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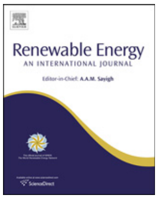

Review

# Use of ionic liquids in converting lignocellulosic material to biofuels

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ABSTRACT

Lignocellulosic materials are potentially a relatively inexpensive and abundant feedstock for biofuel production. The key to unlocking lignocelluloses recalcitrance is in part, the development of an effective pretreatment process. A promising new pretreatment method for lignocellulosic materials is the use of ionic liquids (ILs). ILs are non-volatile solvents that exhibit unique solvating properties. In this review, the dissolution of cellulose and lignocellulose in various ionic liquids is described including key properties such as high hydrogen-bonding basicity, which increases the ability of the IL to dissolve cellulose. As a pretreatment in biofuel production, the review details aspects such as the regeneration of cellulose from ionic liquids, structural changes that arise in the regenerated cellulose and its effect on enzymatic hydrolysis, the potential for IL recycling and finally, exploiting ILs in an integrated bioprocess.

## 1. Introduction

The search for sustainable methods to produce transportation fuels is driven by concerns associated with its supply and demand and its impact on climate change and greenhouse gas (GHG) emissions. Global petroleum demands have increased steadily from 57 × $10^6$ barrels/day in 1973, to 82 × $10^6$ barrels/day in 2004. By 2025, projected economic growth is anticipated to increase global demands for liquid fuels by approximately another 50% [1]. However, taking into account current production and existing reserves, we may have or soon will, approach Hubbert's predicted 'peak oil' levels [2]. Growing dependency on oil and the inability to protect supply lines from global political intrigues and ensuing price volatility is another reason for pursuing alternative fuels.

In selecting alternative transportation fuels, due consideration must be given to those which serve to combat climate change and produce cleaner air. Since the industrial revolution atmospheric $CO_2$ level has increased from ~275 to ~380 ppm owing to the burning of fossil fuels. Consequently, atmospheric temperatures have risen by $0.6 \pm 0.2$ °C during the twentieth century. If left unchecked, $CO_2$ level could easily surpass 550 ppm by the middle of this century [3]. Policies outlining strategic guidelines for reducing net greenhouse gas (GHG) emissions from traditional automotive fuels are currently being prepared and implemented.

The only current sustainable source of organic carbon is plant biomass. Biomass is defined as organic matter available on a renewable basis. Biomass includes forest and mill residues, agricultural crops and wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, fast growing trees, and municipal and industrial wastes. Biofuels derived from plant biomass are currently the only sustainable class of liquid fuels [4–7]. They include bio-alcohols (ethanol, butanol etc), biodiesel, bio-oils and syngas derivatives.

First-generation biofuels mainly utilize plants rich in carbohydrates (i.e. sugar and starch) to produce ethanol or oils such as canola and soybean for biodiesel production. The problem with first-generation biofuels is that as their use increases, demand for the feedstock will intensify and ultimately clash with fundamental agricultural endeavors such as food and fiber production. Second-generation biofuels are derived from the inedible and/or unexploited part of the plant (lignocellulose) and can be sourced from plant residues or organic waste such as crop straw, forestry thinnings or contents of landfill. Lignocellulosic materials are of interest as raw materials for bio-energy production since they are available in large amounts and are relatively cheap. The current challenge with using lignocellulosic biomass as a feedstock rests with technological advances to economically convert it into liquid fuel [8].

Production of bioethanol from lignocellulosic biomass typically involves three steps: (1) size reduction and pretreatment which makes the lignocellulosic material amenable to enzymatic/microbial/chemical hydrolysis; (2) hydrolysis of cellulose and hemicellulose to fermentable reducing sugars; and (3) fermentation of

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the sugars to ethanol or other fermentation products [9–11]. However, the physiochemical, structural and compositional features of lignocellulose which inherently provide tensile strength and barriers against pests and pathogens, also confers resistance to its hydrolysis. This recalcitrance is a major barrier to cost effectively converting lignocellulosic material to sugars and ethanol accordingly [12].

