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# Utilization of Ionic Liquids in Wood and Wood-Related Applications — A Review

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## 1. Introduction

The development of potentially “green” technologies based on renewable feedstock’s is one of the main challenges for mankind in the next decades and centuries underlining the social and economic importance of research conducted in this area [1]. Wood is one of the most versatile biological raw materials that is available today in large, renewable reserves around the world. Wood products have countless important industrial applications, such as in design, furniture and construction. These applications have a bright future ahead. At the same time, chemical and mechanical wood processing provides the basis for a growing range of globally significant fiber-based tissue, paper and packaging applications and solutions. At the sharp end, advances in the use of the individual chemicals and polymers that make up wood are creating the foundation for future biorefineries and helping change the shape of society for the better. The human use of wood reaches back thousands of years. The nowadays escalating global population and limited natural resources, however, call for new ways of improving the efficiency of our use of this vital natural resource. This opens up significant opportunities for products based on renewable, non-food materials (‘non-food bio-products’) [2].

In addition, the fading fossil resources with the simultaneously increasing demand for global energy and arising environmental concerns generate a strong need for new technologies based on renewable and inexhaustible resources. Thus in the face of the current oil prices and the sustainability challenges, the bio-economy concept is the fast winning ground. The question arises, can we increase the share of “consumer products” using renewable raw materials, like wood, instead of the non-renewable resources, like oil? The forest-based industry sees this opportunity and believes that the industry will play a decisive role in the development towards a bio-economy. With this goal in sight, diversifying the product output of the primary wood

refining process – pulping – is a rational strategic starting point. The pulp mills of today are being redefined as the biorefineries of tomorrow [2].

Fossil fuel resources are limited so alternative renewable resources are needed to fill the gap that inevitably will be created once the fossil resource supplies start to dwindle. Biomass has the potential to fill this gap. To utilize this renewable resource in the production of fuel and chemicals, the so called “biorefineries” specialized in fractionation and making use of all components of the biomass are needed [3].

The development of potentially “green” technologies based on renewable feedstocks is one of the main challenges for mankind in the coming years underlining the social and economic importance of research conducted in this area. On this regard, biomass is expected to have the potential to fill the gap of the dwindling fossil fuel resources. Replacement of fossil fuels with new sustainable resources is becoming crucial due to the depleting petroleum reserves, increasing global energy demand, and arising environmental concerns. In particular, lignocellulosic biomass can be an alternative to fossil resources as a sustainable and environmentally-friendly feedstock for producing chemicals and fuels. However, today, only a small portion of the world’s annual production of biomass is utilized by mankind, while the rest is allowed to decay naturally.

With the inevitable depletion of petroleum-based resources, there has been an increasing worldwide interest in renewable resources such as biomass. One reason for the current approaches being taken to utilize biomass is the difficulty in processing lignocellulosic materials and the energy needed for separation of their components. The three major components of biomass (cellulose, lignin, and hemicellulose) are covalently bonded together, which makes dissolution and further separation of these components difficult. This has been recognized as the grand challenge for biomass utilization [4]. Ionic liquids (ILs) are relatively new family of solvents for dissolution of cellulose and could aid in this task.

The use of ILs for cellulose dissolution stems from the unique properties of these solvents to interact with the strong hydrogen bonds of polysaccharides. The scientific discovery of the dissolution of cellulose in ILs is being translated into new processing technologies, cellulose functionalization methods and new cellulose materials including blends, composites, fibers and ion gels. These materials can replace current analogs to overcome the environmental issues associated with petroleum-based products. Although there are many ILs available that can dissolve cellulose, the processing difficulties such as fractionation need to be overcome to support large-scale use. The dissolution and functional modification of cellulose in ionic liquids based on previous researches have been reviewed and summarized by reference [5]. However, due to the chemical versatility of both cellulose and ILs new developments leading to the next generation of cellulosic materials are expected in the near future [6].

Dissolution of cellulose in ILs allows the comprehensive utilization of cellulose by combining two major “green” chemistry principles; using environmentally-preferable solvents and bio-renewable feed-stocks. However, the utilization of cellulose or cellulosic materials has not been developed entirely because of its poor solubility in common organic solvents. But the cellulose dissolved in ILs can be regenerated with anti-solvents such as water, ethanol and acetone.

Ionic liquids are organic compounds that contain at least one ionic bond. ILs consist of organic cations and organic or inorganic anions. ILs are salts with melting points below 100 °C, which possess many advantageous properties. Moreover, ILs are non-volatile, non-toxic, nonflammable and thermally and chemically stable. Due to their larger molecular radii, ILs exhibit only weak cohesion compared with common salt.

In 2002, it was discovered that cellulose is soluble in ILs. Later ILs have been investigated as powerful solvents and reaction media for cellulose in its pure form and in its naturally surrounding matrix including hemicelluloses and lignin. ILs can dissolve cellulose as well as remove or reduce the lignin content in lignocellulosic materials. But it was shown that these solvents are not entirely inert and thus have to be selected carefully.

Hundreds of papers have been published in the literature in the past few years alone. Some ionic liquids such as [Amim]Cl and [Emim][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 [7].

Investigation of the dissolution mechanism of lignocellulose in ILs revealed an ongoing degradation of the solute in dependence of temperature and solvent purity. Finally, ILs were shown capable to significantly reduce the energy demand of mechanical crushing steps in wood-based technologies as a consequence of their lubricating nature [1].

The bulk of the cellulose currently employed by industry is isolated from wood through Kraft pulping; a process which traditionally involves a barrage of environmentally detrimental chemicals and is undeniably “non-green”. 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 [8].

A promising new pretreatment method for lignocellulosic materials relies on their solubility in solvent systems based on ILs and the interaction of natural polymers (present in wood) with ILs. The precipitated cellulose and lignin act as a natural binder for the wood particles thus avoiding the use of toxic organic resins as adhesives. The obtained composites present good water stability and compressive mechanical strength. Additionally, carbohydrates are important natural products that play important biological and commercial roles as food, drug and chemical feedstock. However, the use of natural carbohydrates has two main drawbacks: low solubility in most solvents and their complex highly chiral structures [9].

Lignin, a readily available form of biomass, is a potential source of renewable aromatic chemicals through catalytic conversion. Recent work has demonstrated that ILs are excellent solvents for processing woody biomass and lignin. Seeking to exploit ILs as media for depolymerization of lignin, the reactions of lignin model compounds in or with ILs has been investigated [10].

Looking at the solubility of lignocellulosics in ionic liquids, a thorough literature review was performed by reference [11]. The survey combined with additional screening of a range of in-house ionic liquid structures allows identifying potential opportunities with regard to efficiency of cellulose and lignin dissolution as well as wood fibrillation.

Ionic liquids have shown great potential in the field of biomass processing in general and in the pretreatment of lignocellulose in particular. However, a few things need to be addressed before any large-scale processing can be considered: Finding new routes for IL synthesis that make “on-site” production possible; investigation into the challenges facing IL pretreatment of lignocellulose such as possible depolymerization of cellulosic material during the pretreatment and investigating what influence different ILs have on the pretreatment of cellulosic material by methods like enzymatic hydrolysis [3].

Lignocellulose dissolution in ILs is a relatively new biomass pretreatment technology that is receiving growing interest from the biofuels community as a route to provide readily-hydrolyzable holocellulose. Despite its proven advantages over other pretreatment technologies – including feedstock invariance, high monomeric sugar yields over short saccharification times and extensive delignification– there are several core issues that stand in the way of commercialization. These include the relative high cost of the ILs themselves, a lack of knowledge in terms of process considerations for a biorefinery based on these solvents, and scant information on the coproducts this pretreatment technology could provide to the marketplace. An initial techno-economic model of a biorefinery that is based on the IL pretreatment technology has been presented and identified by reference [12], through a comprehensive sensitivity analysis, the most significant areas in terms of cost savings/revenue generation that must be addressed before IL pretreatment can compete with other, more established, pretreatment technologies. This new pretreatment technology has been evaluated through the perspective of a virtual operating biorefinery, and although there are significant challenges that must be addressed, there is a clear path that can enable commercialization of this novel approach.

Although some basic studies of ILs, such as their economical syntheses and toxicology are eagerly needed and some engineering problems still exist, research for application of ILs in wood-related industries has made great progress in recent years. The use of ILs has provided a new platform for efficient utilization of wood. A comprehensive database on toxicity of ILs has been established by reference [13]. The database includes over 4000 pieces of data. Based on the database, the relationship between IL's structure and its toxicity has been analyzed qualitatively. Furthermore, quantitative structure-activity relationships (QSAR) model has been conducted to predict the toxicities ( $EC_{50}$  values) of various ILs toward the Leukemia rat cell line IPC-81.

In this chapter, applications of ILs in wood and wood-related industries are reviewed. First, the use of ILs in wood preservation and the improvement of wood anti-electrostatic and fire-proof properties are illustrated. The dissolution of wood main constituents (cellulose, lignin, and hemicellulose) in ILs and its application are described along with “green” wood processing with ILs. Finally, application of ILs in dissolution of wood biomass and product retrieval media are briefly reviewed. A summary table of the abbreviations of the ionic liquids used in this chapter is presented in the Appendix.

## 2. Ionic liquids as wood preservatives

Wood is a widely-used, economical, and renewable building resource. However, untreated wood is subject to attack by insects and microorganisms, for example, decay, stain, mould fungi, and bacteria. To ensure long-term structural performance, wood must be protected from biotic wood degradation factors. Preserved wood can be defined as lumber or plywood that has been treated with wood preservatives to protect it from termites and fungal decay. Many preservatives have been used in wood industry, and still many efforts are made to develop new preservatives. The reason is that most of the wood preservatives in current use are chemicals that might be harmful to human health or are not eco-friendly [14].

Natural fibers are made up from different components; cellulose, hemicellulose and lignin are the main elements, but many natural fibers also contain pectin, small amounts of ash and may exhibit a thin wax layer on the surface [15]. Lignin is a 3-D, heavily cross-linked copolymer with aliphatic and aromatic structures. The aromatic structures are formed by the removal of water from a sugar unit. Several monomers can form lignin and the types and properties depend on the source material. In contrast to cellulose and hemicellulose, lignin is hydrophobic in nature. Together with the hemicellulose, it provides matrix for the strong cellulose fibrils [16]. Lignin also resists most microorganisms and its aerobic breakdown is slow, and therefore it protects the load bearing cellulose from a premature degradation [17,18].

Different types of lignin can be found in different plants and even within different plant structures. This can have a strong effect on not only biodegradation but also susceptibility to microbial activity and therefore fiber-retting during fiber processing [19].

Like cellulose, lignin is considered one of the most abundant bio-polymers of the world. However, to date, most of the industrially processed lignin is mainly used as an energy source for the paper industry and finds only few industrial applications [20]. Lignin is hydrophobic in spite of being completely amorphous. Lignin is found in close proximity to the cellulose micro-fibrils in natural fibers [21]. The varying interaction of cellulose, hemicellulose and lignin with moisture is responsible for the complex swelling behaviour of natural fibers [16].

ILs have shown great potential in becoming the eco-friendly, as well as free of both arsenic and pentachlorophenol, and yet they also show effectiveness as wood preservatives. An extensive research has been done on this subject in [22-24]; ILs in wood preservation has been addressed in [22] and protic ILs with organic anion as wood preservative has been discussed in [23]. Some ILs with a nitrate counter ion, such as 3-alkoxymethyl-1-methyl-imidazolium tetrafluoroborates and hexafluoro-phosphates, didecylmethyl-ammonium and benzalkonium nitrates, exhibited good fungicidal activity and could be potential candidates as wood preservatives [24]. In addition, the use of ILs in strategies for saving and preserving cultural artifacts has been discussed in [25].

