



## Review Article

# Ionic liquids (ILs): advances in biorefinery for the efficient conversion of lignocellulosic biomass

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## KEYWORDS

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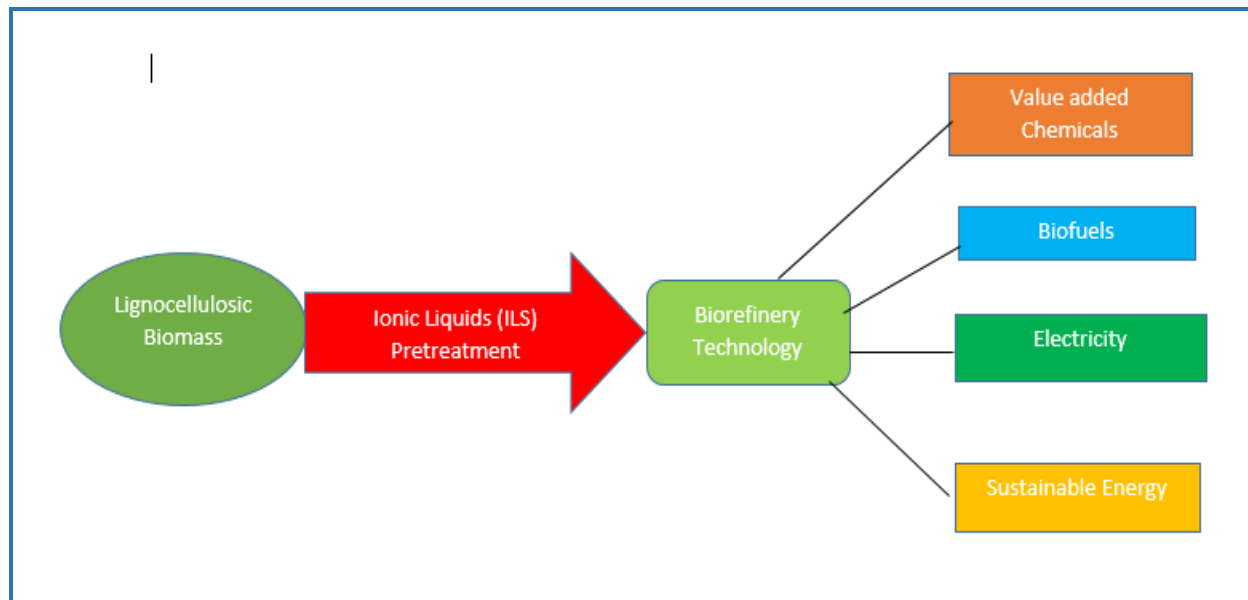
Biorefinery

Biofuels

## ABSTRACT

Lignocellulosic biomass contains polymers of cellulose, hemicellulose, and lignin, bound together in a complex structure. Many physicochemical structural and compositional factors hinder the hydrolysis of cellulose present in biomass to sugars and other organic compounds that can later be converted to fuels. These factors hindering access to sugars contained in lignocelluloses are summed up as “recalcitrance”. As a result, pretreatment is required to allow liberal access to the full contents of lignocellulosic biomass. Production of value-added co-products along with biofuels through integrated biorefinery processes creates the need for selectivity during pretreatment. Pretreatment is an important tool for biomass-to-biofuels conversion processes and is the subject of this review article. The major target of pretreatment is to make the cellulose accessible to hydrolysis for conversion to fuels. Various pretreatment techniques change the physical and chemical structure of the lignocellulosic biomass and enhance the degree of hydrolysis. During the past few years a large number of pretreatment methods have been developed, including alkali treatment, ammonia explosion, and others. Many methods have been shown to result in high sugar yields, for lignocellulosic biomasses such as woods, grasses, corn, rice straw, etc. In this review, we discuss the ionic liquids (ILs) pretreatment method in biorefinery and the recent literature that has been reported on the use of these so-called green solvents for the pretreatment of various lignocellulosic biomasses, ionic liquids have recently become very popular solvents for the dissolution of biomass due to their unique features as compared to conventional solvents.

## Graphical Abstract



## Biographies



**Hitler Louis** is a Master degree student of Physical Chemistry and belongs to Professor He Tao research group at institute of National Centre for Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing, China. Professor He Tao's research group is mainly focus on photo-catalytic/photo-electrochemical reduction of carbon dioxide ( $\text{CO}_2$ ) to liquid fuels (e.g., alcohols) using energy from renewable sources. Louis research focuses on using Density Functional Theory (DFT) to investigate the elementary mechanism that controls selectivity and rate of hydrocarbon products on metal and metal oxide semiconductor catalysts as a key step toward rational design of feasible catalysts for electrochemical or photo-electrochemical reduction of Carbon dioxide ( $\text{CO}_2$ ). In September 2016, He was awarded a full scholarship by the China Scholarship Council (CSC) which made him to move from Nigeria to China to pursue his graduate studies. Louis is also a full time Lecturer with the department of Pure and Applied Chemistry, School of Physical Sciences, University of Calabar, Calabar, Cross River State, Nigeria. Louis has written and published about 20 peer-reviewed science citation index (SCI) journals both within and outside his country.



**Thomas Odey Magu** currently works at the department of Pure & Applied Chemistry, University of Calabar. He is a researcher student at University of Chinese Academic of Sciences, Institute of Chemistry in Beijing. Thomas does research in Physical/Theoretical Chemistry, Environmental Chemistry and Corrosion Studies.



**Aderemi. T. Adeleye** is a graduate of University of Ibadan, Nigeria where he studied Chemistry. He works on the synthesis and characterization of catalysts and use them majorly in the synthesis of high-grade diesel and/or jet fuel and value added chemicals from biomass-derived source (lignocellulosic biomass).



**Monday Philip** is currently a Master student at the National Center for Nanoscience and Technology, Chinese Academy of Sciences, Beijing, China. He does research on electrochemical CO<sub>2</sub> reduction into value added fuel.



**Pigweh I. Amos** works independently and is a versatile writer/researcher in specialized fields. His primary research focuses on solar energy utilization (i.e. CO<sub>2</sub> reduction and artificial photosynthesis) and renewable energy sources.

