for typical pretreatment. When $CO_2$ is used for plant biomass pretreatment, the fluid system is actually a $CO_2$–$H_2O$ binary system because of the moisture in the biomass. Takenouchi and Kennedy [71] published a series of experimental phase diagrams for the $CO_2$–$H_2O$ system, one of which is shown in Figure 2. At a fixed temperature and pressure, any $CO_2$ mol% pre-equilibrium mixture falling between the two sets of equilibrium curves (on the left hand side and the right hand side) will give two equilibrium phases at concentrations indicated by the two intersection points of a horizontal isothermal line with the equilibrium curve. One phase is $H_2O$-rich and the other phase $CO_2$-rich. This is why supercritical $CO_2$ pretreatment is also known as biphasic $CO_2$–$H_2O$ pretreatment.[66]

At least three different mechanisms are thought to contribute to the effectiveness of supercritical $CO_2$ explosion pretreatment. As a supercritical fluid, $CO_2$ is able to penetrate the micro pores in biomass under pressure. Upon pressure release, it ruptures the pores and exposes more cellulose surfaces to cellulase enzymes during hydrolysis step. Scanning electron micrograph (SEM) images of corn stover [69] and rice straw [63] before and after the $CO_2$ explosion pretreatment clearly show the rupture. $CO_2$ explosion pretreatment of Avicel at 3000 psi and 35°C resulted in considerably better glucose yields than nitrogen and helium [62] at the same pressure and temperature. Another mechanism was proposed by Zheng et al. [61] who noticed a 50% reduction in cellulose crystallinity in treated Avicel. They also observed a loosening of Avicel's cellulose crystalline structure after the pretreatment from their solid-state NMR data. For corn stover, however, Narayanaswamy et al. [69] did not find a significant change in crystallinity from X-Ray Diffraction (XRD) data. They speculated that corn stover is a lignocellulosic biomass with cellulose microfibrils embedded in hemicelluloses, lignin and glycoproteins, unlike Avicel, that is pure cellulose. This observation is supported by the unchanged crystalline structure of corn stover after ammonia pretreatment.[72] The third mechanism is that $CO_2$ dissolution in water present in the wet biomass increases the acidity considerably. In fact, pretreatment was found ineffective for dry biomass.[62,69] The pH in supercritical $CO_2$ explosion pretreatment is slightly above 3, which can be estimated from the data by Meyssami et al.[73] and Toews et al.[74]

Many operating parameters impact the effectiveness of supercritical $CO_2$ explosion pretreatment of different types of biomass. They include temperature, pressure, time, moisture, dry biomass/$CO_2$ ratio and pressure release gradient.

### 3.1.1. *Effect of pressure*

A higher pressure during supercritical $CO_2$ explosion pretreatment allows better $CO_2$ penetration through micropores of the biomass, and a more powerful explosion upon pressure release. Table 1 indicates that a typical pretreatment pressure is between 2900 and 4000 psi, much higher than the $P_c$ of 1071 psi for $CO_2$. Figure 3 shows

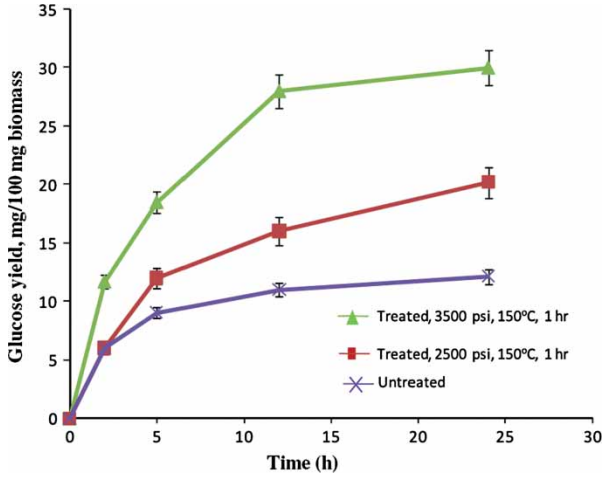


Figure 3. Effect of pretreatment pressure for $CO_2$ explosion pretreatment of corn stover (figure reprinted from [69] with permission from Elsevier).

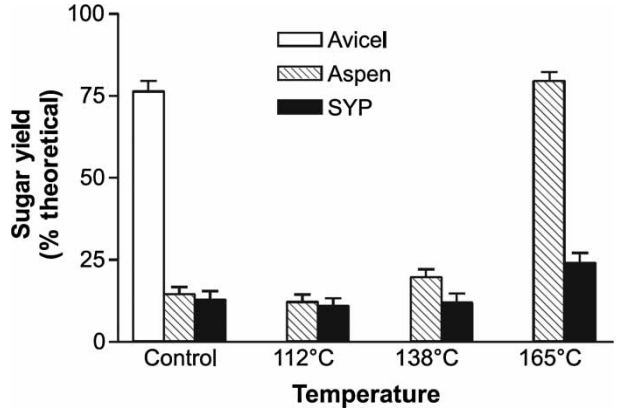


Figure 4. Effect of pretreatment temperature for $CO_2$ explosion pretreatment at 3100 psi for 60 min (figure reprinted from [70] with permission from Elsevier).



the post-pretreatment enzyme hydrolysis time courses for untreated and treated (150°C for 1 h) corn stover.[69] The pretreatment pressure of 3500 psi more than doubled the gain in glucose yield (from 12 to 30 g glucose/100 g dry mass) from corn stover over the untreated control compared with 2500 psi. Zhang et al. [62] found that the improvement in glucose yield from Avicel's post-pretreatment enzyme hydrolysis was around 5% when pressure was increased by 1000 psi increments between 1000 and 4000 psi at 35°C. Surprisingly, Kim and Hong [70] noticed a considerable drop in sugar yield when aspen (hardwood) was treated at 4000 psi compared with 3100 psi at 160°C for 1 h.