On the other hand, four pyridinium-based ILs have been successfully tested in [26] as components of potential wood preservatives: 1-alkoxymethyl-3-dimethylamino-pyridinium chlorides, 1-alkoxymethyl-4-dimethylamino-pyridinium chlorides, 1-alkoxy methyl-3-dimethylamino-pyridinium acesulfamates and 1-alkoxymethyl-4-dimethylamino-pyridinium

acesulfamates. These ILs are new biocides that penetrate well into wood. The tested pyridinium ILs with an alkoxyethyl substituent, consisting of 8, 9 or 10 carbon atoms, exhibited fungicidal activity against the basidiomycetes *Coniophora puteana* and *Trametes versicolor* and the blue-stain fungus *Sclerophoma pityophila*.

However, the doses and toxic values of tested 1-decyloxymethyl-4-dimethylamino-pyridinium chloride and acesulfamate were found comparable with benzalkonium chloride and didecyl dimethyl ammonium chloride but the ILs tested were found largely unextractable from wood by water [26]. The mechanical properties of the wood treated with the former two ILs were lower than natural wood. Wood treated with the chloride and acesulfamate was, however, characterized by lower absorption of free water than the control wood. Only in the case of treatment with acesulfamate was the hygroscopicity of the treated wood distinctly lower than that of control wood. The durability of the wood was increased by 1-decyloxymethyl-4-dimethylamino-pyridinium chloride and acesulfamate.

Due to the high interest in the applications of ILs, new, cheaper, multifunctional ILs which are easy to prepare are highly desired. A new group of air- and moisture-stable, hydrophobic ammonium-based ILs and their properties, including the single-crystal X-ray structure of benzethonium nitrate has been presented in [24]. These salts have utility as anti-bacterial, anti-fungal agents. Additionally, the potential application of these ILs for wood preservation was tested with positive results. The toxicity of benzalkonium and didecyl dimethyl ammonium nitrates were studied and are presented therein.

Ranke [27] presented tabulated and referenced data to show that the use of conventional molecular solvents as a reference for IL toxicity to microorganisms and cell cultures has become common practice. On the other side of the activity spectrum, both cationic surfactants with antimicrobial or germicidal activity and reactive biocides have been chosen for convenient comparison of biological effects. The numerical results given in these studies suggest that IL toxicities toward microorganisms and cell cultures cover the whole range of biocidal potencies from rather inactive molecular solvents, such as ethanol or dimethyl sulfoxide that are biocompatible up to very high aqueous concentrations, up to highly active biocides, leading even to the proposal of some ILs as wood preservatives [23]

The use of ILs has provided a new platform for efficient utilization of wood. The applications of ILs in wood-related industries have been reviewed by [14]: dissolution of wood in ILs and its application, ILs used for wood preservation and improvement of wood anti-electrostatic and fire-proof properties, and finally, 'green' wood processing with ILs.

ILs with low hydrogen-bond basicity are not able to break the hydrogen bonds in the matrix and therefore do not expand it at all or only minimally, as observed for [Bmim][OTf] IL at 120°C. Since these ILs cannot dissolve the cellulose fibers, the wooden ultrastructure is preserved and no extraction is observed [28].

The wettability of wood surface protected with three ILs differing in terms of cation and anion structure as well as fungicidal properties has been tested and measured by [29]. [Ciech][1] IL with didecyl dimethyl ammonium cation and herbicidal anion; [DDA][ABS] didecyl dimethyl ammonium dodecyl benzene sulfonate, and [ArqC35][NO<sub>3</sub>] nitrate(V) with cation derived

from natural coconut oil. The tests were carried out on *Pinus sylvestris* L. wood. The results indicated that the ILs containing 12-carbon hydrophobic alkyl chain in their structure, i.e. [DDA][ABS] and [ArqC35][NO<sub>3</sub>], worsened wood wettability, thus improved the protection of wood against water.

The results of tests on the effectiveness of the action of a new group of synthesized biocidal ILs are presented in [30]. These ILs are derivatives of the leading structure, i.e. didecyl dimethyl ammonium nitrate, and demonstrated strong action against mould fungi. Natural quaternary ammonium salts, mainly extracts from coconut and soybean, and from vegetable fats, were the basis for syntheses. Mycological tests were carried out on the *Pinus sylvestris* L. sapwood in accordance with the method assumed binding for the assessment of biocide efficacy.

The impregnation of wood with wood preservatives may have an influence on its physical and mechanical properties. The knowledge about the character of that influence is of great importance for characterisation of functional properties of wood and, as a consequence, determination of its use classes. The ILs of imidazolium tetrafluoroborates series, which penetrate very well into Scots pine wood, are active against wood-destroying fungi and generally have a positive, although insignificant, influence on physical and mechanical properties of wood, especially on its resistance to colour change during exposure to light. However, various ILs may differ widely in that respect. A research has been carried out in [31] to clarify the influence of dodecyl dimethyl ammonium nitrite, [DDA][NO<sub>2</sub>], and IL with dodecyl dimethyl ammonium cation and anion of herbicide character, [DDA][herbicide], on selected physical and mechanical properties of Scots *Pinus sylvestris* L. wood. The miniature sapwood samples were subjected to sorption with the ILs by vacuum method.

Strongly hydrophobic ammonium ILs penetrating the wood structure and protecting solid wood from water absorption have been developed by [32] and found that by covering the surface of the wood with ammonium IL, the wood became hydrophobically and antiseptically protected for a long time. The swelling and water absorption of the protected wood was several times less compared to unprotected wood and its dimensional stability was also improved.

The application of didecyl dimethyl ammonium nitrate, [DDA][NO<sub>3</sub>], and benzalkonium nitrate, [BA][NO<sub>3</sub>], ILs in preservation of panels resistant to biotic factors has been investigated by [33]. The method for application of ILs to particleboards, the type and amount of chosen ILs, as well as their influence on standard parameters of the panels were also investigated. The amine resin available on the domestic market and particles obtained from debarked Scots pine chips were used in the tests. The results demonstrated that ILs worsened parameters of the panels, but improved their resistance to decay fungi.

The subject of wood finishes that are often used to improve the durability of wood by protecting it from scratching and wearing, minimizing swelling when in contact with water or acting as UV stabilizers for lignin and cellulose has been addressed by [34]. Traditional wood finishes include tung oil or polymerized linseed oil-based products, wax, shellac, rosin, paraffin, synthetic polyurethane, acrylic resin and epoxy-based products. One disadvantage of traditional wood finishes include the use of volatile organic solvents, such as toluene, acetone, or ethanol-acetone mixtures, which are expensive and possess an environmental risk,



also by their capacity to transform their selves in the atmosphere, under the influence of UV radiation and the catalytic action of the nitrogen oxides, in more aggressive species with carcinogenic potential. As consequence, the replacement of the traditional volatile solvents from wood industry with less toxic and volatile solvents became an important aim for the scientists working both in material science and in environmental protection.

The solubility of four frequently used wood finishing products, namely Paraloid B72 thermoplastic resin, paraffin, rosin and bees wax in three types of alkylimidazolium-based ILs: [Bmim]Cl, [Hmim][BF<sub>4</sub>] and [Hmim][PF<sub>6</sub>], at 23 °C and 90 °C, by using the turbidimetric method also determined by [34] and found that the selected ILs were able to dissolve the respective wood finishes, in amounts higher than those achieved by using traditional volatile organic solvents. It was also found that the solubilities of Paraloid B72 in these ILs are higher than those reported for the traditional organic solvents. For paraffin, rosin and bees wax the obtained solubilities are similar to those reported by using volatile organic solvents. Taking into account that the studied ILs are non-volatile, electrically conductive, that they possess anti-fungal character and they are able to plastify wood, their use as solvents for finishes could impart some useful properties to the treated wood, such as higher workability and durability.

The influence of the two ILs [Bmim][BF<sub>4</sub>] and [Bmim][PF<sub>6</sub>] on the properties of sycamore maple (*Acer pseudoplatanus*) veneers at different temperatures by using contact angle measurements and Fourier transform infrared spectroscopy analysis has been studied in [35]. The measurements showed that the wood wettability is increased by IL treatment. It has been determined that the ILs decrease the crystallinity and improve the flexibility of the cellulose matrix. Also, it has been determined that at 60 °C and 80 °C delignification of wood occurred, thus making the studied ILs useful alternatives to traditional toxic and expensive reagents used in wood industry.

The Wood Technology Institute in Poznan (Poland) conducts innovative research on the use of ILs (derivatives of quaternary ammonium salts) in wood preservation technology and wood materials in order to increase the sustainability of wood. The research resulted in the development of "multi-tasking" fungicides, which are alternative to commercial wood preservatives that are environmentally toxic and contain heavy metals. One of the goals of such research is the development of innovative technologies of increasing durability of wood and composite wood materials using ILs. This goal has been established through the development of bioactive derivatives of azoles in the form of ILs in order to intensify biocidal activity, increase penetration, and minimize the necessary amount of these biocides introduced to protect lignocellulosic materials [36]. The activity of azole-derivative ILs against decaying *Coniophora puteana* fungus (pine *Pinus sylvestris* L.) have been determined. Thanks to innovative solutions, a new type of biodegradable biocides with low threshold values against fungi and bacteria (pathogens of wood) was developed. The threshold values for [Azole][Cytr] are ED<sub>50</sub>: 1 ppm; ED<sub>100</sub>: 10 ppm; LD: 50 ppm, and for [[Azole][HCl] are ED<sub>50</sub>: < 0.1 ppm; ED<sub>100</sub>: 5 ppm; LD: 5 ppm. These biocides have significant economic and environmental effects and at the same time no adverse effects on humans. The result is an original in the world. The ILs used in the tests were prepared in the Poznan University of Technology laboratory, according to the method described by [30]. The main substances used in the tests were didecyldimethyl ammonium

nitrite ([DDA][NO<sub>2</sub>]) and IL with didecyl dimethyl ammonium cation and anion of herbicide character ([DDA][herbicide]). The concentration of each of the tested ILs was 91–97% and they were easily dissolved in propanol-2 and water-propan-2-ol mixture. The FTIR spectra of the treated wood confirmed the bond of ammonium ILs to wood. Formation of ammonium carboxylate in the chemical structure of wood and wood modification by long alkyl chain was observed [36].

The use of ILs in protecting technologies for wood-based panels and plywood allowed development of novel protic ILs that can be used as hardeners of adhesive amine resins [36]. The designed structure of these compounds, their parallel multi-activity, plays a role in curing resins and biocides, which is extremely desirable in the process of protection of wood materials. It was concluded that (1) the innovative nature of proposed solutions lies in creating stable and sustainable, deeply wood-penetrating new ILs as wood preservatives of specific properties with respect to microorganisms responsible for wood degradation, and at the moment of (insignificant) wood leaching easily degradable by the micro-flora in soil and water environment; (2) the results of physico-chemical research on the effect of ILs on material allowed identification of bonds of new biocides and wood, which is indispensable for identifying application of ILs in wood preservation; and (3) the ability of combining ILs with other biocides, e.g. boron or copper compounds, is an offer of new generation of antifungal preparations for the chemical and wood industries as well as building construction [36].

The biotic properties of novel structure of tebuconazole IL derivatives: tebuconazole hydrochloride, allyl tebuconazole chloride, methyl tebuconazole iodide, tebuconazole dihydrocitrate have been examined in [37]. Their investigation against wood-degrading fungi contained also the dodecyl dimethyl ammonium 3-aminotriazolate as well as didecyl dimethyl ammonium nitrate(V), [DDA][NO<sub>3</sub>], with tebuconazole or with (tebuconazole+propiconazole). It was found that the most active compound against brown and white rot fungi were precursor of ILs tebuconazole hydrochloride. The fungistatic dose (ED<sub>50</sub>) for *Coniophora puteana* reached 0.1 ppm, the fungitoxic dose (ED<sub>100</sub>) 5 ppm and the lethal dose (LD) 5 ppm. The fungicidal value of didecyl dimethyl ammonium nitrate(V) with tebuconazole for *Coniophora puteana* were < 0.73 kg/m<sup>3</sup>, for *T. versicolor* ranged from 0.81 kg/m<sup>3</sup> to 1.76 kg/m<sup>3</sup>. The investigation of protic triazole-based ILs demonstrated the strongest action against blue stain and mold fungi. The growth of mycelium on the surface of wood samples was inhibited in the amount of application 15 g/m<sup>2</sup>. The penetration depth into Scots *Pinus sylvestris* L. wood of didecyl dimethyl ammonium nitrate(V) including the tebuconazole reached 6.2 mm [37].