The importance of and general interest in lignocellulosic bioconversion is supported by a large body of published reviews dealing with various aspects of 'cellulosic to ethanol' processes. Representative reviews encompassing this research include: the structure and physicochemical pretreatment of cellulosics [13–16]; lignocellulosic feedstocks [17–21]; ethanogenic microorganisms [22–24]; integrated ethanol process design [25–28]; and environmental benefits and process economics [29–32]. The intension of this review is to provide the reader with an overview of ionic liquids (ILs) and their use in lignocellulosic pretreatment. Specifically, how ILs are used to dissolve cellulose/lignocellulose, the structural changes that occur to regenerated cellulose from dissolved lignocellulose/ionic liquid solutions and how these affect enzymatic hydrolysis, and IL recycling. Research into integrated bioprocesses which use a combined ILs pretreatment and hydrolysis step will also be outlined, along with a discussion on potential research options and opportunities.

## 2. Pretreatment

The goal of pretreatment is to make cellulose accessible to hydrolysis for conversion into sugars and subsequently into ethanol. Hydrolysis of cellulose/lignocellulose to monosaccharides is usually catalyzed by enzymes [33]. Enzymatic hydrolysis of lignocellulosic materials without pretreatment is generally inefficient, with less than 20% theoretical maximum yield [34]. Most pretreatment options change the physical and chemical structure of the lignocellulose biomass and improve hydrolysis for conversion to constituent sugars [9,10,35,36]. An effective lignocellulosic pretreatment and fractionation method should have several or all of the following features: (1) produces high monomeric sugar yields (2) generates highly digestible cellulose for rapid hydrolysis with lower enzyme use; (3) fractionate lignocellulose components for better economy; (4) minimizes production and/or release of sugar and lignin degradation products; (5) low energy consumption and/or has potential for re-generating energy, chemicals and/or enzymes; (6) low capital and operational costs; and (7) broad substrate applicability for a variety of feedstocks [3,37].

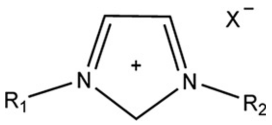
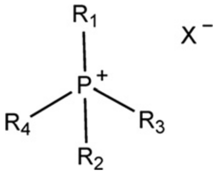
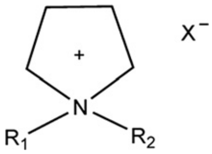
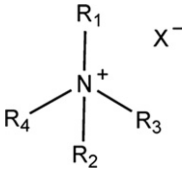
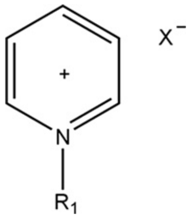
Besides cellulose release, most pretreatment processes liberate natural biomass inhibitors and often generate toxic degradation products which inhibit subsequent hydrolysis and fermentation processes [13]. Current pretreatment options strongly impact on the success and viability of other process variables such enzyme loadings, mixing power, ethanol concentration and purification, waste treatment demands, and power generation [28]. A potential solution to these and other problems associated with traditional pretreatments options may rest with the green chemical solvents ionic liquids (ILs).

## 3. Ionic liquids

Ionic liquid solvents are a promising new approach in the pretreatment of lignocellulosic material because of their ability to dissolve large amounts of cellulose at considerably mild conditions with close to 100% recovery [38]. ILs are a class of organic salts, comprised entirely of cations (usually organic) and anions (usually inorganic) (see Table 1). Unlike molten salts such as sodium chloride which is an ionic liquid at high temperatures, room temperature ionic liquids exist as liquids at relatively low temperatures.