### 3.1.2. *Effect of temperature*

For supercritical $CO_2$ explosion pretreatment of corn stover at 3100 psi for 1 h, Narayanaswamy et al. [69] discovered that 80°C pretreatment temperature was inadequate because the glucose yield improvement was barely noticeable (13 vs. 12 g glucose/100 g dry biomass). However, increasing the temperature to 120°C and 150°C, the pretreatment process released 24 and 30 g glucose/100 g dry biomass, respectively. For aspen and southern yellow pine (softwood), supercritical $CO_2$ explosion pretreatment at 112°C for 1 h under 3100 psi was found to be completely ineffective, even though it was much higher than the $T_c$ of $CO_2$ [70] (Figure 4). Furthermore, there was only a small increase for aspen and no increase for southern yellow pine in sugar yield when the temperature was increased to 138°C, compared with the untreated control. At 165°C, the sugar yield for southern yellow pine almost doubled, but it was still quite low (25% of theoretical maximum sugar yield). A dramatic increase in the percentage of theoretical maximum sugar yield was seen for aspen at 165°C, reaching 80% compared with the 15% for the untreated control (Figure 4).

Recently, Benazzi et al. [65] used ultrasound to assist supercritical $CO_2$ pretreatment of bagasse at a pressure between 100 and 250 bar with a depressurization rate of 50–200 kg $m^{-3}$ $min^{-1}$. It is known that ultrasound introduces cavitation that enhances water penetration into crystalline cellulose. It also creates more surface areas for cellulase enzymes.[65] They found that 40°C pretreatment temperature could double the sugar yield, while 80°C nearly tripled the sugar yield compared with the untreated control that had a fermentable sugar yield of 127 g per kg of dry bagasse. Their pretreatment temperatures were considerably lower than the typical ones discussed above, probably because their process used ultrasound assistance. Although pretreatment temperatures as high as 210°C have been used for guayule, switchgrass and mixed hardwood (Table 1), higher temperatures require more energy input and greater demand on processing equipment. Excessive pretreatment time may actually be undesirable because sugar degradation may occur, leading to the formation of fermentation inhibitors.[65]

### 3.1.3. *Effect of time*

The reported supercritical $CO_2$ explosion pretreatment times in the current literature range from 0.25 to up to 2 h (Table 1). For rice straw treated at 110°C under 30 MPa, Gao et al. [63] reported that a 45 min pretreatment time yielded no further improvement in glucose yield compared with 30 min. Similarly, 30 min was found sufficient for aspen and southern yellow pine treatment at 165°C and 3100 psi. However, for corn stover treated at 150°C and 3500 psi, the glucose yield data reported by Narayanaswamy et al. [69] suggested that 1 h should be used rather than 30 min because a much higher glucose yield (29.9 vs. 18.4 g glucose/100 g corn stover) could be achieved at 150°C and 3500 psi. Luterbacher et al. [67] recommended a pretreatment time of 1 min for switchgrass and 16 min for mixed hardwood at 210°C followed by 1 h at 150°C and 200 bar. It should be noted that excessive pretreatment time at a relatively high temperature may lead to more fermentation inhibitors due to undesired sugar degradation.

### 3.1.4. *Effects of other parameters*

Biomass should be pre-wetted before pretreatment because $CO_2$ dissolution in water brings the benefit of acidity to the pretreatment process as discussed earlier.[61,69] Recently, Benazzi et al. [65] used ultrasound-assisted supercritical $CO_2$ explosion pretreatment for sugarcane bagasse. When the biomass moisture content was 45–65 wt%, no significant changes in glucose yield was noticed after enzyme hydrolysis. This is consistent with the finding by Kim and Hong.[70] They concluded that 57% moisture was sufficient when they evaluated 40%, 57%, 73% moisture contents in aspen wood (hard wood) and southern yellow pine (soft wood) for supercritical $CO_2$ explosion at 3100 psi and 165°C for 0.5 h. Their data indicated that 40% was inadequate while 73% showed only a small improvement over 57%. Luterbacher et al. [66] used 40% solid loading (60% moisture) in their pretreatment

for mixed hardwood and switchgrass with glucose yield as high as 85% of the theoretical maximum.