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**Introduction**

The present energy system is unsustainable as a result of equity issues as well as environmental, economic, increase in global populations and geopolitical concerns that have implications far into the future. At present, fossil fuels still remain key players contributing greater percent to energy supply of the entire world. The high dependence and large usage of fossil fuels creates environmental challenges which demand urgent attention, such as greenhouse gases, which has given incentive for the search for alternative, renewable fuel options [1–5]. Biomass as a renewable resource provides a clean way to productively, secures our environment and improves our economy and energy security. [Figure 1](#) shows the key factors behind the search for the renewable fuels. All organic matters are known as biomass, and the energy released from biomass when it is utilized, burnt, transformed or converted into fuels is called biomass energy ([Figure 2](#)). Biomass energy generates far less air

emissions as compared to fossil fuels [6–8]. Renewable energy is one of the most capable ways to dynamically attain sustainable developments.

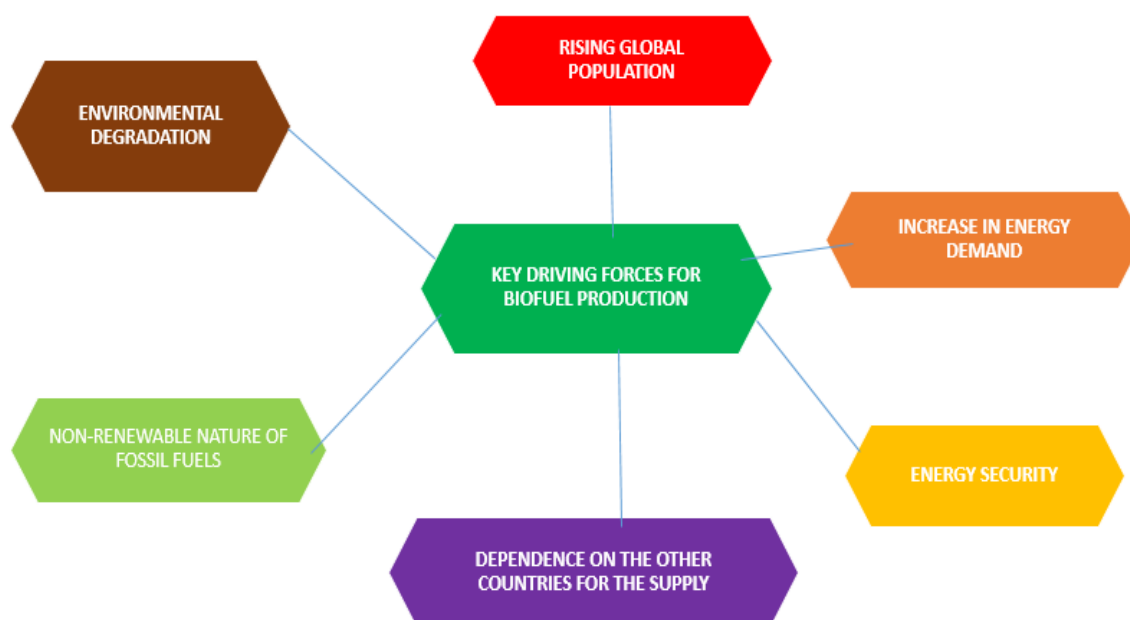
### **Potential of lignocellulosic biomass for the production of environmental friendly fuels and value added chemicals**

Lignocellulosic biomass is the most abundant and renewable resource on earth. It offers potentially carbon-neutral alternative to petroleum. Lignocellulosic biomass represents a promising renewable feed stock for commercial large-scale biorefining, as it is diverse in nature, widely distributed and available in every part of the world, and also can be grown on a billion-ton scale [1]. Agricultural wastes (e.g., wheat straw, sugarcane bagasse, corn stover) or bioenergy crops, which do not engage the use of arable land (e.g., *Miscanthus*, *Switchgrass*, tree wood), and do not raise issue of the food vs. fuel debate, avoid competition with food production and result in a higher reduction of net CO<sub>2</sub> emissions. Unfortunately, the conversion technique of lignocellulosics requires energetically demanding pretreatment paths to separate lignin from cellulose [3], and subsequent cellulosic sugar as the biofuel production depends on slow biocatalytic transformations (Enzymatic saccharification and microbial fermentation) [4]. As global energy supply stands today, biomass accounts for around 12% of the global energy usage, but is mostly used for low-grade heat applications [7]. Biomass is an important feedstock for the environmental-friendly and renewable production of fuels, chemicals, and energy. In order to replace or supplement petroleum, the utilization of lignocellulose needs to be explored [8, 9]. One major key option is to separate the main components of wood and valorize them individually *via* chemical and biological processing. Lignocellulose which is a natural composite material consists of roughly 65% sugar polymers (40% cellulose and 25% hemicellulose), 25% lignin and *ca.* 10% other, minor components. Environmentally benign methods of value-added product extraction from biomass-based feedstocks can drive greater independence from fossil resources and definitively assure a more sustainable future for the next generations. Thus, the maximal valorization of abundant feedstock, i.e. residues from agricultural and food industries, positively contributes positively to the development of bio-based economies achieving sustainability which in turn go in line with principles of green chemistry.

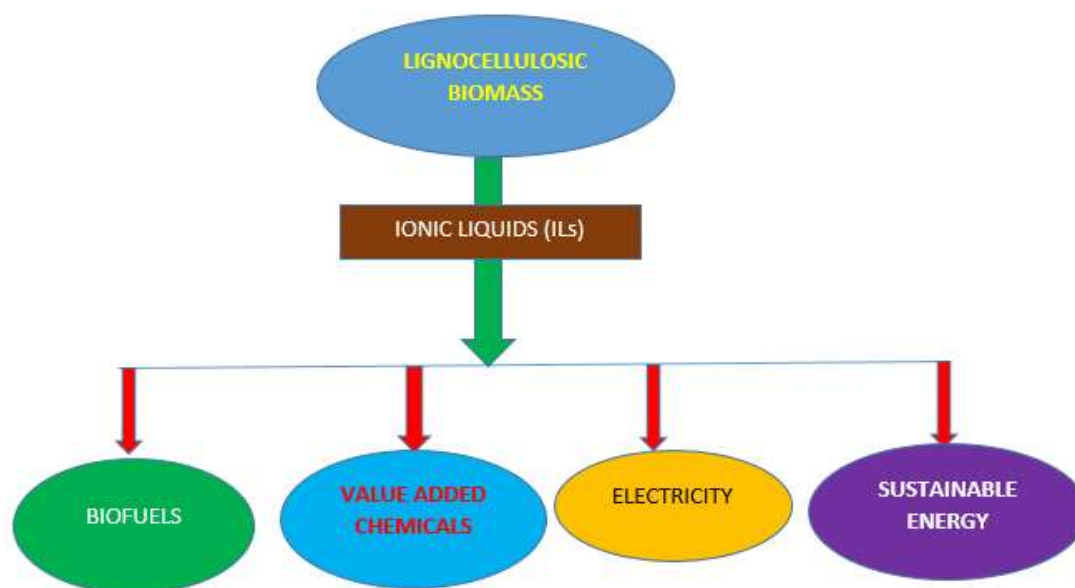
### **Biorefinery**

A biorefinery is a facility that integrates biomass conversion processes with equipment in order to produce fuels, power, heat, and value-added chemicals from biomass. The biorefinery concept is undifferentiated to today's petroleum refinery, which manufactures multiple fuels and products from petroleum [10]. The IEA bioenergy task 42 on biorefineries has defined biorefining as the