It was also found that the most active compound against brown and white rot fungi were precursor of ILs tebuconazole hydrochloride [37]; the fungicidal values for *C. puteana* and *T. versicolor* reached was < 0.2 kg/m<sup>3</sup>. In the case of tebuconazole dihydrocitrate the biocidal activity for *T. versicolor* was at the level of 0.86–1.38 kg/m<sup>3</sup>. Ammonium-based ILs with a cation containing a substituent derived from coconut oil exhibited fungicidal values against *C. puteana* at levels ranging from 2.7 to 4.6 kg/m<sup>3</sup>. Dissolution of 15% tebuconazole or its mixture with propiconazole in didecyl dimethyl ammonium nitrate or nitrite reinforced the biocidal action of this compound (<0.73 kg/m<sup>3</sup> for *C. puteana*) and increased the penetration depth into wood up to 6.2 mm. This allowed effective protection of processed wood against blue stain

fungi comparable with the reference preparation of Sadolin base (150 g/m<sup>2</sup>). Quaternary tebuconazole derivatives with methyl and allyl substituents demonstrated a slightly weaker fungicidal action than tebuconazole. The majority of the examined salts were characterized by a strong anti-mould action when only 15 g/m<sup>2</sup> were applied onto the surface of pine wood. Hydrophobic ILs did not undergo leaching from treated wood. Water-soluble triazole-based ILs with 3-aminotriazolate anion got fixed in treated wood. The ATR spectra analysis of treated Scots pine wood indicated the presence of the cation [DDA]<sup>+</sup> and the 3-aminotriazolate anion in the structure of wood. The positive results of the investigations of the novel functional ILs presented in this study make their potential application in wood protection possible [37].

A very interesting group of ILs is that with a long chain quaternary ammonium cation. They are formed by direct synthesis or by an anion-exchange reaction in quaternary ammonium halides. Popular and cheap precursors for the preparation of ILs are dodecyl dimethyl ammonium chloride and benzalkonium chloride. These compounds have biological activity and are widely used in industry [38]. Use of cations with long alkyl chains suggests that the resulting ILs will have biocidal and wood preservative properties [39,40]. It has been found that didecyl dimethyl ammonium and benzalkonium bisulfates (IV), propionates, sorbates and undecyls are hydrophobic compounds and thus have the ability to preserve wood and refresh its surface [38].

A study aimed at improving the functionality of linen fabric by antimicrobial finishing with the use of IL, i.e., quaternary ammonium salt has been carried out in [41]. Antimicrobial activity of ILs strongly depends on their structure. The study included testing the susceptibility of linen fabric protected with didecyl dimethyl ammonium nitrate, [DDA][NO<sub>3</sub>], IL to the biodegradation process with special attention paid to fungi resistance. Finished linen fabric was tested in relation to the action of five mildew mixtures. The degree of microorganism growth and its effect on physico-mechanical properties of the fabrics were evaluated. The antimicrobial effectiveness of the IL applied to linen fabric was determined by the use of SEM. Applying this biocide in the finishing processes of natural textile materials allows the attainment of antimicrobial barrier properties.

The influence of three types of imidazolium chlorides ILs, namely, [Bmim]Cl, [Hmim]Cl, and [Dmim]Cl, on the surface properties of wood (*Populus sp.*) veneers has been studied in [42] by using contact angle and electrical conductivity analysis. The measurements showed that wood wettability has increased by IL treatment, thus enabling a higher compatibility of wood with polar additives or adhesives. The electrical conductivities of treated wood by the method presented in [42] are in the 0.8-1.65 mS/cm range, higher than the ones reported in the reference literature, which confers the treated wood anti-electrostatic properties. The treatment of wood veneers with ILs could be useful in improving the workability of wood by decreasing its rigidity, and in preventing the build-up of static electric charges on the surface of the wood during finishing, as well as improving its wettability, thus increasing its compatibility with polar adhesives or additives. Still further studies need to be conducted in order to assess also the influence of weathering conditions (humidity, temperature, UV irradiation) and duration on the surface properties of the wood treated with ILs. Another direction of study should focus on evaluating the antibacterial properties of the wood treated with the selected ILs, in order

to have a complete overview of the plethora of useful properties that IL treatment may impart to wood materials [42].

### 3. Dissolution of wood biomass in Ionic liquids

Dissolution of wood biomass in common solvents is practically difficult due to the 3-D network structure of lignin which binds the plant cells together, providing mechanical strength to it. Therefore, to break this network and for further wood biomass processing, various types of methods have been used to manipulate its properties for various applications. But each of these methods has some drawbacks. Biological methods require long time of treatment [43]. Physical methods (mechanical milling) are energy demanding, expansive and ineffective in complete removal of lignin. Chemical methods (acid or base treatment) are costly and not environmentally benign [44]. Physiochemical methods (steam explosion), even though considered as very promising methods require high pressures/ temperatures and the use of catalysts [45].

Cellulose is one of the most abundant biological and bio-renewable materials in the world, with a long and well-established technological base. Derivatized products have many important applications in the fiber, paper, membrane, polymer, and paints industries. The application of cellulose is widely distributed among various industries such as fiber, paper, pharmaceutical, membrane, polymer and paint. However, the utilization of cellulose or cellulosic materials has not been developed entirely because of its poor solubility in common organic solvents. Cellulose dissolved in ILs can be regenerated with anti-solvents such as water, ethanol and acetone. It was pointed out that dissolved pulp cellulose (subjected to certain heating methods) is soluble in [Bmim]Cl, [Bmim]Br, [Bmim][SCN], and [Hmim]Cl; insoluble in [Bmim][BF<sub>4</sub>] and [Bmim][PF<sub>6</sub>]; and slightly soluble in [Omim]Cl [46].

The efficient dissolution of cellulose is a long-standing goal in cellulose research and is still of great importance. Cellulose can be dissolved in several ILs and can easily be regenerated by contacting with water. A short survey of the relevant literature with respect to historical developments and potential industrial uses of ILs is given in [47], which then proceeded to the latest results in cellulose/IL chemistry. The dissolution and reconstitution experiments, fiber characteristics and molecular mass distribution data have been also described in [47].

Dissolution of cellulose with ILs allows the comprehensive utilization of cellulose by combining two major green chemistry principles: using environmentally preferable solvents and bio-renewable feed-stocks. The dissolution of cellulose with ILs and its application is reviewed in [48] and found that (1) cellulose can be dissolved, without derivation, in some hydrophilic ILs, such as [Amim]Cl and [Bmim]Cl; (2) microwave heating significantly accelerates the dissolution process; (3) cellulose can be easily regenerated from its IL solutions by addition of water, ethanol or acetone; and (4) the ILs can be recovered and reused after its regeneration. Typical applications include fractionation of lignocellulosic materials and preparation of cellulose derivatives and composites. It was concluded that although economical syntheses and toxicology of IL studies are still much needed, commercialization of these processes has made great progress in recent years [48].

It was demonstrated that both hardwoods and softwoods are readily soluble in various imidazolium-based ILs under gentle conditions [49]. More specifically, a variety of ILs can only partially dissolve wood chips, while ILs such as [Amim]Cl and [Bmim]Cl have good solvating power for Norway spruce sawdust and Norway spruce and Southern pine thermo-mechanical pulp (TMP) fibers. Despite the fact that the obtained solutions were not fully clear, these ILs provided solutions which permitted the complete acetylation of the wood.

Alternatively, transparent amber solutions of wood could be obtained when the dissolution of the same lignocellulosic samples was attempted in 1-benzyl-3-methylimidazolium chloride, [Bzmim]Cl. This realization was based on a designed augmented interaction of the aromatic character of the cation of the IL with the lignin in the wood. After dissolution, wood can be regenerated as an amorphous mixture of its original components. The cellulose of the regenerated wood can be efficiently digested to glucose by a cellulase enzymatic hydrolysis treatment [49]. It was thus demonstrated that the dissolution of wood in ILs now offers a variety of new possibilities for its structural and macromolecular characterization, without the prior isolation of its individual components. Furthermore, considering the relatively wide solubility and compatibility of ILs with many organic or inorganic functional chemicals or polymers, it is envisaged that this research could create a variety of new strategies for converting abundant woody biomass to valuable biofuels, chemicals, and novel functional composite biomaterials [49].

A simple and a novel alternative approach for processing of lignocellulosic materials that relies on their solubility in solvent systems based on the IL [Bmim]Cl has been presented in [8]. Dissolution profiles for woods of different hardness are presented, making emphasis on the direct analysis of the cellulosic material and lignin content in the resulting liquors. The cellulose obtained can be readily reconstituted from the IL-based wood liquors in fair yields by the addition of a variety of precipitating solvents. Spectroscopic and thermogravimetric studies indicated that the polysaccharide obtained in this manner is virtually free of lignin and hemicellulose and has characteristics that are comparable to those of pure cellulose samples subjected to similar processing conditions.

The effect of the anion of ILs on air-dried pine (*Pinus radiata*) dissolution has been investigated in [28]. All ILs used in that study contained the 1-butyl-3-methylimidazolium cation; the anions were trifluoromethane sulfonate, methyl sulfate, dimethyl phosphate, dicyanamide, chloride and acetate. Using a protocol for assessing the ability to swell small wood blocks (10 × 10 × 5) mm, it was shown that the anion has a profound impact on the ability to promote both swelling and dissolution of biomass. Time course studies showed that viscosity, temperature and water content were also important parameters influencing the swelling process. The Kamlet-Taft parameters were used to quantify the solvent polarity of the ILs and found that the anion basicity described by the parameter  $\beta$  correlated with the ability to expand and dissolve pine lignocellulose. It was shown that 1-butyl-3-methylimidazolium dicyanamide, [Bmim][DCA], dissolves neither cellulose nor lignocellulosic material. It was also shown that the lignocellulosic components, particularly the carbohydrate polymers, are rich in hydroxyl groups and the IL anions that can strongly coordinate these hydroxyl groups (high  $\beta$ ), are able to weaken the hydrogen-bonding interactions in the wood matrix and allow the chips to expand [28].

A challenge in producing wood-plastic composites (WPCs) with a high wood content using extrusion processes is the poor processability, which gives rise to inadequate properties of the resulting WPC. Plasticizing the stiff wood cell walls can be a strategic response to this challenge. Two thoughts to improve the plasticity of wood particle cell walls: use of ILs or use of low molecular weight organic thermal conductors is addressed in [50]. An IL can dissolve the cell wall surface and therefore reduce the stiffness of the cell wall during the extrusion process. Incorporation of ILs can also impart anti-microbial and antistatic properties to the resulting composites, as well as improving the fire retardancy and resistance against fungal decay. However, high cost and leachability of ILs are the main issues that impede their application in wood-plastic composites (WPCs) processes. In addition, ILs exhibit extremely high polarity and can absorb moisture from surrounding environment, which may cause dimensional instability of the resulting WPC. The presence of ILs may also cause the formation of a weak interfacial layer between wood particles and plastic matrices [50].

One other achievement of the Wood Technology Institute in Poznan (Poland) project was the development of a method for cellulose isolation from lignocellulosic raw materials using developed new morpholine ILs. The project focused on development of a novel method of dissolving papermaking raw materials and semi-finished products in ILs in order to extract the carbohydrate from the lignin fraction and ultimately obtain cellulose from a chemical-morphological conglomerate that wood is. The results of the investigation of application of ILs blends as cellulose solvents is expected to be an innovative R&D trend in the forest-based sector [36].