The dry biomass/$CO_2$ ratio depends on how much $CO_2$ is needed to soak the wet biomass. If this ratio is too high, the amount of the $H_2O$-rich phase relative to the amount of the $CO_2$-rich phase (Figure 2) will be increased based on the lever rule. Narayanaswamy [75] used a dry biomass/$CO_2$ ratio of 1:10 (w/w) in the pretreatment of corn stover, similar to the 10 wt% solid loading used in acid hydrolysis by Jensen et al. [76] and the 10:1 liquor/solid mass ratio in hydrothermal pretreatment by Garrote et al. [77] In comparison to this 1:10 ratio that was not optimized, the optimized dry biomass/ammonia ratio used by Lau et al. [78] was 1:1 (w/w).

Pressure release gradient obviously can impact plant biomass pore rupturing. A faster release gives a more powerful explosion and thus the effect on pore rupturing would be more pronounced. Benazzi et al. [65] reported that the depressurization rate in the range of 50–200 kg $m^{-3}$ $min^{-1}$ during the pretreatment of sugarcane bagasse with ultrasound-assisted supercritical $CO_2$ explosion pretreatment did not produce a significant change in glucose yield after hydrolysis. This could be explained by a far slower rate of pressure release that they used compared with a very fast pressure release in an explosion. Unfortunately, no other parametric study on depressurization rate has been reported in the literature as of March 2013.

### *3.2. Pretreatment using ILs*

The glucan chains of cellulose self-assemble into paracrystalline microfibrils. The extensive intermolecular and intramolecular hydrogen bonds that mediate microfibril architecture (Figure 1) make cellulose very difficult to dissolve in common solvents and require the use of special solvents.[79] While hemicelluloses lack the ability to form microfibrils, only a small fraction can be extracted with hot water. Complete solubilization of hemicellulose requires the use of alkaline and choatropic conditions.[79] Ion salts known as ILs have been used to efficiently dissolve cellulose and other plant cell wall polymers. ILs exist as solids at moderate temperatures (mostly inorganic salts), but some organic ILs can also exist as liquids at temperatures of below 100°C and even at room temperature.[80] Much like oils, they are far more viscous than traditional organic solvents. Unlike oils, most of ILs are heavier than water.[81] ILs are considered green solvents because they emit no or very little vapour pressure, and have been used as solvents to replace volatile organic solvents in conventional chemical reactions,[82] enzymatic reactions [83] and separations [84]. However, most ILs are non-biodegradable and need to be recycled.

ILs have a unique capacity for dissolving many materials that are considered insoluble in traditional solvents. In 2002, Swatloski et al. [85] published a work on the dissolution of cellulose in various ILs, which ignited interests from biomass processing researchers. The trend has intensified greatly in the last two or three years due to the push for lignocellulosic ethanol. Many new ILs are being investigated for biomass pretreatment.[79] Some common cations and anions in ILs used in biomass pretreatment are listed in Table 2. It shows that the cations are all organic while most anions are inorganic. An extensive list of ILs for cellulose pretreatment was provided by Wang et al. [79] including ILs with additional types of cations and anions.

There are several ways that ILs can be used for biomass pretreatment. ILs can be used to dissolve the whole lignocellulosic biomass or selectively some of the components (i.e. lignin, hemicellulose or cellulose) at temperatures lower than those for other pretreatment methods and without the need for pressurization. The undissolved and the

Table 2. Some cations and anions in ILs for biomass pretreatment.

| Ion | Abbreviation | Full Name |
|---|---|---|
| Cation | $[AMIM]^+$ | 1-allyl-3-methylimidazolium |
| | $[C_1MIM]^+$, $[MMIM]^+$ | 1-methyl-3-methylimidazolium |
| | $[C_2MIM]^+$, $[EMIM]^+$ | 1-ethyl-3-methylimidazolium |
| | $[C_3MIM]^+$ | 1-propyl-3-methylimidazolium |
| | $[C_4MIM]^+$, $[BMIM]^+$ | 1-butyl-3-methylimidazolium |
| | $[C_5MIM]^+$ | 1-pentyl-3-methylimidazolium |
| | $[C_6MIM]^+$, $[HMIM]^+$ | 1-hexyl-3-methylimidazolium |
| | $[C_7MIM]^+$ | 1-heptyl-3-methylimidazolium |
| | $[C_8MIM]^+$, $[OMIM]^+$ | 1-octyl-3-methylimidazolium |
| | $[Cholinium]^+$ | 2-hydroxy-N,N,N-trimethyl-ethanaminium |
| | $[C_2CNBIM]^+$ | 1-propyronitrile-3-butylimidazolium |
| | $[C_2CNAIM]^+$ | 1-propyronitrile-3-allylimidazolium |
| | $[C_4DMIM]^+$ | 1-butyl-2,3-dimethylimidazolium |
| | $[C_4MPY]^+$ | 3-methyl-N-butylpyridinium |
| Anion | $ABS^-$ | Alkylbenzenesulfonate |
| | $Ac^-$ | Acetate |
| | $Br^-$ | Bromide |
| | $HSO_4^-$ | Hydrogen sulphate |
| | $MeSO_3^-$ | Methane sulfonate |
| | $MeSO_4^-$ | Methyl sulphate |
| | $CF_3SO_3^-$ | Trifluoromethanesulfonate |
| | $Cl^-$ | Chloride |
| | $DEP^-$ | Diethyl phosphate |
| | $Gly^-$ | Glycine |
| | $HCOO^-$ | Formate |
| | $Lys^-$ | Lysine |
| | $Phe^-$ | Phenylalanine |
| | $Pro^-$ | Proline |
| | $Trp^-$ | Tryptophan |