"sustainable processing of biomass into a spectrum of bio-based products (Food, feed, chemicals, materials) and bioenergy (Biofuels, power and/or heat)." The biorefinery is not a single or fixed technology. It is the collection of processes that utilize renewable biological or bio-based sources, or feedstocks, to produce an end-product, or products, in a system that is a zero waste producing, and whereby each component from the process is converted or utilized efficiently in a productive system to add value, and hence sustainability to the plant. Several different paths from feedstocks to products are being developed as they demonstrate that multiple biorefinery designs will emerge for the future use. By producing multiple products, a biorefinery utilizes various components in biomass and their intermediates by taking advantage and, thereby, maximizing the value derived from the biomass feedstock. A biorefinery could, for example, produce one or several low-volume, but high value chemical or products and a low-value and high-volume liquid transportation fuel such as biodiesel or bioethanol, while also generating electricity and processing heat through combined heat and power (CHP) technology for its own use, and possibly enough for sale of electricity to the local utility. In this sense, it leads to high profits in high-value products. The produced high-volume fuel produced helps meet energy demands as the power production reduces energy costs and also helps address greenhouse gas emissions, as compared to the traditional power plant facilities. Although some facilities exist that can be called biorefineries, the technology is not stereotype. Future biorefineries may play a key role in the production of chemicals and materials that are traditionally produced from petroleum-based sources.



**Figure 1.** Factors responsible for renewable fuels production



**Figure 2.** Applications of ionic liquids in biorefinery

### Pretreatment and biomass recalcitrance

#### *Pretreatment*

Pretreatment is very important to break the crystalline structure of cellulosic biomass in order to gain access to the enzymes, which can then attach to the cellulose and hydrolyze the carbohydrate polymers into fermentable sugars. The major aim of pretreatment is to pre-extract hemicellulose, disrupt the lignin seal and have full access to the cellulose from the plant cell wall matrix. Pretreatment is considered to be one of the most expensive processing steps in biomass conversion technology, but it also has great potential to improve the productivity and lower the costs through research and development [11–13]. Many pretreatment technologies have been developed and evaluated for various biomass materials. However, each pretreatment method has its own cons and pros, and it is worth mentioning that one pretreatment approach does not applicable to all biomass feedstocks. There are many pretreatment technologies available for biomass processes such as alkaline pretreatment, hot- water pretreatment, dilute-acid pretreatment etc. However, for the sake of this review attention is solely focused on ionic liquids (ILs) pretreatment since there many reports else where in the previous years regarding the other pretreatment methods. The recalcitrance of plant cell wall is constructed by its chemical compositions that build a spatial network as a protection bulwark. Generally, the factors that hinder the accessibility of biomass cellulose can be divided into direct and indirect factors. The direct factor refers to the accessible surface area. It is the most crucial



factor hindering the enzymatic hydrolysis of biomass, because the digestibility of pre-treated biomass is directly limited by the degree of cellulose accessibility. The indirect factors include biomass structure-relevant factors (Pore size and volume, particle size, and specific surface area), chemical compositions (Lignin, hemicelluloses, and acetyl group), and cellulose structure-relevant factors (Cellulose crystallinity and DP (*i.e.*, degree of polymerization)). Pretreatment actually is the process to alter indirect factors and improve direct factor (Increase accessible surface area) thus facilitating the accessibility of cellulose and improving the overall performance of the process.

#### *Requirements for the pretreatment of lignocellulosic biomass*

Using pretreatment as a means by which recalcitrance force is broken for liberal accessibility of the contained contents (Lignin, cellulose and hemicellulose) in lignocellulose has been long recognized. However, better and suitable pretreatment method is required for each type of biomass. The key target of pretreatment technique is to give room for the removal of lignin and hemicellulose, reducing the crystallinity of cellulose, and increasing the porosity of the lignocellulosic materials. For the pretreatment to be considered as an effective method, it must therefore achieve the followings [14]: 1) improve the formation of sugars or the ability to subsequently form sugars by hydrolysis, 2) avoid the degradation or loss of carbohydrate, 3) avoid the formation of by products that are inhibitory to the subsequent hydrolysis and fermentation processes, and 4) be cost-effective.

#### *Biomass recalcitrance*

The material is recalcitrant toward mild chemical and biological composition and thus requires a pretreatment step before the sugars contained in the biomass can be processed biologically (Fermentation) or chemically. Biomass recalcitrance encompasses the multiscale structural features that disallow the conversion of the biomass components into the intermediate or full final desired products [15–17]. Lignocellulose recalcitrance is determined by the composition and molecular structure of the individual components of the feedstocks (Cellulose, hemicellulose, and lignin), and the nature of their intra and intermolecular correlations. Several chemical and physical pretreatment methods have been reported, including the use of steam [18], ammonia [19], dilute acid [20], the organosolv process [21], and most recently, ionic liquids [22], liquid organic salts with tunable solvent properties. Pretreatment to overcome the recalcitrance of lignocellulosic biomass is very important for the efficient and economically viable utilization of lignocellulosic biomass (Figure 2) [23–25]. However, the use of traditional pretreatment methods has disadvantages, including low efficiency and high pollution, seriously hindering their large-scale application [8, 15–17, 26–30]. Pretreatment technologies such as dilute (Aqueous) acid and steam explosion allow the hydrolysis



of the sugar polymers without prior removal of lignin (*i.e.*, delignification). However, pretreatment using a fractionative, lignin-extracting solvent offers a number of advantages, including lower enzyme loadings in the saccharification step, due to the reduced non-productive binding of enzymes [27], and higher saccharification yields for hardwoods and softwoods because of the reduced steric hindrance from lignin binding to the cellulose [15]. Other benefits attached are higher quantity of fermentation products obtained in the absence of carbohydrate and lignin derived inhibitors, smaller reactors for hydrolysis and fermentation, and a lignin that is more appropriate for further valorization. Recently, ionic liquids (ILs) based solvent systems have emerged as promising solvents for lignocellulose, as they serve as an effective tool for the pretreatment of biomass [31–34].