An ideal IL for cellulose transformation should possess the following properties: (1) high dissolution capacity for cellulose; (2) low melting point; (3) good thermal stability; (4) non-volatile; (5) non-toxic; (6) chemically stable; (7) no cellulose decomposition; (8) easy cellulose regeneration, and (9) low cost and simple process [51]. Imidazolium is one of the most commonly used cations of ILs, while anions include quite a number such as chloride, hexa-fluorophosphate, tetrafluoroborate and others. To improve the solubility of cellulose and lignocellulose in ILs, it is important to optimize the suitable anions and cations in ILs, sometimes necessitating structural modifications [52].

The dissolution of cellulose and lignocellulose in various ILs including key properties such as high hydrogen-bonding basicity, which increases the ability of the IL to dissolve cellulose has been described in the review by [9]. As a pretreatment in biofuel production, the review in [9] details aspects such as the regeneration of cellulose from ILs, 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. The review in [9] also presented the solubility of assorted lignocellulosic material and constituent polymers using different ILs. The outcomes clearly show that some ILs such as [Bmim]Cl are beneficial in dissolving biomass samples (cellulose solubility of up to 25 wt.%), whilst other ILs containing large non-coordinating anions [PF<sub>6</sub>]<sup>-</sup> and [BF<sub>4</sub>]<sup>-</sup> are unsuitable as a solvent for either cellulose [46] or lignin liquefaction [53]. Longer chained substituted ILs such as [Hmim]Cl and [Omim]Cl also appear to be less efficient in dissolving cellulose [46,53]. 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 discovery of [Bmim]Cl, which is reported to completely dissolve cellulose without the formation of derivatives, has created a basis for studying the use of ILs in wood processing. This finding paved the way for a many studies on interactions between cellulose and ILs [54]. 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 possess the capacity to rapidly dissolve greater amounts of cellulose [9]. The poor performance of ILs containing [PF<sub>6</sub>]<sup>-</sup> and [BF<sub>4</sub>]<sup>-</sup> anions was attributed to the weak hydrogen-bonding basicity of these anions [55]. However, weak activity associated with longer-chained substituted ILs such as [Hmim]Cl and [Omim]Cl may be ascribed to a reduction in the effective chloride concentration of these ILs [9].

ILs based on polar organic solvents such as dimethyl formamide (DMF), dimethyl acetamide (DMAc), dimethyl imidazolidinone (DMI) or dimethyl sulfoxide (DMSO) and usually coupled with charged species such as LiCl, are frequently used for dissolving cellulose. Methylsulfate imidazolium-based ILs showed excellent results when dissolving softwood Kraft lignins [52].

The research efforts in processing of lignocellulosic biomass using ILs as solvents is described [4]. Cellulose composite fibers were prepared based on IL solution with dispersion of the additives. Wood and bagasse were completely dissolved in ILs. Partial separation of the components was obtained using selected reconstitution solvents. High temperature and fast dissolution was found to be an efficient method for both dissolution and separation of biomass components. Biomass composite fibers can be prepared directly from such biomass solutions. With selected catalysts in solution, improved dissolution and separation was achieved, making the delignification and pulp yield comparable to the Kraft pulping process [4].

The interaction of natural polymers (Avicel, wood, "beech" cellulose) with the [Emim]Cl IL and their structural features before and after the regeneration process have been investigated in [56]. The observed dissolution mechanisms were found to be fully controlled by the physical and chemical organizations of the macromolecular chains. The XRD results indicated that the crystalline structure of the substrates regenerated from the IL is mostly disrupted.

One of the major challenges of biomass-based technologies is to extract sugars that are covalently trapped inside the lignocellulosic biomass efficiently. ILs have been recognized as promising solvents for mild and rapid hydrolysis of biomass feedstocks with higher sugar yields. An IL-based biomass hydrolysis strategy for large-scale production of fermentable sugars from corn stover has been developed and evaluated in [57]. Toward this aim, a process simulation model based on literature experimental studies and a simulated-moving-bed (SMB) system has been developed. The IL cost has been identified as the major cost driver. Analysis suggested that process alternatives with lower IL consumption and/or separation strategies that would allow higher recycle of ILs should be studied [57].

Pine and eucalyptus woods were dissolved in ILs [Emim][OAc], [Amim]Cl, [Bmim]Cl and [Emim]Cl, and successfully regenerated lignin from the solutions of these woods in the chloride-based ILs after 24 h at 150 °C in a thermostatic bath using methanol or ethanol as anti-solvents or after 1 h at 170 °C in a microwave oven [58]. Similarly, cellulose was recovered from

the wood solutions in [Amim]Cl after 20 min at 120 °C in the microwave oven. The regenerated products were found to be similar to the reference samples [58].

The [Bmim]Cl IL was used to dissolve two lignocellulosic materials including bagasse soda lignin and *Populus deltoides* wood flour at 70 °C for 72 h while stirring in [59]. The lignin and wood flour samples were acetylated with addition of acetic anhydride to each container with a 1:1 ratio and heated for 3 days at 110 °C. The functional groups and the number and type of carbon as well as their structure were examined and identified.

The dissolution and regeneration of both hardwood and softwood dissolving pulps with and from the two ILs ([Bmim][OAc] and [Bmim]Cl) were investigated in [60]. The impact of treating cellulose with ILs was also evaluated by using different analytical techniques (size exclusion chromatography, thermal gravimetric analysis and scanning electron microscopy).

Regarding IL recyclability, the new classes of 'switchable' and 'distillable' ILs can effectively lignocellulose. Whereas previous structures have low recyclabilities, the new structures can be converted from their 'ionic' form into "neutral" species, which allows for distillation of the materials in high yields and recovery. This increases the overall sustainability of the prospective processes, beyond what was capable before and offers significant energy savings [11].

A route for IL synthesis making use of alcohols and carboxylic acids both commonly found in a biorefinery is presented in [3]. Some of these ILs have also been tested for their ability to dissolve cellulose. He addressed the possibilities but also challenges upon IL-mediated lignocellulose processing. This includes investigating several ILs and their efficiency as a pretreatment solvent for enzymatic hydrolysis; these studies involve a large variety of different cellulosic materials. It has been demonstrated that depolymerization during the IL pretreatment is a possibility and that this can complicate the recovery processes and gives guidance into what type of ILs might be suited as pretreatment solvents for different cellulosic materials, including amorphous and crystalline cellulose, processed and native lignocellulose, different types of wood samples and hemicellulose [3].

Pretreatment of lignocellulosic biomass materials from poplar, acacia, oak, and fir with different ILs containing 1-alkyl-3-methylimidazolium cations and various anions was carried out [61]. The dissolved cellulose from the biomass was precipitated by adding anti-solvents into the solution with vigorous stirring. Commercial cellulases were used for the hydrolysis of untreated and pretreated lignocellulosic biomass. The hydrolysis of the cellulose was facilitated by the pretreatment with [Emim][OAc] and [Emim][CF<sub>3</sub>COO]. Among the tested ILs, [Emim][OAc] showed the best efficiency and resulted in highest amount of liberated reducing sugars. It was also found that enzymatic hydrolysis using combined pretreatment techniques could result in significant improvements of enzymatic hydrolysis efficiency. Combined pretreatment of the lignocellulosic biomass using glycerol-ILs and dilute acid-ILs were evaluated and compared with single pretreatment using glycerol, ILs or dilute acid [61].

Lignin was isolated from rubber wood using 1,3-dimethylimidazolium methyl sulfate IL in [62], and the optimum parameters to isolate lignin, namely, concentration of IL (0.5 mol), isolation duration (120 min) and isolation temperature (100 °C) investigated. Lignin could be isolated from rubber wood up to 13.03 wt.% by IL which is less than that obtained using acid



(22.15 wt.%) and alkaline (18.56 wt.%) isolation methods. The lignin preliminary structures isolated by IL have been confirmed based on Fourier transform infrared (FTIR) results. However, the isolated lignin by IL provides a lignin without other related isolatives. In addition, the IL can be recycled up to three times compared to acid and alkaline isolation methods [62].

A new composite material was obtained by using a waste resulted from wood industry, namely spruce wood flour and an ecologic green solvent for lignocellulose, namely 1-butyl-3-methylimidazolium chloride, [Bmim]Cl [63]. The method consists of dissolving wood in ILs followed by precipitation by water addition. The precipitated cellulose and lignin act as natural binders for the wood particles thus avoiding the use of toxic organic resins as adhesives. The obtained composites showed good water stability and compressive mechanical strength. Taking into account that the studied IL is non-volatile, the proposed method is more ecological than other traditional fiberboard-obtaining processes, which are energetically inefficient and contribute to the pollution of the atmosphere [63].

Lots of reports are available on dissolution of cellulose in ILs and its applications (48,64). Dissolution of cellulose samples in some imidazolium-based ILs, collected from references [46, 65-69] is available in [70]. Selected results for cellulose dissolution in ILs are presented in [4]. Recently, the extent of cellulose solubility in the most commonly used ILs is summarized in [6]. On the other hand, a summary table on the dissolution behavior of various types of wood-based lignocellulose in different ILs, based on data from [49] and [71], are provided in [72].

However, dissolution of wood in ILs is far more complicated than cellulose dissolution due to the wood complex structure from the 3-D lignin network [49]. Up to now, wood dissolution in ILs is limited to the imidazole-based ones [14]. A summary of the ILs used for wood dissolution according to various published sources [8,49,73,74] is presented in [14].

Wood fractionation through IL-mediated pretreatment for obtaining simple fermentable sugars, namely oligo- and mono-saccharides, and in particular hexoses (and pentoses) has been investigated in [75] focusing on softwood, Scots pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*), exposed to 1-ethyl-3-methylimidazolium chloride, [Emim]Cl, IL. Since both [Emim]Cl and the mono-saccharides are water-soluble and dissolve readily in similar solvents, the separation of this hydrophilic IL from sugars is difficult. Moreover, the analysis of mono-saccharides released from lignocellulosics with the help of [Emim]Cl is challenging [75].

It was found that both softwood (southern yellow pine) and hardwood (red oak) can be completely dissolved in the IL 1-ethyl-3-methylimidazolium acetate, [Emim][OAc], after mild grinding [76]. Complete dissolution was achieved by heating the sample in an oil bath, although wood dissolution can be accelerated by microwave pulses or ultrasound irradiation. It was shown that [Emim][OAc] is a better solvent for wood than 1-butyl-3-methylimidazolium chloride, [Bmim]Cl, and that variables such as type of wood, initial wood load, particle size, etc. affect the dissolution and the dissolution rates; for example, red oak dissolves better and faster than southern yellow pine [76].

Lipophilic wood extractives composition is currently a big concern of pulp and paper industries due to their negative impacts on the quality of the pulp and on the environment. Because of the shortcomings of different extraction procedures using volatile organic solvents in capturing residual lipophilic extractives in pulp, the use of ILs as an effective approach for such extraction is reported in [77]. The capacity of [Bmim][OAc] and [Bmim]Cl ILs to recover wood extractives was compared and observed that [Bmim]Cl recovered a higher amount of extractives than [Bmim][OAc]. Thus, the effectiveness of the IL in this process was due to the anion and not the cation of the solvent [77]. Based on the fact that ILs are biodegradable, non-volatile and non-flammable, this approach of analysis is definitely a highly green process for the determination of lipophilic extractives in dissolving pulp.

Lignin is an aromatic, amorphous, heterogeneous polymer that represents the second most abundant natural polymeric material on Earth [78]. It is known that the bulk of lignin in wood consists of non-phenolic aryl-glycerol- $\beta$ -O-aryl ether units. Other units, such as phenylcoumaran ( $\beta$ -5), resinol ( $\beta$ - $\beta$ ), and dibenzodioxocins(5-5/ $\beta$ -O-4,  $\alpha$ -O-4) are also present within the lignin macromolecule [79]. Furthermore, lignin is usually covalently linked to carbohydrates forming a refractory lignin-carbohydrate network [80].