Table 3. Some reported ILs and their biomass pretreatment conditions.

| Biomass | IL | *T* (°C) | *t* (h) | Dissolved component | Ref. |
|---|---|---|---|---|---|
| Agave bagasse | $[C_2MIM]Ac$ | 160 | 3 | All | [86] |
| Bamboo | [Cholinium]Ac | 110 | 3 | All | [87] |
| Bamboo | $[C_2CNBIM]Cl$ | 120 | 24 | Lignin | [88] |
| Bamboo | $[C_2CNAIM]Cl$ | 120 | 24 | Lignin | [88] |
| Cassava pulp | $[C_2MIM]DEP$ | 180 | 24 | All | [89] |
| Corn stover | $[C_2MIM]Ac$ | 160 | 3 | All | [90] |
| Cotton stalk | $[C_2MIM]Ac$ | 150 | 0.5 | All | [91] |
| Energy cane bagasse | $[C_2MIM]Ac$ | 100 | 2 | All | [92] |
| Eucalyptus | $[C_2MIM]Ac$ | 160 | 3 | All | [93] |
| *Pinus radiate* wood | $[C_2MIM]Ac$ | 120 | 3 | Mostly Hemicellulose | [94] |
| Rice hull | [AMIM]Cl | 90 | 4 | Hemicellulose | [95] |
| Rice hull | [AMIM]Cl | 110 | 8 | Hemicellulose and cellulose | [95] |
| Rice straw | [Cholinium]AA/Water (1:1 w/w) | 90 | 12 | All | [96] |
| Southern yellow pine | $[C_2MIM]Ac$ | 110 | 16 | All | [97] |
| Southern yellow pine | $[C_4MIM]Cl$ | 110 | 16 | All | [97] |
| Sugarcane bagasse | [AMIM]Cl | 140 | 1 | All | [98] |
| Sugarcane bagasse | $[C_2MIM]Ac$ | 150 | 1.5 | All | [99] |
| Switchgrass | $[C_2MIM]Ac$ | 160 | 3 | All | [86] |
| Spruce wood chip | $[C_2MIM]Ac$ | 120 | 15 | All | [100] |
| Yellow pine | $[C_6MIM]Cl$ | 150 | 5 | All | [101] |
| Wheat straw | $[C_2MIM]Ac$/water (1:1 w/w) | 158 | 3.6 | (Undissolved slurry wanted) | [102] |
| Wood flour | $[C_4MIM][CF_3SO_3]$ | 90 | 24 | Lignin | [103] |
| Wood flour | $[C_1MIM][MeSO_4]$ | 90 | 24 | Lignin | [103] |



dissolved lignocellulosic biomass (or biomass components) are far less recalcitrant toward enzyme hydrolysis. Dissolved biomass can be precipitated using an antisolvent such as water.[80] Table 3 lists some examples of ILs used in treating lignocellulosic biomass. The sugar yields from IL pretreatment are equally excellent compared with other effective pretreatment methods such as dilute acid and Ammonia Fibre Explosion pretreatment methods.[80]

By disrupting the extensive intermolecular and intramolecular hydrogen bonds in cellulose, some ILs are capable of dissolving cellulose. Experimental results suggest cellulose solubility in ILs depends on their anions' hydrogen bonding accepting abilities.[104] Some researchers argue that cations also play an important role based on experimental and molecular simulation data.[79,105] For example, it was found that $[C_3MIM]Cl$ and $[C_5MIM]Cl$ are poor solvents for cellulose while $[C_2MIM]Cl$, $[C_4MIM]Cl$ and $[C_6MIM]Cl$ are good choices.[79] The XRD patterns for untreated and treated cotton stalk in Figure 5 show depressed intensity peaks at 15° and 22° for IL treated cotton stalk at 150°C for 30 min compared with the untreated control, indicating reduced crystallinity after the IL pretreatment.[91] The SEM images in Figure 6 clearly demonstrate that pretreatment of cotton stalk using $[C_2MIM]Ac$ disrupted its compact framework and exposed more surfaces for enzyme hydrolysis.[91]

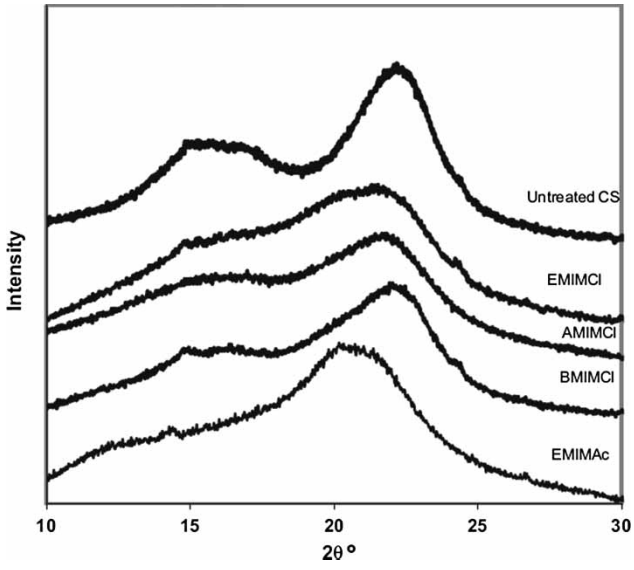


Figure 5. XRD patterns of untreated and IL treated (at 150°C for 0.5 h) cotton stalk samples (figure reprinted from [91] with permission from Elsevier).