### **Ionic liquids (ILs)**

As a point of argument in “The Paris UN Climate Conference 2015”, the world needs a new model of growth that is safe, durable and beneficial for all to address the climate change challenge. Hence, researchers both from the academia and the industry have to pay greater attention to the detrimental effects of chemicals and chemical-related activities on the environment. Recently, efforts to achieve a sustainable development in the chemical fields have become important task, which is expected to be achieved by applying green chemistry practices [28]. One of the most important criteria for green and sustainable chemical processes is the use of eco-friendly solvents having minimum or zero impact on aquatic organism as well as on environment by putting 12 principles of green chemistry to effective use [35]. The best choice of alternative solvents for the chemical reactions is the ionic liquids. Application of green technology is the demand of time in the view of environmental concerns. it can be found that these noble solvents called ionic liquids (ILs) are very useful in many other fields with thier recycle ability and without any adverse effects on environment which is the most impressive factor in the present era that environmental degradation has become order of the day [36]. Ionic Liquids (ILs) are usually composed of heterocyclic organic cations and various anions and have unique properties such as non-volatility, non-flammability, and a wide temperature range for liquid phase. The reality is that ionic liquids can be liquid at temperatures as low as -96 °C and some are liquid at over 400 °C [37]. Furthermore, room-temperature ionic liquids (RTILs) are frequently colorless, fluid, and easy to handle. In the patent and academic literature, the term “ionic liquids” now refers to liquids composed entirely of ions that are fluid around or below 100 °C [37]. Keeping in view of the noble properties of ionic liquid and its detailed knowledge, the applications of ionic liquids can be explored in many other areas. Ionic liquids are the liquids that make new technologies possible through environmental feasibility.

### *Chemical structure of ionic liquids*

Ionic liquids are formed from organic cations which are usually large and asymmetric like; derivatives of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium. Common anions include; halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis(Trifluoromethylsulfonyl) imide which are inorganic and organic anions like alkyl sulfate, alkyl sulfonate, p-toluenesulfonate (Tosylate) and trifluoroacetate.

### *Ionic liquids greener chemistry (greener solvents)*

Ionic liquids have several tremendous characteristic features (Figure 3) that render them preferably over other traditional types of solvents. Figure 4 shows in chart format the characteristic features of ionic liquid, while Scheme 1 and Scheme 2 show some common cations and anions respectively used in ionic liquid synthesis

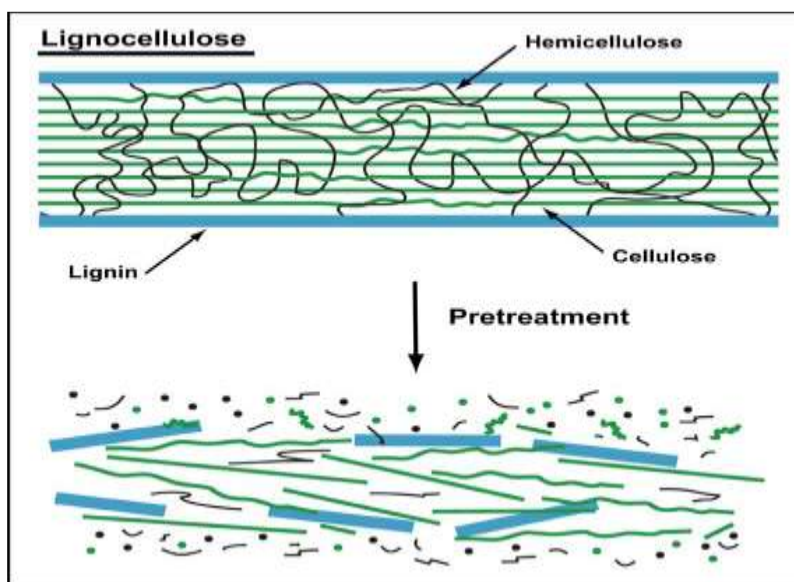
### *Overview of ionic liquid synthesis*

The synthesis of ionic liquids is quite simple and, by controlling the synthesis, it is also possible to control the purity of the products formed in the process [38]. Ionic liquids composed of the 1-*n*-butyl-3-methylimidazolium cation are the most commonly, widely studied and discussed compounds. Scheme 3 shows the general method for synthesis of ionic liquids [39]. A synthetic method for the preparation of these salts starts with alkylation of 1-methylimidazole with a butyl halide, usually a chloride or bromide. 1-methylimidazole is refluxed with excess of butyl halide for about approximately 24 hours. This excess is then evaporated and 1-*n*-butyl-3-methylimidazolium chloride (or bromide) is obtained [40].

The resulting organic salt synthesized can be used in three different ways: directly as an ionic liquid; it can be mixed with aluminum chloride or other halometallates leading to the formation of chlorometallate-based ionic liquids, widely studied in the literature; or for subsequent metathesis [41]. The metathesis reaction is simply an exchange between cations and anions of the involved compounds. An example is the reaction of 1-*n*-butyl-3-methylimidazolium chloride with sodium tetrafluoroborate in acetone at room temperature, resulting in the production of a nearly quantitative yield of [BMI] [BF<sub>4</sub>] after 24 hours of reaction time (Scheme 4) [42]. Another method to prepare alkyl sulfonate esters such as butyl methanesulfonate to obtain higher yields is by treating *n*-butanol with methanesulfonyl chloride in the presence of a base such as triethylamine. Finally, 1-methylimidazole is alkylated with the ester produced in the absence of solvents at room temperature, leading to the formation of organic salt 1-*n*-butyl-3-methylimidazolium methanesulfonate after 48-72 hours in a nearly quantitative yield. The methanesulfonate anions can easily be replaced in the