Ionic liquids, especially those based on imidazolium cations, are capable of dissolving cellulose in a wide range of values of the polymerization degree (even bacterial cellulose) without covalent interactions [81,82]. Scientists are currently investigating the application of ILs as the solvent for the chemical modification of cellulose [See for example, 81,83-86].

The dissolution mechanism of cellulose in ILs involves the oxygen and hydrogen atoms of the cellulose-OH groups in the formation of electron donor-electron acceptor (EDA) complexes which interact with the IL. On the basis of the analysis of experimental and theoretical data, it was found that hydrogen-bond interactions are created between H-atom of OH-groups in cellulose and electron-donor center of the anion of the IL [87]. The cation of the IL doesn't interact with the cellulose directly. The cations role is considered as a steric obstacle for the prevention of interactions between polymeric chains, shielding them from each other after dissolution [87].

Lignin contributes to the recalcitrance of lignocellulosic biomass and affects enzymatic activity during biorefinery operations, therefore, it must be removed before further processing [88]. Organic solvents and ILs are two important pretreatments for delignifying lignocellulosic biomass; both have been proven beneficial for fractionating and recovering cellulose and hemicellulose, as well as lignin with useful physicochemical properties. Volatility and harsh conditions of the acidic systems that result in toxicity, corrosion, and pollution are the main problems of organic solvents. Ionic liquids, generally recognized as green solvents, have also been proposed as a possible solution to the challenge of using lignocellulosic biomass. Ionic liquids can either dissolve the lignocellulosic biomass completely or dissolve it into individual fractions. The advantages and disadvantages of organic solvents and ILs were considered, since both are important methods to fractionate lignocellulosic biomass in their main components which can be converted into value added products [88].

The application of selected ILs as aprotic green solvents for dissolution of lignin (isolated from pine Kraft pulp) were examined in [53]. Up to 20 wt.% lignin could be dissolved in [Hmim][CF<sub>3</sub>SO<sub>3</sub>], [Mmim][C<sub>1</sub>SO<sub>4</sub>] and [Bmim][C<sub>1</sub>SO<sub>4</sub>]. For the [Bmim]<sup>+</sup>-containing ILs, the order of lignin solubility for varying anions was: [MeSO<sub>4</sub>]<sup>-</sup> > Cl<sup>-</sup> ~ Br<sup>-</sup> ≫ [PF<sub>6</sub>]<sup>-</sup>, indicating that the solubility of lignin was principally influenced by the nature of the anions. ILs containing large, non-coordinating anions [PF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> were unsuitable as solvents for lignin [53].

The enzymatic pretreatment of wood biomass for degrading lignin, which is a complex aromatic polymer, has received much attention as an environmentally safe or "green" process. However, this process for lignin degradation has been found to be very slow, even needed several months. To overcome this limitation, a new approach for enhanced enzymatic delignification of wood biomass using ILs—a potentially attractive "green" and "designer" solvent-as co-solvents and/or pretreated agents has been reported in [89]. This approach comprised pretreatment of wood biomass prior to enzymatic delignification in ILs-aqueous systems with the aim of overcoming low delignification efficiency associated with the difficulties in enzyme accessibility to the solid substrate and the poor substrate and products solubility in aqueous system. The results showed that IL [Emim][OAc] was a better solvent for wood delignification than IL [Bmim]Cl. The recovered cellulose rich materials obtained from combination effects of IL and biological pretreatment contained significantly lower amounts of lignin as compared to the amounts found when each method applied alone. It is believed that this newly developed process will play a great role in converting cellulosic biomass to biomaterials, biopolymers, biofuels, bioplastics and hydrocarbons [89].

The [Bmim]Cl and [Bmim][MeSO<sub>4</sub>] ILs have been examined to dissolve wood flour, cellulose and chemical-mechanical pulp (CMP) in [90]. The overall evaluation indicated the inability of [Bmim][MeSO<sub>4</sub>] in full dissolution of lignocellulosic materials and sample treatment with this solvent led to water-soluble degradation products, whereas, [Bmim]Cl was able to dissolve lignocelluloses. Density, clarity, water absorption and thickness swelling of regenerated cellulose films were significantly higher than those of CMP and wood flour, and CMP higher than wood flour. Also, cellulose film has the lowest water vapor permeability compared to wood flour and CMP. Tensile strength, Young's modulus and strain at breaking point of cellulose film were significantly higher than the CMP and wood flour samples [90].

The state of art on the dissolution of cellulose, lignin and wood using ionic liquids is presented in [91] with emphasis on the relationship between the properties of ionic liquids and the dissolution capacity. The impact of the solvation parameters, namely, Hildebrand solubility parameter and hydrogen-bond basicity were related to the dissolution of lignocellulosic material. Good solvents for cellulose are [Bmim]Cl, [Amim]Cl and [Emim][OAc], whereas for lignocellulosic material the best solvents are [Emim][OAc] and [Amim]Cl [91]. In the allyl group, the ethylene functionality facilitates B-interactions with the aromatic lignin structure. Furthermore, small polarizable anions are also powerful when aiming at dissolution of cellulose. The properties of the regenerated cellulose and the reconstituted lignin were compared with those of the native materials and the results from the regeneration and reuse of ionic liquids were presented [91].

The dissolution of ball-milled poplar wood (PW), chemical-mechanical pulp (CMP), and cotton linter (CEL) in two imidazolium ILs, namely, 1-butyl-3-methyl-1-imidazolium chloride, [Bmim]Cl, and 1,3-methylimidazolium dimethyl sulfate, [Dimim][MeSO<sub>4</sub>] have been tested in [92]. The overall evaluation indicated the inability of [Dimim][MeSO<sub>4</sub>] in complete dissolution of lignocellulosic materials, and sample treatment with this solvent did not lead to water soluble degradation products. However, [Bmim]Cl was able to dissolve all used lignocellulosic materials by destroying inter- and intra-molecular H<sup>+</sup>bonds between lignocelluloses. The physical and mechanical properties of the regenerated CEL films were much higher than those of CMP and PW composites. In addition, CEL film showed the lowest water vapor permeability compared to the WF and CMP composite films [92].

#### 4. Lignin extraction in ionic liquids

Biodegradable plastics and biocompatible composites, generated from renewable biomass feedstock, are regarded as promising materials that could replace synthetic polymers and reduce global dependence on fossil fuel sources [93]. Wood cellulose, the most abundant biopolymer on earth, holds great potential as a renewable biomass feedstock for the future. The lignocellulosic biomass composes a diversity of feedstock raw materials representing an abundant and renewable carbon source and a key sustainable source of biomass for transformation into biofuels (e.g. bioethanol) and bio-based products (feedstock molecules for the chemical industry such as phenols and other aromatics). Because of the worldwide energy shortage and environmental pollution, the world has to make full use of lignocellulose in order to develop clean energy and bio-products in the future. However, the great diversity of lignocellulosic biomass opens a great opportunity for the production of various commodities using the wise valorization processes [94].

In majority lignocellulose is constituted by carbohydrate macromolecules, namely, cellulose (30-50 wt.%) and hemicellulose (15-30 wt.%), and by lignin (10-30 wt.%); a poly-phenylpropanoid macromolecule. Between these bio-macromolecules, there are several covalent and non-covalent interactions defining an intricate, complex and rigid structure of lignocellulose. The deconstruction of the lignocellulosic biomass makes these fractions susceptible for easier transformation to large number of commodities including energy, chemicals and material within the concept of biorefinery [94].

Cellulose is a major component in plant cell walls, which is made up of 6 carbon sugar (glucose) in the form of long chains. Hemicellulose is composed of 5 carbon sugars (xylose) which is the second most abundant source in the plant cell walls, and it is interconnected with cellulose molecules. Lignin provides the structural strength for the plant. Due to the complex structure of lignocellulose, it is resistant to traditional solvents, which inhibits hydrolysis and commercial utilization. Since different lignocellulosic materials have different physico-chemical characteristics, it is necessary to adopt suitable pretreatment methods for the lignocellulosic biomass [95]. However, the separation of lignin from cellulose and hemicellulose is a vital step. Also lignocellulosic biomass is highly recalcitrant (unmanageable) to biotransformation, both

microbial and enzymatic, which limits its use and prevents economically viable conversion into value-added products. As a result, effective pretreatment strategies are necessary, which invariably involve high energy processing or results in the degradation of key components of the lignocellulose [96]. To unlock the entire scope of potential benefits of this feedstock, the wood components, namely cellulose, hemicellulose and lignin, need to be separated and processed individually [93].

Lignin is a renewable bio-resource with a variety of applications. It is an important component of the biomass from which several useful chemicals can be derived as indicated by the work initiated in the second half of the last century and the renewed interest today. Lignin valorization constitutes an important component of the modern biorefinery scheme, and the structure and composition of lignin offer unique routes to produce several fine and bulk chemicals. The different approaches and strategies currently available for catalytic lignin valorization are presented in [97]. Generally, lignin reduction catalytic systems produce bulk chemicals with reduced functionality, whereas lignin oxidation catalytic systems produce fine chemicals with increased functionality [97].

The development of green processes for wood dissolution and lignin regeneration would be really useful in the context of biorefinery and biomass efficient employment. One of the most traditional methods to lignin extraction used in the industry is by the Kraft process. Even though most of the lignin is extracted, the Kraft process has several major disadvantages: (1) high temperature and pressure; (2) pollution; (3) odor problem (due to the use of sulphite); (4) high water usage; and (5) large plant size [98]. Several other methods to extract lignin from lignocellulose have been designed and developed in the past. These include physical (limited pyrolysis and mechanical disruption/comminution), physiochemical (steam explosion, ammonia fiber explosion), and chemical (acid hydrolysis, alkaline hydrolysis, high temperature organic solvent pretreatment, oxidative delignification) methods [52]. The above extraction methods have one main disadvantage; the lignin starts to degrade after a certain amount of lignin is extracted.

Generally, the biomass pretreatment depends on the final goal in the biomass processing. The recalcitrance of lignocellulose materials is the main limitation of its processing once the inherent costs are excessively high for the conventional pretreatments. Furthermore, none of the currently known processes is highly selective and efficient for the satisfactory and versatile use, thus, new methodologies are still broadly under study [94].

The IL technology on biomass processing is relatively recent and first studies were focused on the lignocellulosic biomass dissolution in different ILs. The dissolution in IL drives to the structural changes in the regenerated biomass by reduction of cellulose crystallinity and lignin content contrasting to the original biomass. These findings provided ILs as tools to perform biomass pretreatment and the advantageous use of their specific properties over the conventional pretreatment processes [94].

ILs have played an important role in the production of clean energy owing to their excellent physico-chemical properties and outstanding performance in the dissolution and separation

of lignocellulose. However, the research in this area is still at its infant stage and some problems have to be solved. In the future work, the following main issues are suggested [70].

1. To study the interaction mechanism between ILs and cellulose, hemicellulose or lignin further through macroscopic and microcosmic methods, and to know how cations and anions of the ILs disrupt the cross-linked structure, and the intra-and inter-molecular hydrogen bonding of lignocellulose.
2. To develop the knowledge of the relationship between the structure of ILs and their dissolution performance for cellulose, hemicellulose and lignin, and then to design and prepare more new task-specific ILs which are ought to have low viscosity, low melting points and high dissolution and separation capability for lignocellulose.
3. To develop inexpensive methods for the recovery and recycle of ILs, and to promote the application of microwave heating and other intensification technologies in the dissolution and separation of lignocellulose components with ILs.
4. To investigate the effect of precipitation solvents on the crystalline state and thermo-physical properties of regenerated cellulose, hemicellulose and lignin, and then to regulate the structure and properties of the regenerated components for different applications.