ILs (such as $[EtNH_3][NO_3]$) were first described in 1914 [39]. In 1980, there were only a few ILs based patent applications, increasing to 100 by the year 2000 and 800 by the end of 2004 [40]. Today, ILs are recognized as one of the most promising green chemical solvents due to their desirable properties. Owing to their non-volatile and non-flammable properties, they are considered ideal replacements for conventional environmentally harmful molecular solvents which are used in catalytic and organic

**Table 1**
Examples of ionic liquid types and structures. The anion (X−) can be a variety of species, including nitrate [$NO3^-$], acetate [$CH_3CO_2^-$], trifluoroacetate [$CF_3CO_2^-$], tetrafluoroborate [$BF_4^-$], triflate [$CF_3SO_3^-$], hexafluorophosphate [$PF_6^-$], and bos(trifluoromethylsulfonyl)imide [$(CF_3SO_2)^2N^-$].

| Type of ionic liquid | Structure | Type of ionic liquid | Structure |
|---|---|---|---|
| Imidazolium |  | Tetra alkylphosphonium |  |
| Pyrrolidinium |  | Quaternary ammonium |  |
| Pyridinium |  | | |

reactions. They have a wide liquidus range (for example [BMIM]Cl has a melting point of 41 °C and decomposition temperature of 254 °C [41]). The asymmetric nature of the ions prevents compact packing of the ions, and makes them very useful in reactions which require both high and low temperatures. Other beneficial properties of ILs include their high thermal stability, high ionic conductivity, large electrochemical window, miscibility, water stability, density, viscosity, polarity and refractive index.

Referred to as "designer solvents", Ionic liquid solvent's chemical and physical properties can be adjusted and set by using different anion and cation combinations (Table 1). ILs miscibility with water is controlled by the choice of anion and cation. Water interacts mainly with the anion via the formation of hydrogen bonds. The cation contributions are secondary, acting as a weak hydrogen bond donor [42]. Examples of water immiscible anions include $[PF_6]^-$ and $[(CF_3SO_2)N]^-$, while water miscible anions are epitomized by $[CH_3COO]^-$, $[CF_3COO]^-$, $[NO_3]^-$, $BR^-$, $I^-$ and $Cl^-$. ILs miscibility with organic solvents also varies according to the design of the cation and anion components. For example, $[BMIM][Tf_2N]$ is miscible with dichloromethane and ketone but immiscible with alkanes and ether, $[BMPy][BF_4]$ is miscible in benzene, toluene and styrene but immiscible in higher alkyl benzenes [43]. NoIL is able to dissolve $CO_2$. Variability in miscibility properties of different ILs in diverse media imparts a great advantage to process design, mainly because the ILs can be recovered and recycled through extraction.

### 3.1. Biomass dissolution in ionic liquids

Cellulose is very difficult to dissolve due to the extensive network of inter- and intra-molecular hydrogen bonds and van der Waals interactions between cellulose fibrils. Remsing and coworkers [44] investigating the solubilizing mechanism of cellulose in IL [BMIM]Cl using NMR spectroscopy found that cellulose dissolution is mainly driven by the chloride anion which has a strong hydrogen-bonding basicity. The dissolution mechanism of cellulose in [BMIM]Cl involves the formation of hydrogen bonds between the chloride anions of IL and the hydroxyl groups of the sugar, in stoichiometric ratios [44].

Solubility of assorted lignocellulosic material and constituent polymers using different ILs are presented in Table 2. The outcomes clearly show that some ILs such as [BMIM]Cl are beneficial in dissolving biomass samples (cellulose solubility of up to 25 wt%),