Apart from the early practice of using ILs to dissolve cellulose, some nitrile-based ILs (e.g. $[C_2CNBIM]Cl$) and biomaterial-based ILs (e.g. [Cholinium]Gly) have recently been synthesized to selectively dissolve lignin in


Figure 6. SEM images of untreated (a) and [$C_2$MIM] Ac treated (at 150°C for 30 min) (b) cotton stalk samples (figure reprinted from [91] with permission from Elsevier).



lignocellulosic biomass.[87,106] The delignified biomass is much more susceptible to enzyme hydrolysis. Chen and Dixon [107] found that the lignin content and composition in the stem of alfalfa influenced enzyme hydrolysis of its cellulose. After IL pretreatment, the sugar yield from cellulose directly correlated with reduced lignin content. [$C_2$MIM]Ac pretreatment of eucalyptus at 120°C and 160°C for 6 h broke down roughly 50% more S-lignin than G-lignin, while for switchgrass, roughly three times more G-lignin broke down than S-lignin.[108] It was reported that the removal of 40% of the lignin from a wood flour by [$C_2$MIM]Ac did not result in cellulose dissolution, but reduced cellulose crystallinity, leading to greater than 90% cellulose hydrolysis by cellulase.[103] Lignin solubility in excess of 0.5 g/g [$C_1$MIM][$MeSO_4$] and [$C_4$MIM][$CF_3SO_3$] at 90°C has also been reported.[103]

IL pretreatment can reduce the need for the energy-intensive milling step for biomass. Pretreatment of spruce wood chips using [$C_4$MIM]Ac and [$C_2$MIM]Ac at 120°C for 15 h increased the yield of enzymatic hydrolysis in terms of % theoretical yield from 1.8% (untreated control) to 56.9% (32-fold) and 66.4% (37-fold), respectively compared with the 7- to 9-fold increases for spruce wood powder.[100] Many pretreatment operating conditions impact the pretreatment outcome for a particular biomass, including IL selection, temperature and time, water content, pH, and dry biomass/IL ratio. Some of the pretreatment conditions are listed in Table 3.

### 3.2.1. *Selection of IL*

For cations, methylimidazolium and methylpyridinium cores with allyl-, methyl, ethyl-, or butyl- side chains are generally considered good at dissolving cellulose.[79] This is why they dominate the list of cations in Table 2. Cholinium-based ILs such as [Cholinium]AA and nitrile-based ILs such as [$C_2$CNBIM]Cl and [$C_2$CNAIM]Cl have been found to be good at dissolving lignin.[88,106]

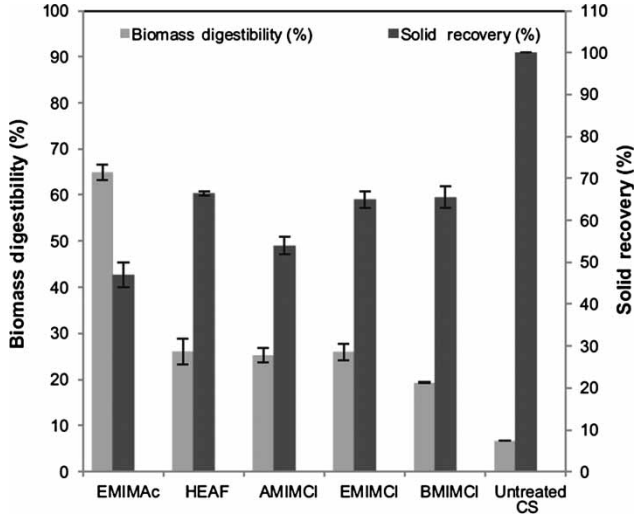


Figure 7. Effect of IL selection on the pretreatment of cotton stalk at 150°C for 0.5 h. (figure reprinted from [91] with permission from Elsevier).

Table 3 shows that $[AMIM]^+$, $[C_2MIM]^+$ and $[C_4MIM]^+$ are most popular cations. Haykir et al. [91] found that [AMIM]Cl, [$C_2$MIM]Cl and 2-hydroxy ethyl ammonium formate (HEAF) achieved comparable biomass digestibility when they were used to pre-treat cotton stalk at 150°C for 30 min, and showed significantly better performance compared to [$C_4$MIM]Cl (Figure 7) [91].