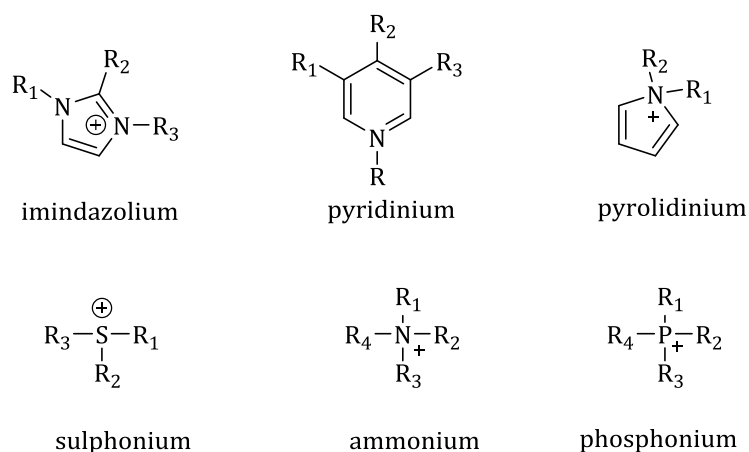
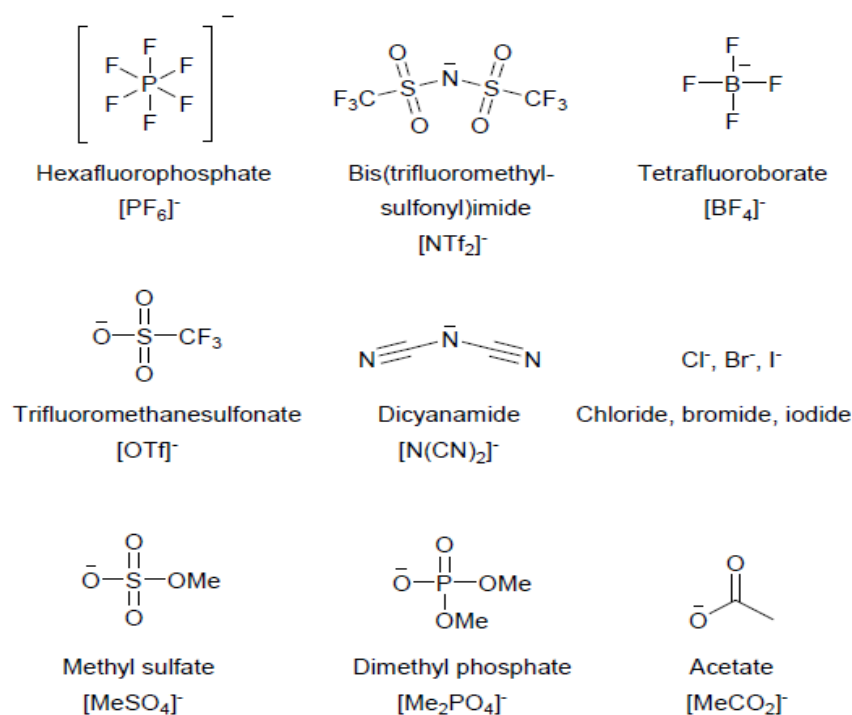
process by other anions such as  $\text{BF}_4$  and  $\text{PF}_6$  through metathesis in aqueous medium at room temperature, presenting yields of 80-95% (Scheme 5) [43]. The reactions described above are only examples, and a wide variety of ionic liquids can also be prepared applying these procedures with slight modifications and varying the anions, cations and alkyl chain lengths of both. The cations play a vital role to define the physical properties of ionic liquids (Such as melting point, viscosity and density), while the anion determines its chemical properties and reactivity [38]. One major factor that may be taken into consideration while designing an ionic liquid is its hydrophilic/hydrophobic chemistry, which affects the solvation properties of ionic liquids.

**Figure 3.** Pretreatment of lignocellulose



**Figure 4.** Characteristic features of ionic liquids

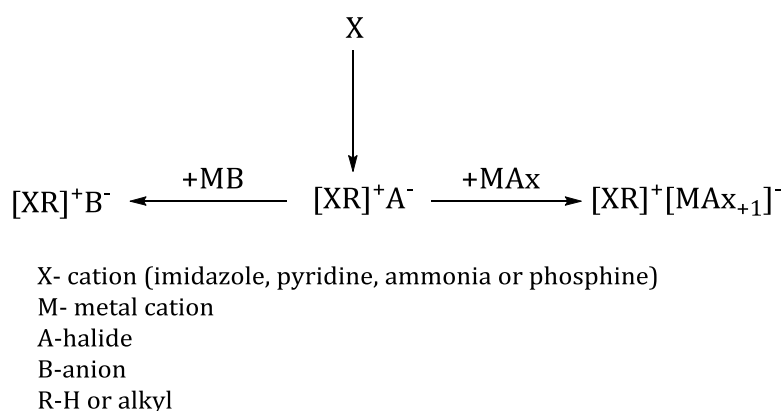


**Scheme 1.** Some common cations used in ionic liquid synthesis**Scheme 2.** Some common anions used in ionic liquid synthesis*Applications of ionic liquids in various fields*

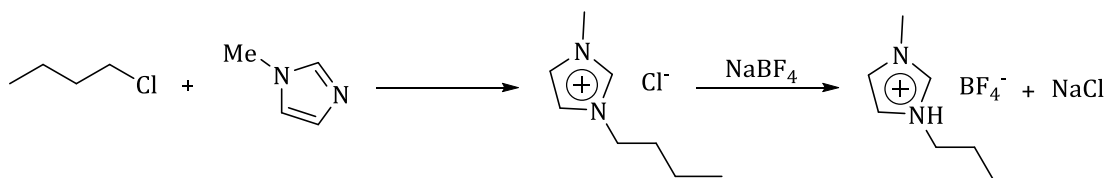
The fascinating attention of ionic liquids lies in their extraordinary set of characteristic features when compared to conventional solvents. As salts consisting of distinct anions and cations, ILs are basically binary (or higher order) systems. The anions and cations can be independently selected to tune the IL's physicochemical properties (Melting point, conductivity, viscosity, density, refractive

index, etc.) while at the same time introducing specific desired features for a given application (hydrophobicity vs. hydrophilicity, controlling the degree of solute solubility, adding functional groups for catalysis/reactivity purposes, chirality, etc.). As a result of their unique features mentioned in this review they have been used in various fields (Figure 5). Ionic liquids (ILs) have found to possess a number of industrial applications and have also been investigated as green solvents in biomass conversion technology.

The most popular ionic liquids are the salts composed of 1,3-dialkylimidazolium cations. The associations of the 1-*n*-butyl-3-methylimidazolium cation (BMI) with bis{(trifluoromethyl)sulfonyl} amide (NTF<sub>2</sub><sup>-</sup>), tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) or hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) anions (Scheme 6) are well-studied examples of these salts.