ILs have proven the inordinate potential in reactions and separation including biomass processing. The pretreatment of lignocellulosic biomass can affect its physical properties, such as alter the structure of cellulosic biomass to make cellulose more accessible to the enzymes that convert carbohydrate polymers. Subsequently, when lignocellulose is separated into its components, it can be hydrolyzed to fermentable sugars (monosaccharaides) using mineral acids or enzymes. Mono-saccharides can then be further converted to other valuable bio-based chemicals [95].

ILs can dissolve extensive quantities of biomass, and even be designed to be multifunctional solvents [99]. In the past decade, ILs have been used as solvents for natural polymers, including cellulose and starch [e.g., 8,46,48]. Current methods to separate wood components, such as Kraft pulping for example, suffer considerable drawbacks and cannot be considered environmentally benign [85]. These drawbacks lead researchers to trying to design and develop ILs that are able to dissolve lignin and thus, extracting them from the lignocellulosic biomass with the aim of minimizing lignin degradation. In order to separate lignin from plant constituents using ILs, the ideal IL should possess properties such as: high dissolution capacity for lignin; low melting point; good thermal stability; non-volatile; non-toxic; chemically stable; no lignin decomposition; easy lignin regeneration; low cost and simple process [51,52].

The tremendous chemical and physical breadth of ILs can be exploited in the design of new ILs with improved lignin extraction capability while providing a ready source of highly degradable cellulose and hemicellulose. Further studies, such as precipitation or extraction of lignin and removal or reuse of ILs by ion exchange, are needed to evaluate the efficient removal of the pristine lignin from the IL, thereby providing a new source for highly functionalized natural product [96].

The unique solvating properties of ILs foster the disruption of the 3-D network structure of lignin, cellulose, and hemicellulose, which allows high yields of fermentable sugars to be produced in subsequent enzymatic hydrolysis. Lignocellulosic biomass pretreatment in ILs is a promising alternative, with comparable or superior yields of fermentable sugars, than conventional pretreatments. The broad number of ILs that can be synthesized allows the design of solvents with specific physicochemical properties that play a critical role interacting with lignocellulosic biomass subcomponents [72]. Today, these interaction mechanisms are better understood. However, future challenges rely on the ability to make this process economically attractive. This might be achieved by optimizing large-scale pretreatment conditions, performing post-pretreatment steps in ILs, reusing ILs, recycling the ILs with reduced energy consumption and enhancing process efficiency, and producing high-value products in addition to ethanol (e.g., products traditionally derived from petroleum, fine chemicals or fuels with higher energy value). Moreover, the potential high-value of lignin suggests that it might instead be used in the large-scale diversified manufacture of high value chemicals, traditionally obtained from petroleum [72].

The physico-chemical properties of ILs that make them effective solvents for lignocellulose pretreatment, including mechanisms of interaction between lignocellulosic biomass subcomponents and ILs, along with the several recent strategies that exploit ILs and generate high yields of fermentable sugars suitable for downstream biofuel production, and new opportunities for use of lignocellulosic components, including lignin, have been summarized and highlighted in [72].

A variety of ILs have been used to dissolve lignocellulosic biomass. The mostly reported efficient ILs used to dissolve lignocellulose are those containing Cl<sup>-</sup> anion, e.g. [Amim]Cl and [Bmim]Cl. The ions in these ILs dissociate to individual cations and Cl<sup>-</sup> ions. The free Cl<sup>-</sup> ions associate with the cellulose hydroxyl proton, which are the hydrogen-bond accepters and the free cations are moderate hydrogen-bond donators that complex with the cellulose hydroxyl oxygen. This leads to the disruption of hydrogen bonds in cellulose and to the dissolution of cellulose [95]. However, chlorine has been proved as an ecologically destructive element in the industrial utilization and its by-products are also harmful for human. Therefore, finding new chlorine-free ILs that also provide good dissolution ability on lignocellulosic biomass (cellulose, hemicellulose and lignin) is underway [95].

Recently, a number of publications introduced a variety of technical developments and solvent systems based on several types of ILs to fractionate lignocellulose into individual polymeric components, after full or partial dissolution [100]. Many new technical advances are apparent, including more refined ILs, electrolytes, pretreatments and processing techniques. However, the application of fundamental knowledge related to the connectivity of wood biopolymers, morphology, ultrastructure, and even the wood solubility in ILs seems to have been largely neglected. Increasing awareness related to IL reactivity has brought both challenges and possibilities to wood fractionation. Depolymerization during fractionation can result in undesired products. This is most relevant when molecular weight distributions should be maintained, e.g. for the production of cellulosic pulps. However, in some cases degradation

may be beneficial, e.g. for dissolving the lignin-carbohydrate complexes (LCC) network or reducing the recalcitrance of wood for biofuel production [100].

On the other hand, the polar nature of ILs has the ability for dissolution and fractionation of wood biomass for various applications. Dissolved wood biomass fractions are regenerated by the addition of non-solvents, i.e., water, acetonitrile, etc. [46,101]. Using ILs for the preparation of cellulose and wood biomass composites and derivatives will contribute towards reducing the dependency on petroleum as raw material whilst enhancing the use of wood biomass. Though ILs are considered as green solvents, there are some drawbacks associated with them such as non-biodegradable, expensive and the toxicity is still not known. This calls for further research in order to understand their toxicity and also to develop new economically viable methods for producing ILs at industrial scale [102].

The application of ILs in cellulose dissolution has promising futures due to three factors: (i) ILs properties such as like extremely low vapor pressure, high polarity, and high chemical and thermal stabilities, and the most important properties of ILs is the possibility of reaction at high temperature without hazard; (ii) cellulose abundance, biodegradability and biocompatibility; and (iii) the dissolution of cellulose in ILs takes place in wide temperature range (60–130°C) which may help in applying different types of modifiers in the blending process of grafting copolymerization [103].

Modification of cellulose in ILs media provides possibilities for preparation of various advanced materials, including cellulose derivatives and composites, which may replace synthetic polymers, which biodegrade slowly or to a less extent. The important target for this technology is how to increase the solubility efficiency, which may be achieved by careful design of what is called “Task-Specific IL (TSIL)” [104]. TSIL is a design specific type of ILs produced by introducing functional groups at the imidazolium cation to make the IL more effective in the cellulose dissolution process [55]. A reactive extrusion process to modify the cellulose has been successfully applied where a specific IL has been used with cellulose and cyclic anhydride to modify the cellulose by using twin screws. This process may open a new horizon for cellulose modification through melting process or may lead to regeneration of cellulose through melting process [103].

In a typical process of lignocellulose biomass pretreatment, lignocellulose and IL are heated up to 100°C for a certain time. The dissolution time depends on the structure of the cellulose and the type of the IL. The dissolved cellulose in the IL can be precipitated by adding a non-solvent (anti-solvent), such as water, methanol, ethanol, or acetone and separated by filtration. The filtrated IL can be recovered and reused through the distillation of the anti-solvent [95].

The dissolution of three wood species in the IL [Amim]Cl, followed by pretreatment with small amounts of hydrochloric acid, has been studied as a function of time in [105]. The materials regenerated from the IL solutions were determined to contain significantly higher amounts of lignin than the original wood. Detailed analyses of the recovered IL revealed the presence of typical wood degradation compounds. Thus an IL-based acid pretreatment of wood may offer a potential platform for the efficient conversion of woody biomass to readily digestible carbohydrates and other valuable chemicals.



The effect of temperature on enhancing the enzymatic hydrolysis of cellulose wheat straw in the IL [Amim]Cl has been studied and the morphology, enzymatic hydrolysis rate, the recovery and the composition of the recovered solid have been investigated in [106]. It was concluded that treatment with [Amim]Cl is an efficient pretreatment method to enhance the enzymatic hydrolysis of wheat straw; too intense treatment condition would induce degradation of wheat straw and the most easily degradable component is hemicellulose. Heating at 150°C for 2 h is a suitable condition for the pretreatment [106].

The chemical interaction of dissolving pulp with ILs, where softwood and hardwood industrial dissolving pulps were pretreated with ILs [Bmim][OAc] and [Bmim]Cl have been investigated in [107]. Time (28-330 h) and temperature (80 °C and 105 °C) dependence of the dissolution process as well as the impact of the pretreatment on the molecular weight properties, thermal stability, morphology, and crystallinity of the cellulose were evaluated. It was shown that the dissolution of cellulosic material in ILs is a temperature-dependent process; however, the viscosity of the IL affected the efficiency of dissolution at a given temperature. Molecular weight properties were affected negatively by increased dissolution temperature, while the type of anti-solvent for the regeneration of cellulose had no major impact on the degree of polymerization of the cellulose. Water was found to be more efficient than ethanol for the regeneration of cellulose when performed at an elevated temperature. The pretreatment decreased the crystallinity of the cellulosic material. This might lead to the increased accessibility and reactivity of the cellulose [107].

Various wood samples (subjected to some mechanical pretreatment) were dissolved in some Cl-containing ILs, namely, [Amim]Cl, [Bmim]Cl, and [Bzmim]Cl for 8 h at temperatures between 80 and 130 °C and results showed that wood can be dissolved in some ILs, including [Amim]Cl and [Bmim]Cl, with high wood regeneration yield [49].

Cellulolytic enzymatic hydrolyses of wood regenerated from IL solutions was determined to produce higher saccharification yields than those of untreated wood. When these ILs were used for additional wood pretreatment cycles, it was observed that the hydrolysis rate of the cellulose increased, accompanied by lignin degradation. As such, it became of interest to investigate the effect of small amounts of acid in ILs on wood degradation and its hydrolytic conversion during such a pretreatment stage. In this effort, three wood species pretreated with dilute hydrochloric acid in water and in [Amim]Cl have been compared. The lignin contents of the regenerated wood were determined, and the components that remained within the recycled IL were examined [49]. However, studies on the recycled ILs from the pretreatment of wood revealed that the ILs contain carboxylic acids from the dissolved hemicelluloses [108].

The IL [Emim][ABS] has been used for extraction of lignin from sugarcane bagasse. The results showed that the lignin extraction increases with elevating temperature (170-190 °C), and when the extraction time increases from 30 min to 120 min. Also, a lignin extraction with more than 93% yield was successfully attained at atmospheric pressure [109].

The pretreatment of oil palm frond (OPF) lignocellulosic feedstock with the IL [Bmim]Cl, followed by regeneration of cellulose using an anti-solvent, to facilitate the conversion of the OPF into fermentable sugar (glucose) has been investigated [110]. SEM analysis showed a

significant destruction of the biomass structure after pretreatment with the IL, which in turn reduced the crystallinity and improved the enzymatic digestibility of the biomass. An optimum 100% glucose recovery was found with pretreatment conditions of 80 °C, a 15-min retention time and 10% solid loading [110].

Some difficulties in dissolving and extracting lignin from maple wood flour were faced by [96] using the same ILs used earlier in [53], namely, [Hmim][CF<sub>3</sub>SO<sub>3</sub>], [Mmim][MeSO<sub>4</sub>] and [Bmim][MeSO<sub>4</sub>]. However, Cl<sup>-</sup>-containing ILs, [Amim][Cl] and [Bmim][Cl], have shown better capabilities. This might be due to the high solubility of the wood flour as a whole. However, Cl<sup>-</sup> ions are good H<sup>+</sup> acceptors and are able to interact with the OH groups of the sugars, causing dissolution of cellulose too. It was also found that [Emim][OAc] IL provides a balance between good lignin extraction and low wood flour solubility [96]. Hence, lignin extraction can be done using [Emim][OAc] without much disruption of the cellulose and hemicellulose structures [98]. On the other hand, an extensive summary on lignin dissolution in ILs is presented in [96] while solubilities and extraction efficiency of lignin in various ILs are presented in [97].