While [$C_3$MIM]Cl and [$C_5$MIM]Cl appeared to be less efficient in dissolving cellulose in various biomass types, [$C_2$MIM]Cl, [$C_4$MIM]Cl and [$C_6$MIM]Cl performed better.[79] For cellulose dissolution, Swatloski et al. [85] and Klemm et al. [109] suggested the following order for decreased cellulose solubility exists for the selection of anions based on some experimental data:

$$(CH_3CH_2O)_2PO_2^- \approx Ac^- > SHCH_2COO^- > HCOO^- > Cl^- > Br^- \approx SCN^-.$$

Table 3 shows that $Ac^-$ and $Cl^-$ are most popular anions. Between these two, $Ac^-$ is superior. For example, [$C_2$MIM]Ac more than doubled the biomass digestibility compared with [$C_2$MIM]Cl for the pretreatment of cotton stalk at 150°C for 30 min.[91] Amino Acids (AAs) such as GLy, Lys, Phe, Pro and Trp were also found to be good anions when combined with $[Cholinium]^+$ for dissolving lignin.[88]

[$C_2$MIM]Ac pretreatment of sugarcane bagasse at 150°C for 1.5 h achieved 83 wt% yield of glucan saccharification, considerably higher than the 53% achieved by [$C_2$MIM]Cl and [$C_4$MIM]Cl.[99] Similarly, Katinonkul et al. [110] reported that enzyme digestibility of oil palm empty fruit bunches increased from 20.4% (untreated control) to 96.6% after pretreatment with [$C_2$MIM]Ac at 110°C for 2 h compared to [$C_2$MIM]Cl at 130°C for 2 h. These data proved that $Ac^-$ is superior to $Cl^-$.

### 3.2.2. *IL pretreatment temperature and time*

In general, higher temperatures increase biomass dissolution. However, higher temperatures not only mean higher energy input, but also an increase in IL decomposition, and the formation of undesirable biomass degradation products, which all are considered major concerns. Table 2 shows that a typical pretreatment temperature falls between 90°C and 160°C. It may be beneficial to use a longer pretreatment time for a lower pretreatment temperature. Qiu and Aita [92] found that cane bagasse pretreatment with recycled [$C_2$MIM]Ac at 100°C for 2 h achieved significantly better glucan and xylan yields (>90%), and less IL decomposition than a pretreatment at 120°C for 30 min.

When the pretreatment temperature increased from 120°C to 160°C for the 3 h pretreatment using [$C_2$MIM]Ac, the lignin removal rate increased from 8.2% to 38.4% for switchgrass, and from 16.6% to 45.5% for agave bagasse, respectively.[86] Hong et al. [111] investigated the temperature effect on the [AMIM]Cl pretreatment of cotton-based waste textiles, and found that 110°C was the optimal temperature, with a recommended pretreatment time of 1.5 h. At 130°C, less than 0.5 h was required, but cotton loss due to undesirable biomass degradation was more significant than at 110°C with a pretreatment time of 1.5 h. In addition, for longer pretreatment time, IL solution became darker, indicating more undesirable biomass degradation. Pretreatment at 90°C would reduce cotton loss, but the time for dissolution would be excessively long.

Apart from using a higher temperature to speed up pretreatment, obviously, using a fine biomass powder instead of larger particles will reduce pretreatment time. However, milling is an energy-intensive process. Using a lower dry biomass/IL mass ratio will also speed up biomass dissolution, but it increases the cost of IL. Table 2 shows that a wide range of pretreatment times (from 30 min to 24 h) have been tested by various researchers. The shortest pretreatment time was reported by Uju et al. [112] who found

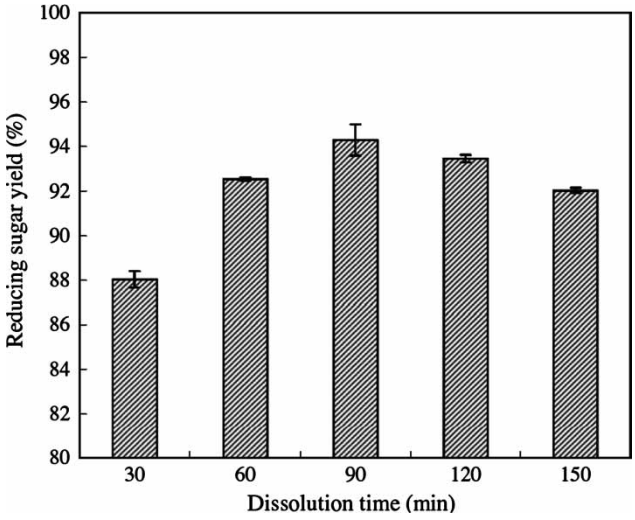


Figure 8. Effect of pretreatment time required on sugar yield in [AMIM]Cl pretreatment of cotton-based waste textiles at 110°C (figure reprinted from [111] with permission from Elsevier).

that pretreatment of bagasse and eucalyptus small particles (<0.2 mm) using [$C_4$MPY]Cl at 120°C for 10 min yielded 89% and 96% regenerated biomass, respectively. Figure 8 shows that for [AMIM]Cl pretreatment of cotton-based waste textiles at 110°C, 1.5 h was the optimal pretreatment time.[111]

### 3.2.3. *Water content and the use of IL-water mixtures for pretreatment*

It is well known that IL solubility of cellulose is reduced if water is present in the IL.[80] It is believed that water is a better hydrogen bond donor and will form hydrogen bonds with the IL rather than the hydroxyls of cellulose. Water molecules compete with cellulose to bind ILs and thus reduce their cellulose solubility.[80] In fact, water is often used as an antisolvent to precipitate dissolved cellulose from an IL solution after pretreatment. Nitrogen sparging can be used to strip water from ILs.[113] Other methods such as freeze drying or vacuum drying of a heated IL have also been used.[80] Because ILs are often hygroscopic, after water removal, a moisture-free nitrogen headspace is sometimes used during pretreatment,[114] which adds to the operating costs.