**Scheme 3.** Typical schematic representation for synthesis of ionic liquids



**Scheme 4.** Synthetic route for 1-*n*-butyl-3-methylimidazolium tetrafluoroborate preparation from 1-methylimidazolium and butyl chloride

### Ionic liquids in biorefinery

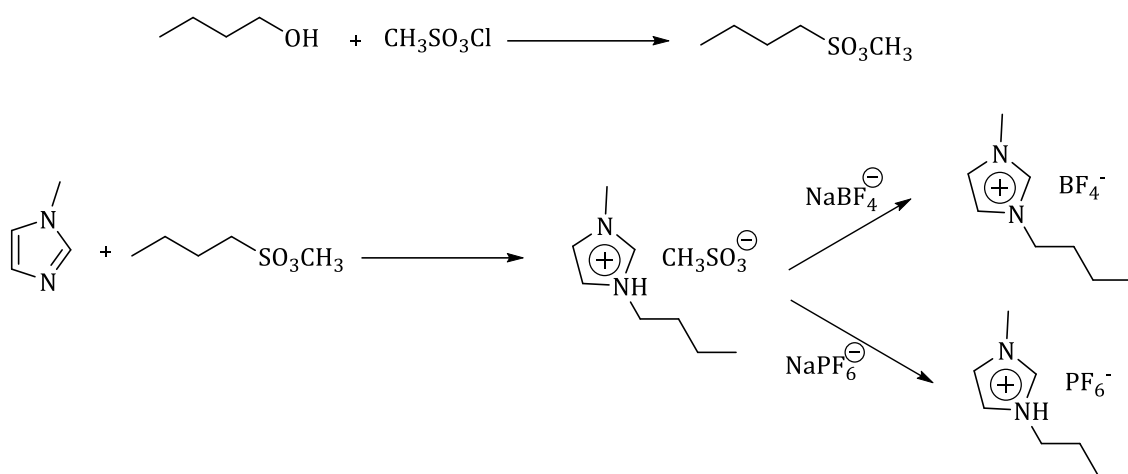
Ionic liquids (ILs) have recently become very popular solvents for the dissolution of biomass. They often have tunable physical properties based on the choice of cation and anion pair used for the synthesis, a negligible vapor pressure, and good thermal stability [44]. In a pioneering study by Rogers and co-workers, several ionic liquids, in particular, 1-butyl-3-methylimidazolium chloride, were found capable of dissolving up to 10 wt% cellulose [45]. Hydrogen bonds formed with non-

hydrated  $\text{Cl}^-$  ions disrupted the intermolecular hydrogen bonding in the cellulose structure, which allowed the dissolution of the cellulose [44]. Since this study, several researchers have investigated the dissolution of biomass, including lignin, using ionic liquids. Lee and co-workers observed that [EMIM] [OAc] was able to selectively extract lignin from wood with less crystalline cellulose remaining [46]. Fort and co-workers used 1-butyl-3-methylimidazolium chloride to dissolve wood and followed the dissolution by  $^{13}\text{C}$  NMR spectroscopy. They found that this ionic liquid was effective for the dissolution of both cellulose and lignin, and they were able to use precipitation solvents to isolate cellulose from the other biomass components [44]. As a result of the previous investigations, the use of ionic liquids as biomass solvents has recently attracted considerable interest, and important developments in the use of ionic liquids for biomass fractionation, analysis, and pollutant removal have been recently achieved. Some ionic liquids commonly used for the pretreatment of lignocellulosic biomass are shown in Table 1.

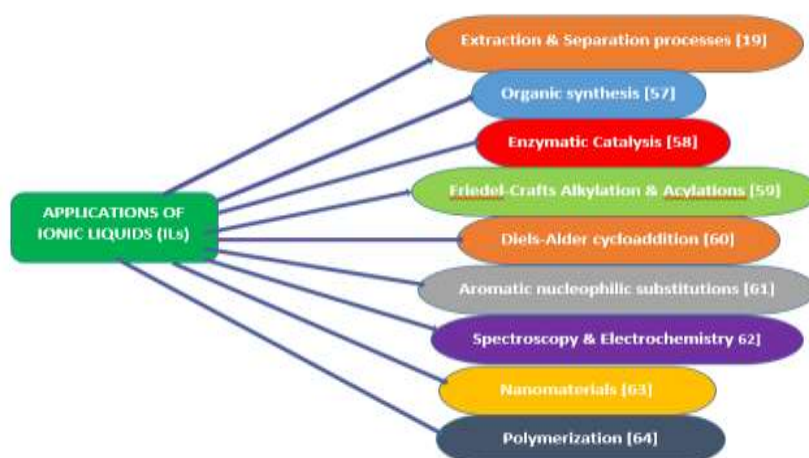
### Solubilisation strength of cellulose in ionic liquids (ILs)

Cellulose, the most abundant carbohydrate contents in biomass, is an important resource for many biomass-derived applications such as fiber, paper, membrane, ethanol, and furan-based products. It is composed of linear glucose polymer chains and is insoluble in water and most common organic solvents. Cellulose can be dissolved in solvents by disrupting its inter and intramolecular hydrogen bonding [47].

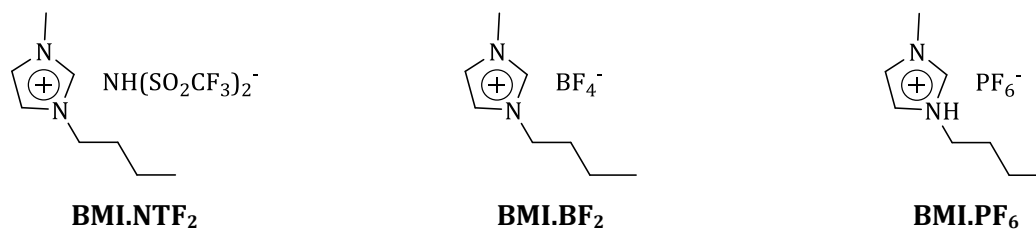
Cellulose dissolution is an industrially attractive application of ionic liquids, due to good solubility (5-20 wt%, depending on the ionic liquid and the reaction conditions), the competitive properties of cellulose regenerated from the ionic liquid solutions [48] the increased stability of ionic liquid cellulose solutions [49] and the low toxicity of certain relevant ionic liquids. Payal et al., indicated that among room temperature ILs, a good solvent for cellulose dissolution contains a strong hydrogen bond acceptor and a moderate hydrogen bond donor [50]. The mechanism of liquid pretreatment resulted from impact of ion that attacks hydrogen bond of cellulose by decreasing the hydrogen dipolar and columbic force. Then, aqueous molecular shell dislocates from cellulose to ionic liquid, and caused the rearrangement of intra and intermolecule interaction. The dissolved cellulose can be modified in solution [51, 52] or regenerated (Reprecipitated) by adding water, mixtures of water with organic solvents (e.g. acetone) or protic organic solvents, such as ethanol resulting to the formation of films and fibres [53, 54]. The ordering of the regenerated cellulose is reduced as compared to the initial state and it is converted into cellulose II [55]. This, in turn, consequently leads to the acceleration of hydrolysis with cellulases as compared to native cellulose [56], an effect that is