The imidazolium-based ILs were used for the study of the dissolution of residual softwood lignin isolated from a southern pine Kraft pulp (at 25-100 °C). It was found that the lignin solubility can be influenced by the nature of the anion when different [Bmim]<sup>+</sup>-containing ILs are used. It was also concluded that ILs containing large, non-coordinating anions like [BF<sub>4</sub>]<sup>-</sup> and [PF<sub>6</sub>]<sup>-</sup> are not suitable for dissolving lignin; and that imidazolium methyl sulfate-based ILs are effective for dissolution of such lignins. The solubilities of lignin in some imidazolium-based ILs (at 50-120 °C) are presented; and almost similar conclusions are still valid [53].

The IL 1-ethyl-3-methylimidazolium glycine [Emim][Gly], which has a high hydrogen-bond basicity, has been used to dissolve bamboo biomass and found to be effective at 120 °C in 8 h. While, 1-ethyl-3-methylimidazolium trifluoroacetate, [Emim][TFA], which contains an acetate-based anion, and choline propionate, which has high hydrogen-bond basicity, none of them could dissolve the bamboo biomass after 24 h [102].

Food additive-derived imidazolium acesulfamate ILs have been used for extraction of lignin from wood flour and showed promising results without disrupting the cellulose crystallinity [93]. Among all, 1-ethyl-3-methylimidazolium acesulfamate [Emim][Ace] IL is desirable for industrial processing due to its physical properties. The extracted lignins have a larger average molar mass as well as a more uniform molar mass distribution compared to that obtained from the Kraft process. This adds to another advantage of using imidazolium acesulfamate ILs. The various extraction conditions: extraction temperature and time; water content; wood load, particle size and species; types of IL cation; effect of IL recycling; multi-step treatment and use of co-solvents were also examined in [93]. Interestingly, the use of dimethyl sulfoxide (DMSO) as a co-solvent in weight ratios of ( $w_{IL} : w_{DMSO} = 9:1$ ) increased the extraction efficiency by almost 50%. It is believed that the penetration and interaction of the lignocellulosic biomass with IL are enhanced due to loosening of the tight hydrogen bond network of the cellulose and the decrease in the overall viscosity of the mixture caused by the use of DMSO [93]. The lignin extract and the wood residues were characterized *via* infrared spectroscopy, elemental analysis, thermogravimetric analysis, differential scanning calorimetry, X-ray diffraction, and gel permeation chromatography. An extraction efficiency of 0.43 of wood lignin was achieved

in one gentle extraction step (100°C, 2 h), and it was found that the presence of a co-solvent increased the extraction efficiency to 0.60. Gentle conditions during IL treatment did not decrease the crystallinity of the wood sample, and the extracted lignin had both a larger molar mass and a more uniform molar mass distribution, compared to commercially available Kraft lignin [93].

On the other hand, lignin extraction can also be done after complete dissolution of the whole cellulosic biomass. A cellulose-lignin mixture system has been separated and recovered from ILs [Bmim]Br and [Bmim]Cl. The cellulose precipitates when water is added to the solution (cellulose-lignin mixture in IL). Lignin is then recovered from the precipitate formed when the filtrate is treated with ethanol. The IL can be regenerated by evaporating the ethanol from the second filtrate with more than 95% yield. On the other hand, lignin yields of 69% and 49% were isolated from [Bmim]Br and [Bmim]Cl, respectively [111]. However, the influence of water on dissolution of cellulose in selected ionic liquids is discussed in [112].

Both softwood and hardwood were dissolved in [Emim][OAc] and lignin was extracted using acetone/water (1:1 v/v) and the effects of IL, particle size, wood species, and initial wood concentration and pretreatment were evaluated [76]. The same method in [102], lignin has been extracted from the solution using acetone/water anti-solvent. The ideal process flow of the dissolution and regeneration of wood in IL is shown in Figure 1.

It was reported also that IL [Emim][OAc] is an effective solvent for lignin extraction from triticale straw, flax shives and wheat straw and the extraction yields were much higher than those of [Bmim]Cl. The extraction capability was found to increase with higher temperatures (up to 150°C) and longer extraction times (up to 24 h) [113].

The structural features of poplar wood lignin extracted using IL [Emim][OAc] has been compared with that using dioxane-water (classical method). A higher yield of extraction was obtained using the IL [114]. Even though the lignins obtained from both extractions have relatively similar methoxy and phenolic hydroxyl contents, the molecular weight of that obtained from classical method is higher. However, the poly-dispersity index (PDI) of IL extraction is lower and thus, indicating that lignin from IL extraction is of rather uniform size. This suggests that some form of depolymerization had occurred. On top of that, thermal behaviour of the lignins were also analyzed. Lignin obtained from classical method has a higher maximum decomposition rate and temperature, indicating that it is thermally more stable [114].

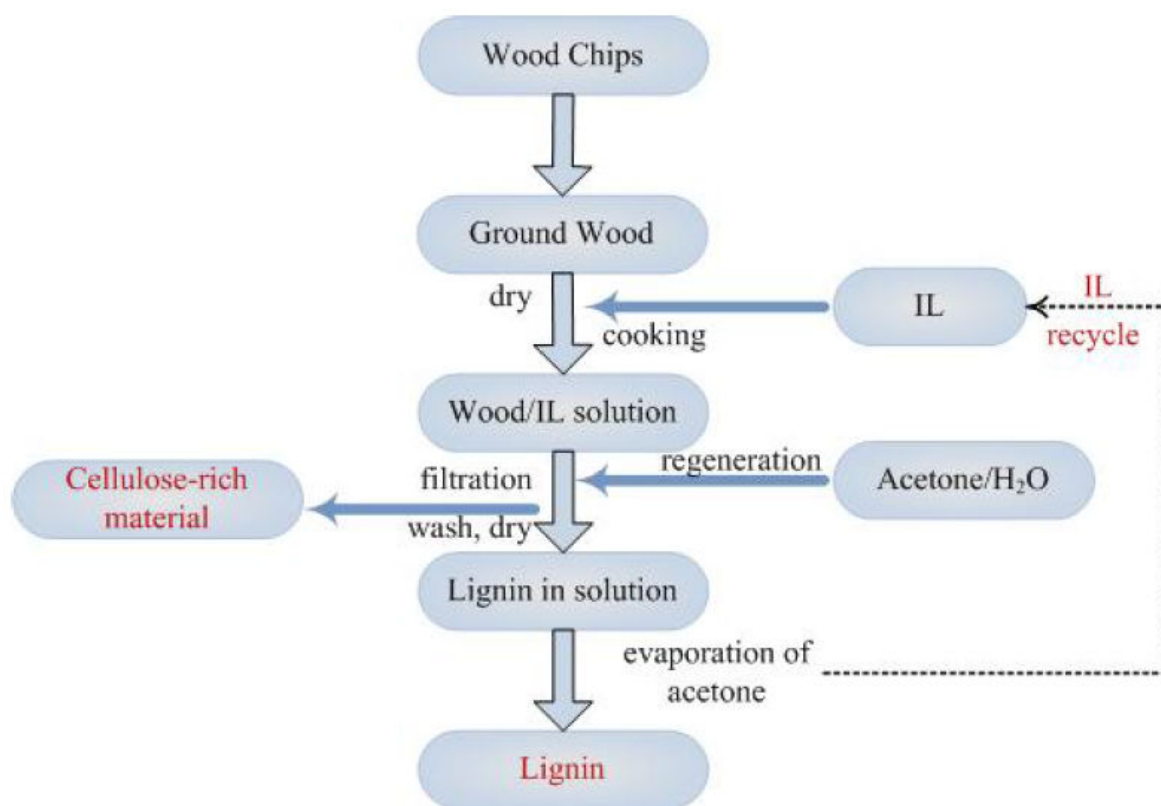
A large number of ILs, sorted by cations and anions, have been screened for their solubility characteristics towards infinite concentrations of cellulose. The calculations show a very well-defined dependency on the anion for the dissolution kinetics. Further calculations concern the influence of water in ILs, because in experiments a very rapid decrease in the solubility of cellulose in ILs has been observed. At this point, a link to experimental results must be established in order to validate the calculations and to develop the routines and databases of a COSMO-RS software. These calculations can then be used as reliable screening method to identify new candidates of eligible ILs for the dissolution of wood [115].

Fractions of pulverized Norway spruce (*Picea abies*) and *Eucalyptus grandis* wood were solvated and precipitated by agitating and heating the lignocellulosic materials in IL [Amim]Cl followed by precipitation using non-solvents, such as acetonitrile (MeCN) and water [116]. The efficiency of precipitation was found to be dependent upon molecular weight, with the dissolved higher molecular weight and partially soluble wood components precipitating first. Moreover, when coarse sawdust samples were fractionated, the selective dissolution of cellulose from the fiber was observed; this allowed for the regeneration of a fraction of delignified and bleachable cellulose. Additionally, finely milled softwood samples, with demonstrated narrowly distributed low molecular weights, did not efficiently fractionate most likely due to the presence of an extensive lignin-carbohydrate complexes (LCC) network [116].

A comparison of the fractionation of coarse and finely pulverized wood from [Amim]Cl identified that fractionation mainly is dependent on molecular weight and not chemical composition. This was observed for softwood (Norway spruce) and hardwood (*Eucalyptus*) species. When finely milled wood is completely dissolved in [Amim]Cl, most of its components can be precipitated in the order of decreasing molecular weight using MeCN and MeOH as non-solvents [116]. Contrary to reports of highly efficient fractionation of cellulose doped with high purity lignin [111], it was only possible to fractionate the finely pulverized and dissolved spruce wood with marginal selectivity. It is likely that the presence of extensive LCCs, especially within the softwood material, is preventing the separation of lignin and polysaccharides. This suggests the need for a pretreatment of wood so as to break the LCCs in order to increase the selectivity of fractionation [116].

In the fractionation of sawdust, it was determined that cellulose preferentially dissolves in the initial dissolution step and that lignin is relatively resistant to being removed from the fiber. After precipitation of the residual insoluble material it was possible to precipitate the dissolved cellulose in bleachable grade and relatively high purity [116]. This result, using [Amim]Cl, is contrary to previous publications [76] using [Emim][OAc] and suggests either a different mode of dissolution of wood between the two classes of ILs or between different species. Additionally, extraction of the residual fibrous and the precipitated materials after the fractionation of sawdust afforded acetylated galactoglucomannan (a water-soluble hemicellulose, consisting of galactose, glucose and mannose) with relatively high molecular weight [116].

On the other hand, the IL [Emim][OAc] was used as a pretreatment solvent to decrease both lignin content and cellulose crystallinity of maple wood flour [96]. The cellulose in the pretreated wood flour becomes far less crystalline without undergoing solubilization. In addition, [Emim][OAc] was easily reused, thereby resulting in a highly concentrated solution of chemically unmodified lignin, which may serve as a valuable source of a poly-aromatic material as a value-added product. The [Emim][OAc] did not dissolve the wood flour; however, facile extraction of the lignin was achieved. A strong inverse relationship was found between the effectiveness of cellulase-catalyzed hydrolysis of wood flour cellulose and both lignin content and cellulose crystallinity. Complete lignin removal was not needed and maximal cellulose degradability (> 90%) was achieved even at 40% total lignin extraction. Finally, [Emim][OAc] was reusable without significant loss in the yield of lignin extracted and subsequent cellulose hydrolyzed after four cycles. Furthermore, chemically unmodified lignin



**Figure 1.** Flowchart for the process of dissolution and regeneration of wood in IL [4].

with high hydrophobicity could be easily precipitated from concentrated lignin solution in [Emim][OAc] by adding excess water [96].