There is a growing trend to use IL-water mixtures in biomass pretreatment instead of moisture-free ILs. Hou et al. [96] used biodegradable [Cholinium]AA-water mixture (1:1 w/w) for the pretreatment of rice straw at 90°C for 12 h. For Lys, Gly, Ala, Ser, Ph, Trp containing ILs, glucose yields greater than 80% were obtained. Pretreatment of sugarcane bagasse using a [$C_4$MIM]Cl solution containing 10–30% water and 1.2% HCl at 130°C for 30 min achieved glucan digestibility of 94–100%.[115] This outcome was due to efficient delignification and xylan removal by the liquid mixture while leaving cellulose in the solid phase.

[$C_4$MIM][$MeSO_4$] and [$C_4$MIM][$HSO_4$] were mixed with 10–40% (w/w) water separately at 120°C were used by Brandt et al. [116] to dissolve lignin and hemicellulose in switchgrass, pine and willow during pretreatment. Up to 90% glucose in the biomass was released after pretreatment in enzyme hydrolysis. The addition of water makes IL solutions less viscous, thus increasing biomass loading. It reduces IL costs by using less ILs. It also makes IL pretreatment more practical because it eliminates the need for biomass drying required by pretreatment using dry ILs to dissolve cellulose in pretreatment.[115]

Fu and Mazza [102] performed an optimization study on the pretreatment of wheat straw using aqueous solutions of [$C_2$MIM]Ac. They found 158°C, 3.6 h and 49.5 wt% IL to be optimal for a predicted combined recovery of 71.4% of glucose and xylose. Unlike the typical IL pretreatment of biomass that hydrolyzes the biomass that initially dissolves in the IL and is subsequent recovered using an antisolvent such as water, only the undissolved slurry after incubation with the aqueous IL (not the material removed from the aqueous IL) was used for hydrolysis to yield glucose and xylose.

Instead of adding water, researchers have also experimented with mixing less-expensive organic solvents with ILs for pretreatment to reduce cost. For example, Xie et al. [117] used a N-methylpyrrolidone/[EMIM]Ac (4:1 molar ratio) for pretreatment of corn stover at 140°C for 1 h, which resulted in 82.9% yield in total reducing sugars.

### 3.2.4. *IL pretreatment pH*

It is well documented that acidic pH is beneficial in biomass pretreatment methods, as an acid acts as a catalyst. When a mixture of IL and water is used, the mixture's pH can be acidified. Zhang et al. [118] investigated the effect of pH on the pretreatment of sugarcane bagasse using aqueous (20 wt% water) [BMIM]$CH_3SO_3$, [BMIM]$CH_3SO_4$, [EMIM]Cl and [BMIM]Cl solutions with pH adjusted by the addition of a 32 wt% HCl solution. Figure 9 shows that acidic pH greatly improved glucan digestibility and delignification at 130°C. When pH < 1 was used, close to 90% or higher glucan digestibility and delignification were achieved, more than doubling those using aqueous HCl pretreatment at a more acidic condition (pH 0.4). Figure 9 also suggests the aqueous solution of ILs [BMIM]$CH_3SO_3$, [BMIM]$CH_3SO_4$, [EMIM]Cl and [BMIM]Cl at pH 6 all performed very poorly in the pretreatment.

### 3.2.5. *Dry biomass/IL ratio*

The recent data gathered by Luo et al. [80] suggested that the typical dry biomass/IL ratio for biomass loading is between 1:20 and 1:30 (g dry biomass/g IL), which is several times smaller than the 1:10 (g dry biomass/g liquid) ratio used in supercritical $CO_2$,[119] acid hydrolysis,[76] hydrothermal [77] pretreatment methods. Thus, it appears that the IL pretreatment method uses relatively more solvents. However, the ratios for ILs were probably not optimized. Ninomiya et al. [87] reported that a biomass loading ratio greater than 1:3 (g dry biomass/g IL) was required to achieve a subsequent cellulose saccharification rate of 80% when [Cholinium]Ac was used to treat bamboo powder at 110°C for 3 h. Haykir et al. [91] used a ratio of 1:10 (g dry biomass/g IL) for the pretreatment of cotton stalk using [AMIM]Cl, [$C_4$MIM]Cl, [$C_2$MIM]Cl and [$C_2$MIM]Ac separately at 150°C for 30 min. Figure 7 shows biomass digestibility data from the pretreatment of cotton stalk using these ILs. It should be noted that using less IL would make the IL solution of biomass more viscous, causing processing difficulties, which can be a setback.