**Table 2**
Substrate dissolution in ionic liquids. TMP- thermomechanical pulp.

| Ionic liquid cation | Anion | Abbreviation | Biopolymer dissolved | Solubility | Reference |
|---|---|---|---|---|---|
| 1-Allyl-3-methylimidazoium | Chloride | [AMIM]Cl | Cellulose | 9 wt% | [54] |
| | | | Maple wood flour | >30 g/kg | [53] |
| | | | Norway spruce sawdust | 5–8 wt% | [51] |
| | | | Norway spruce TMP | 7 wt% | [51] |
| | | | Southern pine TMP | 5 wt% | [51] |
| 1-Ethyl-3-methylimidazoium | Acetate | [EMIM]Ac | Wheat straw | 4 wt% | [50] |
| | | | Miscathus | 4 wt% | [65] |
| | | | Maple wood flour | <5 g/kg | [53] |
| | Diebutyl phosphate | [EMIM][DBP] | Wheat straw | 4 wt% | [50] |
| | Diethyl phosphate | [EMIM][DEP] | Wheat straw | 4 wt% | [50] |
| | | | Cellulose | No data | [59] |
| | Xylenesulfonate | [EMIM][XS] | Sugarcane bagasse | No data | [62] |
| 1-Butyl-3-methylimidazolium | Chloride | [BMIM]Cl | Cellulose | 13 wt% | [33,48,54,66] |
| | | | Wheat straw | 4 wt% | [34,50] |
| | | | Cellulose dissolving pulps | 25 wt% | [45,48] |
| | | | Maple wood flour | >30 g/kg | [53] |
| | | | Cotton cellulose | >10 wt% | [48] |
| | | | Norway spruce sawdust | 8 wt% | [51] |
| | | | Norway spruce TMP | 7 wt% | [51] |
| | | | Southern pine TMP | 5 wt% | [51] |
| | | | Softwood kraft lignin | 13.9 g/L | [46] |
| | Bromide | [BMIM]Br | Cellulose dissolving pulps | 5–7 wt% | [45] |
| | | | Softwood kraft lignin | 17.5 g/L | [46] |
| | Methylsulfate | $[BMIM][MeSO_4]$ | Softwood kraft lignin | 312 g/L | [46] |
| | | | Maple wood flour | 19% | [67] |
| | Tetrafluoroborate | $[BMIM][BF_4]$ | Cellulose dissolving pulps | Insoluble | [45] |
| | | | Maple wood flour | <0.1 g/kg | [53] |
| | Hexafluorophophate | $[BMIM][PF_6]$ | Cellulose dissolving pulps | Insoluble | [45] |
| | | | Maple wood flour | <0.1 g/kg | [53] |
| | | | Softwood kraft lignin | Insoluble | [46] |
| | Tetrafluoromethanesulfonate | $[BMIM][CF_3SO_3]$ | Maple wood flour | <0.1 g/kg | [53] |
| 1,3-Dimethylimidazolium | Methylsulfate | $[MMIM][MeSO_4]$ | Softwood kraft lignin | 344 g/L | [46] |
| | | | Maple wood flour | >0.1 g/kg | [53] |
| 1-Hexyl-3-methylimidazolium | Chloride | [HMIM]Cl | Cellulose dissolving pulps | 5 wt% | [45] |
| | Tetrafluoromethanesulfonate | $[HMIM][CF_3SO_3]$ | Softwood kraft lignin | 275 g/L | [46] |
| 1-Methyl-3-octylimidazolium | Chloride | [OMIM]Cl | Cellulose dissolving pulps | Slightly soluble | [45] |
| 1-Butyl-2,3-dimethylimidazolium | Tetrafluoroborate | $[BM_2IM][BF_4]$ | Softwood kraft lignin | 14.5 g/L | [46] |
| 1-Methyl-3-benzylimidazolium | Chloride | [BZMIM]Cl | Norway spruce TMP | 5 wt% | [51] |
| | | | Southern pine TMP | 5 wt% | [51] |
| | | | Maple wood flour | > 10 g/kg | [53] |
| | Dicyanamide | [BZMIM]Dca | Southern pine TMP | 2 wt% | [51] |
| 1-Methyl-3-m-benzylimidazolium | Chloride | [MBZMIM]Cl | Southern pine TMP | 2 wt% | [51] |
| 1-Methyl-3-methylbenzylimidazolium | Chloride | [MOBZMIM]Cl | Southern pine TMP | 2 wt% | [51] |
| N,N-Dimethylethanolammonium | Acetate | [MM(EtOH)NH]Ac | Cellulose filter paper cotton cellulose | >10 wt% | [48] |
| 1-Ethyl-3-methylbutylpyridinium | Diethyl phosphate | [EMBy][DEP] | Wheat straw | 4 wt% | [50] |
| 1-Butyl-4-methylpyridinium | Hexafluorophosphate | $[BMPy][PF_6]$ | Softwood kraft lignin | Insoluble | [46] |

whilst other ILs containing large non-coordinating anions $[PF_6]^-$ and $[BF_6]^-$ are unsuitable as a solvent for either cellulose [45] or lignin liquefaction [46]. Longer chained substituted ionic liquids [HMIM]Cl and [OMIM]CL also appear to be less efficient at dissolving cellulose [45,46]. At 100 °C, [HMIM]Cl was found to dissolve only 5 wt% of cellulose, whereas [BMIM]Cl dispersed up to 10 wt% of cellulose.