It was also demonstrated in [117] that the IL [Emim][OAc] can be used as a potential solvent for the pretreatment of lignocellulosic biomass such as energy cane bagasse (ECB). Furthermore, the sugar yields obtained post pretreatment have great potential as building blocks in the production of renewable fuels and chemicals. The energy cane bagasse pretreated with recycled [Emim][OAc] resulted in a decrease of lignin removal as compared to bagasse pretreated with the original IL. However, further research is still needed to improve the efficiency of this pretreatment on energy crops. Among the future research work that still to be investigated are the optimal pretreatment conditions with extended design space, assess the efficiency of recycled IL pretreatment at optimal processing conditions, and calculate the cost for the entire conversion process and energy returned on energy invested.

The regeneration of lignin from some woods dissolved in imidazolium-based ILs: [Bmim][OAc], [Emim][OAc], [Emim]Cl, [Bmim]Cl and [Amim]Cl have been studied in [118]. The lignin was successfully regenerated by precipitation with an anti-solvent from solutions of wood in [Amim]Cl, [Bmim]Cl or [Emim]Cl. The regenerated lignin, characterized by Fourier transform infrared spectroscopy,  $^{13}\text{C}$  nuclear magnetic resonance, elemental analysis, thermogravimetric analysis, and differential scanning calorimetry, was compared to Indulin AT lignin, and showed different properties depending on the IL employed and the wood species.

On the other hand, the latest developments and knowledge in the field of fractionation of lignocellulosic materials with ILs have been briefly reviewed and an alternative fractionation method based on the controlled regeneration of components from [Amim]Cl has been introduced in [100]. Norway spruce (*Picea abies*) and *Eucalyptus grandis* woods were dissolved in their fibrous state or by utilizing ball milling to improve solubility. The resulting wood solutions were precipitated gradually resulting into fractions by addition of non-solvents, such as acetonitrile and water. Further water extraction of the crude fractions resulted in better separations. Fractionation efficiency was found to be highly dependent on the modification of the wood cell wall ultrastructure and the degree of reduction of the molecular weights of the main components, arising from mechanical degradation. Isolation of cellulose enriched fractions was achieved with Spruce sawdust and ball milled *Eucalyptus*, evidently following from distinct dissolution mechanisms [100]. It was also demonstrated that wood (sawdust and highly pulverized spruce) is *not* completely soluble in [Amim]Cl in its native state. One possible reason for this is the presence of a lignin-carbohydrate complexes (LCC) matrix in wood that is simply of too high molecular weight and interconnected to dissolve. This property can be utilized to extract cellulose, as it is not covalently bound to the insoluble LCC matrix. Cellulose is extracted and by careful control of non-solvent addition, the insoluble lignin-hemicellulose rich fraction can be first isolated, followed by regeneration of relatively pure cellulose. *This cellulose extraction procedure is not yet at a stage that would yield a technically useful pulp, due to apparent depolymerization, in comparison to technical pulps and holocellulose.* However, the more we learn about the stability of wood and lignocellulose, in technical and pure ILs, the better are our chances of yielding close-to native polymers [100].

Samples of corn stover, Norway spruce, and *Eucalyptus grandis* were pulverized to different degrees, subjected to quantitative analyses, upon the basis of pre-dissolution into imidazolium chloride-based ILs [Amim]Cl and [Bmim]Cl, followed by labeling of hydroxyl groups as phosphite esters and quantitative “wood solubility” using  $^{31}\text{P}$  NMR analysis. Analysis of different pulverization degrees provided semi-empirical data to chart the solubility of Norway spruce in these ILs [119].

The solubility of the Norway spruce wood samples (subjected to varying degrees of mechanical pulverization) in a range of common ionic and molecular solvents, was quantified using a novel  $^{31}\text{P}$  NMR technique [120]. The results showed that intact wood is not soluble under mild treatment conditions, in cellulose-dissolving or swelling solvents. Further refinement afforded an optimized method of analysis of the lignin phenolic functionalities, without prior isolation of the lignin from the fiber. The lignin in the samples was further enriched using cellulase and acidolysis treatments, allowing for comparison with the fibrous samples. Analysis of all samples charts the polymerized-monomer availability for each stage of the treatment. Conditions required for adequate signal-to-noise ratios in the  $^{31}\text{P}$  NMR analysis were established with a notable improvement observed upon the lignin enrichment steps [120].

The critical outlook on the study of biomass dissolution and changes occurred in the biomass during this process as well as on the influence of several crucial parameters that govern the dissolution and further pretreatment process are reviewed in [94]. The currently known methods of biomass fractionation in IL and aqueous-IL mixtures are also discussed and

perspectives regarding these topics are given as well. The review in [94] also shows that ILs have potential to be used in the biomass pretreatment and demonstrated that ILs can be successfully used to obtain cellulose, hemicellulose and lignin fractions with purity and efficiency equal or superior to the classical pretreatment methods. The exploitation of ILs in the lignocellulosic biomass processing demonstrates the enormous potential in this research area, especially in the context of a biorefinery; however, an extensive research is still required to better understand and predict the outcomes of these processes.

The multi-functional use of ILs with respect to lignin processing has been reviewed in [99] and the use of ILs in selectively or non-selectively dissolving lignin, the attempted depolymerization reactions on lignin in ILs, and the observed effect of ILs on such processes have been highlighted. Some of the challenges and issues that must be addressed before the informed and large-scale application of ILs can be realized for lignin processing has been presented and finally it was concluded that, there is both great scope for innovation and huge potential in the sophisticated application of ILs, in order to produce high yields of chosen, monomeric aromatics from a wide variety of lignin sources [99].

The up-to-date progress in selective breakdown of lignocellulose in ILs, especially molecular level understanding of the dissolution of biomass in ILs, strategies for the conversion of lignocellulose into fermentable sugars and furans, and related chemicals have been highlighted [121]. Further research in the area of selective breakdown of lignocellulose, or utilization of biomass incorporating ILs technology, is expected for example in, exploitation of novel chemistry of lignocellulose in ILs or IL-containing media; integration of the ILs processes with other chemical or biological processes; design and preparation of cheaper, greener and process-compatible ILs; developing new strategies for ILs recycling and product recovery.

The complex structure and the 3-D lignin network that binds lignocellulosic components together makes it practically impossible to dissolve lignocellulosic materials in their native form in conventional solvents. The aromatic electron-rich cationic moiety creates strong interactions for polymers which undergo  $\pi$ - $\pi$  stacking (lignin). The chloride anion in an IL is the most efficient in disrupting the extensive inter- and intra-molecular H-bonding interactions present in wood (cellulose) allowing the IL [Amim]Cl, for example, to diffuse into the interior of the material [122].

The conversion of lignocellulosic biomasses has been considered to be economically unfeasible due to the crystalline structure of cellulose. Molecular dynamic simulation (MDS) tools have been applied to (1) determine driving force(s) for the crystalline structure of cellulose, (2) illuminate the interactions between cellulose molecules and candidates of decrystallization chemicals, and (3) search for a novel chemical to allow the decrystallization of cellulose followed by the saccharification without an intervening process [123].

## 5. Future prospects

Use of ionic liquids provided a new platform for comprehensive utilization of wood, although many problems need to be further addressed: First, dissolution of wood in ILs has opened a

new avenue for wood chemistry research and to improve the efficient utilization of wood. Second, the ILs can be used as wood preservatives or to improve wood's anti-electrostatic and fire-proof properties. This will extend the range of wood applications and reduce the use of some dangerous chemicals. Finally, use of ILs is also a competitive alternative exhaust treatment technology in the wood processing, which can reduce the energy consumption and waste of resources [14]. However, application of ILs in wood-related industry at industrial scale still faces some challenges.

1. The cost of ILs hampers the use of ILs at a commercial scale. Therefore, economical synthesis of ILs and efficient recovery and recycling technologies play vital roles in their industrial applications. Depending on the IL used and the application performed on it, a variety of recycling methods were possible. By picking the right purification steps, an individually optimized work-up procedure can be obtained [124]. Several procedures on how to recover ionic liquids from their solution have been reviewed in [125]: distillation/stripping at some suitable temperature ( $< 300\text{ }^{\circ}\text{C}$ ) and under vacuum, liquid-liquid extraction (using objectionable VOCs!), supercritical fluids (using  $\text{CO}_2$  at room temperature and several MPa), and membrane separation (to separate nano size particles from ILs).
2. The biodegradability, toxicology, and thermodynamic data of ILs are still scarce. There are also lots of engineering problems that need to be solved. ILs have the reputation of being "green" chemicals, but not all of them can pass favourably the tests evaluating their environmental effects. For example, reference [126] focused on ionic liquids' environmental impact, ecotoxicity and potential biodegradability, while compiling results of different ecotoxicological studies. A comprehensive database on toxicity of ILs has been established in [13] in a database that includes over 4000 pieces of data. Based on this database, the relationship between IL's structure and its toxicity has been analyzed qualitatively. Furthermore, quantitative structure-activity relationships (QSAR) model has been conducted to predict the toxicities ( $\text{EC}_{50}$  values) of various ILs toward the Leukemia rat cell line IPC-81.
3. The most challenging engineering problem is the high viscosity of ILs, which is expected to cause severe mass and heat transfer problems during their industrial use. Some measures have been taken to reduce ILs viscosity, such as development of low viscous ILs [66] and use of mixtures of ILs [49], but these measures can only partially resolve this problem.

Although these challenges still exist, great progress has been made in research for application of ILs in wood-related industries in recent years. Although many problems associated with application of ILs in wood-related industries need to be solved, it is quite clear that in the near future these applications will be implemented at a full industrial scale and society can be expected to benefit greatly from these applications [14].

Thus understanding of ILs volatility, purity, stability, biodegradability and toxicity is necessary for their recovery, since this determines whether an IL can be sustainably developed. In other words, a long way is still to go before large-scale implementation of ILs becomes feasible



and practical. However, issues over the cost of ionic liquids for industrial applications still exist.

## Appendix: Abbreviations of some of the ionic liquids used in this chapter

Ionic liquid	Abbreviation
1-allyl-3-methylimidazolium chloride	[Amim]Cl
1-butyl-3-methylimidazolium chloride	[Bmim]Cl
1-butyl-3-methylimidazolium chloride	[Bmim]Br
1-butyl-3-methylimidazolium acetate	[Bmim][OAc]
1-butyl-3-methylimidazolium methyl sulfate	[Bmim][C <sub>1</sub> SO <sub>4</sub> ]
1-butyl-3-methylimidazolium trifluoromethane sulfonate	[Bmim][OTf]
1-butyl-3-methylimidazolium tetrafluoroborate	[Bmim][BF <sub>4</sub> ]
1-butyl-3-methylimidazolium hexafluorophosphate	[Bmim][PF <sub>6</sub> ]
1-butyl-3-methylimidazolium sulfo cyanate	[Bmim][SCN]
1-benzyl-3-methylimidazolium chloride	[Bzmim]Cl
1-ethyl-3-methylimidazolium chloride	[Emim]Cl
1-ethyl-3-methylimidazolium glycine	[Emim][Gly]
1-ethyl-3-methylimidazolium trifluoroacetate	[Emim][TFA]
1-ethyl-3-methylimidazolium acetate	[Emim][OAc]
1-ethyl-3-methylimidazolium trifluoroacetate	[Emim][CF <sub>3</sub> COO]
1-ethyl-3-methylimidazolium alkyl benzene sulfonate	[Emim][ABS]
1-ethyl-3-methylimidazolium acesulfamate	[Emim][Ace]
1-hexyl-3-methylimidazolium chloride	[Hmim]Cl
1-hexyl-3-methylimidazolium tetrafluoromethane sulfonate	[Hmim][CF <sub>3</sub> SO <sub>3</sub> ]
1-hexyl-3-methylimidazolium tetrafluoroborate	[Hmim][BF <sub>4</sub> ]
1-hexyl-3-methylimidazolium hexafluorophosphate	[Hmim][PF <sub>6</sub> ]
1,3-dimethylimidazolium methyl sulfate	[Mmim][C <sub>1</sub> SO <sub>4</sub> ]
1-methyl-3-octylimidazolium chloride	[Omim]Cl

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