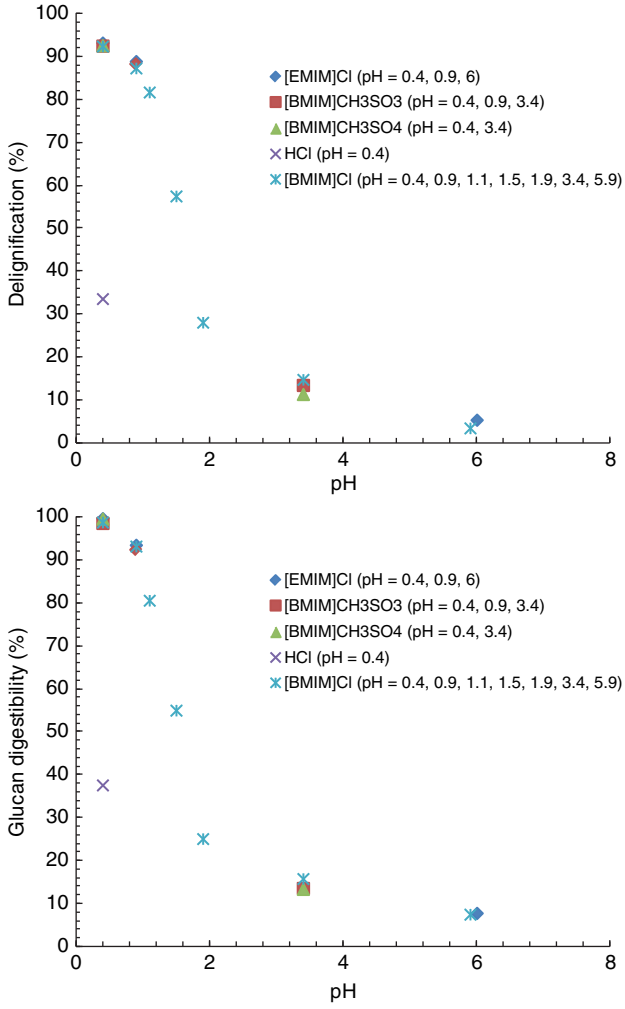


Figure 9. Effects of pretreatment pH on glucan digestibility and delignification for different ILs containing 20% water in the pretreatment of bagasse at 130°C for 30 min (figure plotted with data from [118]).

## 3.3. *IL pretreatment processes and recycling*

ILs are currently very expensive. As research chemicals, they are several US dollars per g or higher.[80] Most of them

are non-biodegradable and some of them are fermentation inhibitors [120] and can also inhibit enzyme hydrolysis.[91] Unlike in supercritical $CO_2$ explosion pretreatment, it is necessary to recycle ILs after biomass pretreatment. Several methods have recently been reviewed by Luo et al.[80] They include (1) precipitation using antisolvents such as water, (2) distillation and evaporation of volatile antisolvents, or volatile ILs after chemical modifications of the ILs,[121] (3) phase separation and liquid-liquid partitioning, (4) membrane filtration, and (5) ion chromatography. Each recycling method has its advantages and limitations for a particular pretreatment process.[122]

Sen et al. [123] proposed a process for IL pretreatment of corn stover. The process used a very capital-intensive simulated moving bed chromatography system instead of an antisolvent, which requires an energy-intensive evaporation step. The process designed by Sun et al. [97] used water and acetone (antisolvents) to precipitate cellulose and lignin, respectively after the $[C_2MIM]Ac$ pretreatment of soft wood and hard wood. The IL was recycled in the process. Acetone is not a green solvent due to its volatility. A less-volatile solvent may be used as a replacement to precipitate lignin from $[C_2MIM]Ac$. In principle, this process is readily scaleable depending on the cost of the IL. Other processes using ILs will certainly emerge once IL prices come down considerably.

## 4. Conclusion

Both supercritical $CO_2$ explosion and IL pretreatment methods use green solvents. $CO_2$ is an inexpensive solvent that can be readily discharged. However, due to the high operating pressure, the equipment requirement is rather heavy. By comparison, ILs require recycling because they are expensive and they can inhibit enzyme hydrolysis and ethanol fermentation. Even if a small fraction of an IL after biomass pretreatment is unrecovered, the residue trapped in the treated biomass can be harmful to enzyme hydrolysis and fermentation. Apart from the high costs, with a few exceptions (e.g. Cholinium ILs), many commonly used ILs are recalcitrant in the environment and are toxic to plants and animals.[124] Compared with supercritical $CO_2$, ILs do not need an elevated pressure for biomass pretreatment. Thus, IL pretreatment is far less demanding on processing equipment. ILs still command hefty prices compared with conventional solvents. Large-quantity prices are certainly much lower, but are still very expensive for real-world applications. It is anticipated that the prices will go down considerably in the future, and perhaps new ILs may be synthesized economically. Although laboratory-scale processes have been developed for both supercritical $CO_2$ explosion [67] and IL pretreatment [123,125] methods, both of them have been deployed in practical applications. More research is needed to move these technologies forward.

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