The superiority of [BMIM]Cl in breaking the extensive hydrogen bond network present in cellulose can be attributed to its high chloride anion concentration. Owing to its strong hydrogen-bonding basicity, ILs with elevated chloride anions possesses the capacity to rapidly dissolve greater amounts of cellulose. The poor performance of ILs containing $[PF_6]^-$, and $[BF_6]^-$ anions is attributed to the weak hydrogen-bonding basicity of the $[PF_6]^-$, and $[BF_6]^-$ anions [47]. However, weak activity associated with longer-chained substituted ionic liquids such as [HMIM]Cl and [OMIM]Cl maybe ascribed to a reduction in the effective chloride concentration of these liquids.

### 3.2. Cellulose regeneration and hydrolysis

Cellulose dissolved in ILs can be regenerated by adding an anti-solvent such as acetone, deionized water or alcohol [48,49]. The choice of anti-solvent does not appear to affect the resulting regenerated cellulose [33,50]. The structural differences between the untreated cellulose and regenerated cellulose have been investigated using Fourier transform IR (FT-IR) spectroscopy [48,50–52], X-ray diffraction (XRD) [50,51,53,54], differential scanning calorimetry (DSC) [45,52], size exclusion chromatography (SEC) [45], scanning electron microscope (SEM) [45], nuclear magnetic resonance (NMR) [55,56] and thermogravimetric analysis (TGA) [45,51]. Cellulose regenerated from ILs were found to be essentially amorphous and porous, and more prone to cellulase saccharifications.

The pretreatment of cellulose and lignocellulose with ILs greatly enhanced enzymatic (cellulase) hydrolysis rates compared to untreated substrates [48,50,53,54,57]. However, it has been found that high molecular concentrations of anions in ILs can lead to enzyme inactivation [48,58]. Zhao and co-workers reported finding trace amounts of the IL [BMIM]Cl in the glucose solution following complete hydrolysis of regenerated celluloses [48]. Thorough rinsing of regenerated cellulose samples prior to enzymatic saccharification is highly recommended, and/or use of enzyme compatible ILs [59,60].

### 3.3. Ionic liquid recycling

After cellulose is regenerated from the IL solution the anti-solvent can be evaporated and the IL reused. It has been found that the IL can be reused up to 4–5 times without affecting sugar yields [50,53,61]. Recycling ILs that have undergone cellulose regeneration results in the accumulation of solubilized lignin [53,62]. This lignin may potentially serve as a raw material in the production of polymeric material or as a starting point for catalytic transformation into liquid hydrocarbons.

### 3.4. Enzyme compatible ionic liquids

One of the disadvantages of ILs is their strong tendency to denature enzymes. Because of this regenerated cellulose produced by the pretreatment of cellulose with ILs needs to be recovered and thoroughly washed before enzymatic saccharification. Work by Kamiya et al. [59] investigated '*in situ*' enzyme saccharification of cellulose in enzyme compatible ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate, with the aim of eliminating the need to recover regenerated cellulose. Cellulase was directly added to the aqueous-IL mixture containing cellulose at 40 °C. The ratio of IL to water (citrate buffer pH 5.0) greatly affected cellulase activity. When the volume of IL to water was greater than 3:2, little cellulase activity was observed. However, decreasing the volume ratio to 1:4 (IL:water) enhanced cellulase activity and resulted over 70% of the starting cellulose being converted to glucose and cellobiose [59]. A similar study conducted by Engel et al. [57] revealed cellulase activity of up to 30% on alpha-cellulose in the presence of 10% (v/v) 1,3-dimethylimidazolium dimethylphosphate. Increasing both viscosity and ionic strength led to a decline in enzyme activity.