**Scheme 5.** Synthetic route for 1-*n*-butyl-3-methylimidazolium tetrafluoroborate and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate preparation from *n*-butanol, methanesulfonyl chloride and 1-methylimidazolium



**Figure 5.** Applications of ionic liquids. Corresponded references in bracket



**Scheme 6.** Structures of 1-*n*-butyl-3-methylimidazolium derived ionic liquids

very impressive in terms of feedstocks utilization in the biorefinery technology and has aroused interest in the use of cellulose dissolution when ionic liquids as green solvents are employed for the



deconstruction of lignocellulose in order to access its contained contents. Mixtures of cellulose dissolving ionic liquids and polar organic cosolvents, such as dimethylformamide, dimethylsulfoxide and 1,3-dimethyl-2-imidazolidinone, have also been successfully applied [57, 58]. The great advantage of such mixtures is the lower viscosities of the cellulose solutions. This enhances the process of cellulose dissolution process from hours down to minutes. It has been observed that the ionic liquid anion plays an important role in determining an ionic liquid's ability in dissolution of cellulose. Suitable ionic liquids identified to date contain anions that can form strong hydrogen bonds with hydroxyl groups, e.g. chloride [53], carboxylates (Acetate, formate, propionate, lactate) [59], dialkyl phosphates, dialkyl and trialkyl phosphonates [60] and amino acid anions. The dissolving strength of these relevant ionic liquids has been typically attributed to strong hydrogen-bonding interactions between the anions and equatorial hydroxyl groups on the cellulose. The dissolution of cellulose with ILs is influenced by many factors, including the composition and structure of ILs, the nature of cellulose and the dissolution conditions. Many experiments have indicated that the anions of ILs play an important role in determining an IL's ability to dissolve cellulose [61–63]. Up to now, these ILs which are identified as being capable of dissolving cellulose generally consist of imidazolium<sup>+</sup>, pyridinium<sup>+</sup>, ammonium<sup>+</sup>, phosphonium<sup>+</sup>, or morpholinium<sup>+</sup> based cations, and anions that can form strong hydrogen bonds with hydroxyl groups, e.g., chlorides, carboxylates (Acetate, formate, propionate, lactate), dialkyl phosphates, dialkyl and trialkyl phosphonates and amino acid anions [61–65]. It is known that the solubility of cellulose in IL corresponds well with the hydrogen-bond basicity of its anion [8, 63, 65]. At the same time, the cations can also indirectly influence the dissolving ability of ILs through impacting their physical properties, such as the melting point, density and viscosity [66, 67]. It should be noted that the ILs containing anions that can form strong hydrogen bonds are not always capable of dissolving cellulose.

#### *The impact effects of water on the solubility strength of cellulose in ionic liquids*

Impurities can affect cellulose solubility, the most prominent being water. Water can easily be absorbed by ionic liquids from air or introduced with wet cellulose biomass and is a potent anti-solvent for cellulose. For example, a study by Mazza et al., of the precipitation of cellulose from [C<sub>2</sub>C<sub>1</sub>im] Cl showed the onset of cellulose precipitation occurring at *ca.* 0.15 wt% water and that it was quite complete at *ca.* 0.25 wt% water; [68] this is less than 3 mol% as compared to the number of ionic liquid ions in the system and only 0.5 equivalents relative to the number of cellulose hydroxyl groups in solution. Gericke et al., found that addition of 20 wt% water influenced solubilisation of cellulose in all the ionic liquids that they employed for the investigation: [C<sub>4</sub>C<sub>1</sub>im] Cl, [C=C<sub>2</sub>C<sub>1</sub>im]Cl and [C<sub>2</sub>C<sub>1</sub> im] [MeCO<sub>2</sub>] [69]. Changes in solvent entropy may also play a role. Finally, it is possible that

different effects are contributing to this noticeable effects at different concentrations of water. Interestingly, *Ohno* and co-workers recently reported the rapid dissolution (5 min) of 15 wt% cellulose in aqueous solutions of tetrabutylphosphonium hydroxide,  $[(C_4)_4P]OH$ , and tetrabutylammonium hydroxide,  $[(C_4)_4N]OH$ , containing 40-50% water by weight were reported to dissolve cellulose at room temperature [70]. In both cases, even large quantities of water did not hinder the degree of solubility, as it typically does with other cellulose solubilizing ionic liquids. The tolerant ability towards water is highly important, as the water is demanded to stabilize the organic hydroxide salt, which would decompose upon drying. The fast dissolution is as a result of the decreased viscosity of the resulting cellulose solutions. Cellulose solubility in cold (4 °C) aqueous hydroxide has been formerly reported [71]. However, the organic hydroxide solution seems to work at temperatures that are more beneficial for processing and in a wider range of concentration. These IL based solvent systems have the potential to maintain (or even to improve) moderate-to-high cellulose solubility, while simultaneously minimizing challenges associated with handling highly viscous solutions of cellulose in pure ILs.

#### *Dissolution of hemicellulose in ionic liquids*

Hemicellulose has the weakest structure in comparison to other components of lignocellulose (That of cellulose and lignin). Because of structural similarity to cellulose, ionic liquids that can dissolve cellulose are expected to dissolve hemicellulose as well, even though few reports show specific dissolution of hemicellulose. It is interesting, however, to note that a  $[BMIM]Cl-H_2O$  mixture selectively removes hemicellulose from the treated legume straw. A maximum of 29.1 wt% legume straw is dissolved in the  $[BMIM]Cl-20$  wt%  $H_2O$  mixture at 150 °C for 2 h. A hemicellulose-free lignin-rich material (64.0 wt% lignin and 35.3 wt% cellulose) was obtained by adding water. Removal of hemicellulose increases the mean pore size of the substrate and therefore increases the probability of the cellulose to get hydrolyzed [72].