### 3.5. Acid catalyzed hydrolysis of cellulose and lignocellulose in ionic liquids

Acid catalyzed hydrolysis of cellulose and lignocellulose in IL has also been examined [12,63] as an alternative to enzymatic hydrolysis. Li et al. (2008) found that under mild conditions (100 °C, atmospheric pressure within 60 min) total reducing sugar yields were up to 66%, 74%, 81% and 68% for the hydrolysis of corn stalk, rice straw, pine wood and bagasse, respectively, in [BMIM]Cl in the presence of 7 wt% hydrogen chloride. They also explored the reactivity of other mineral acids in [BMIM]Cl against corn stalks and found that hydrolysis proceeded more effectively with hydrochloric acid > nitric acid > sulfuric acid > maleic acid > phosphoric acid.

An unusual yet novel outcome of their work was discovering that acidic ILs 1-(4-sulfobutyl)-3-methylimidazolium bisulfate $[SBMIM]HSO_4$ and 1-butyl-3-methylimidazolium bisulfate $[BMIM]HSO_4$ could substitute and acts as an acidic catalyst in place of HCl. They found that corn stalk dissolved readily in the ionic liquid forming a solution with lower viscosity, implying that polysaccharide depolymerization readily occurred. However, low total reducing sugar (TRS) yields were obtained (15–23%). Li and co-workers concluded that the strong acidic ILs may not only promote the depolymerization reaction, but also speed up the rate of sugar degradation. They subsequently hydrolyzed corn stalk in [BMIM]Cl and added the acidic ionic liquids $[BMIM]HSO_4$ and $[SBMIM]HSO_4$ which resulted in an increase in TRS yield to 68% and 71% respectively [12].

### 3.6. Concluding remark

ILs could hold the key to unlocking new and exciting processes for the production of biofuels from lignocellulosic materials. From the review it can be seen that ILs have many advantages over traditional solvents, such as their low volatility which arises from them having no vapor pressure, non-flammability, odourlessness and thermal stability. Moreover, because ILs are composed of two parts (anion and cation), they have a superior flexibility to their design that is not available for single molecular solvents.

ILs liquid's ability to dissolve a variety of polar and non -polar materials makes them useful for dissolving the complex structure of lignocellulose. Cellulose dissolution is controlled by the anion component of the IL and that anions such as $Cl^-$, which have high hydrogen bond basicity, can dissolve up to 25% of cellulose due to the formation of hydrogen bonds with the hydroxyl groups of cellulose. Current literature on the use of ILs as a pretreatment in the production of bioethanol showed that the process is very promising because lignocellulose dissolved in ionic liquids can be easily regenerated by the simple addition of an anti-solvent. Regenerated cellulose is amorphous and porous and much more responsive to enzymatic saccharification. Another advantage of using ILs in biomass pretreatment includes the potential for recycling and reuse.

There are several shortcomings of using ILs in biofuel production, especially in process development and optimization. The choice of IL can be a compromise between solubilizing power and enzyme compatibility. The $Cl^-$ anion is a superior anion for biomass dissolution, but also causes enzymes to denature. For an effective integrated bioprocess which would use enzymes *'in situ'* with ILs, additional research on enzyme compatible ILs is required. The review also touched on alternative integrated bio-processing routes for biofuel production via simultaneous acid catalysts of lignocellulosic material in ILs. Additional investigations into acidic ILs, particularly in manipulating the side chains of the cation, may help to reduce the rate of formation of degradation products.

Current ILs research and their use in lignocellulose pretreatment or as part of an integrated bioprocess are obviously in its infancy. Several research gaps and opportunities are clearly evident, for example in characterizing the products of hydrolysis. Owing to the specific action of cellulase enzymes [33], enzymatic hydrolysis does not posses a significant problem. However, traditional acid hydrolysis produces undesirable degradation products such as hydroxymethyl furfural (HMF) and furfural. These products reduce yield and inhibit subsequent fermentation [64]. Confirming that the hydrolysate sugar streams resulting from ionic liquid pretreatment of lignocellulose are suitable for fermentation is also an area that requires further research.

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