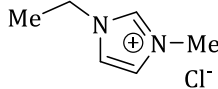
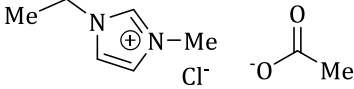
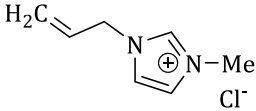
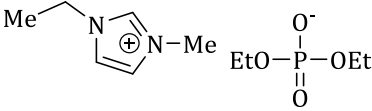
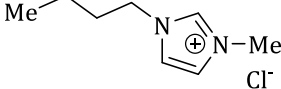
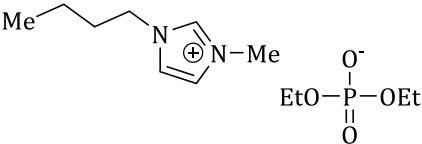
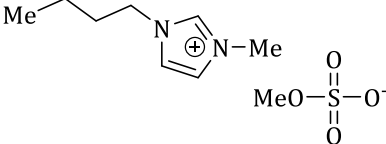
#### *Dissolution of lignin in ionic liquids*

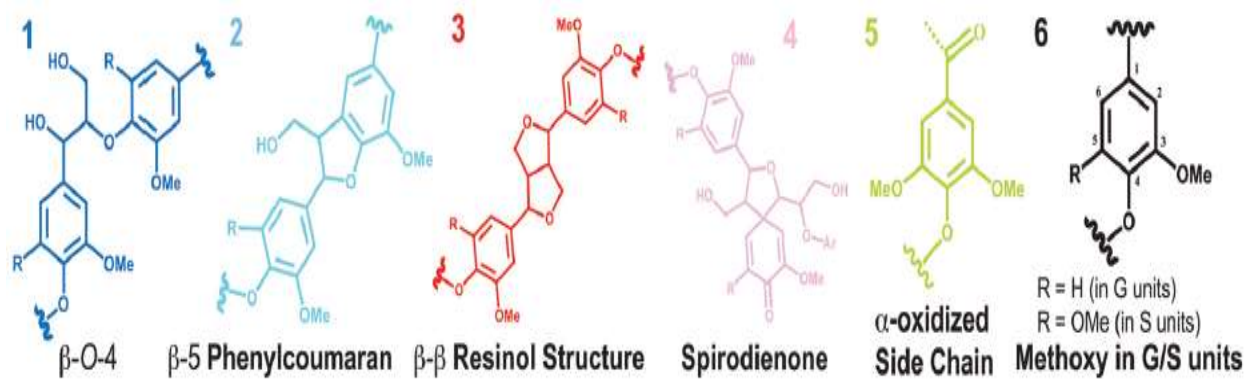
Lignin consists of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units linked by various interunit linkages (Figure 6a), S and G units linked by  $\beta$ -O-4 bonds being the most abundant in hardwoods. 7 biomass recalcitrance comprises the multiscale structural features that hinder the conversion of the biomass components into the final desired products [73–76]. Lignocellulose recalcitrance is determined by the composition and molecular structure of the individual components (Cellulose, hemicellulose, and lignin), and the nature of their intra and intermolecular interactions [76, 77]. The molecular structure of hemicelluloses plays an important role in

modulating the association with cellulose microfibrils [78–81] and the occurrence of covalent linkages with lignins forming so-called lignin carbohydrate complexes (LCCs) (Figure 6b) [82, 83]. Although the occurrence of LCCs is still under debate due to questionable isolation procedures and low frequencies of detected bonds, recalcitrance in biomass fractionation has partly been attributed to these covalent linkages.

The mechanistic path for the dissolution of lignin in ionic liquids lacks sufficient study, likely because of the complexity structural nature of lignin. The reported literature appears to indicate that the dissolution of lignin also follows a similar mechanistic route that involves anions of strong *H*-bonding basicity. Because of the heavily polyaromatic composition of lignin, cations of ionic liquids with unsaturated bonds such as C=C in allyl group also contribute to the overall solubility of lignin [84, 85]. The lignin crust has been identified as one of the major obstacles for an energy efficient biomass deconstruction process [86]. Native lignin not only prevents access of carbohydrate hydrolases to their substrates, but also modifies lignin adhering to the pulp after pretreatment also resulting in unproductive binding of hydrolases [87]. This leads to the need for higher enzyme loadings in the enzymatic carbohydrate hydrolysis and prevents efficient enzyme recycling [88]. Lignin can also be a source of compounds that inhibit hydrolases and fermentative organisms, including syringyl aldehyde and vanillic acid [89]. A number of observations regarding the modification of lignin during ionic liquid deconstruction have been published. *Tan et al.*, reported that lignin extracted with [C<sub>2</sub>C<sub>1</sub>im] [ABS] has a lower molecular weight and a narrower polydispersity than a lignin obtained by aqueous auto-catalysed pretreatment [90]. *George et al.*, also reported the impact of a range of ionic liquids on several commercial lignins and demonstrated a profound anion effect on the fragmentation mechanism and the degree of polymerisation, with liquids containing alkyl sulfate anions having the greatest ability to fragment the lignins and reduce polymer length [91]. The order of molecular weight reduction was sulfates>lactate>acetate>chlorides>phosphates. The functional group of the anion determined the effect rather than its size, while the cation did not play a significant role. The authors conclude that the more active anions act as nucleophiles during lignin depolymerisation. In support of this, an increased sulfur content of the lignin after treatment with ionic liquids with sulfur containing anions such as sulfonates and sulfamates (*e.g.* [ABS] and acesulfamate) [89–92], and sulfates (MeSO<sub>4</sub><sup>−</sup> and HSO<sub>4</sub><sup>−</sup>) [90], has been reported. This may also explain why an attempt to design a “lignin friendly” cation by adding an aromatic side chain had only moderate success [84]. Analysis of the residual lignin in [C<sub>2</sub>C<sub>1</sub>im] [MeCO<sub>2</sub>] pretreated maple wood with 2-dimensional NMR revealed a decrease of the β-O-4 aryl ether bond content as well as deacetylation of xylan [93]. The effect of two lignocellulose dissolving ionic liquids on a lignin model

**Table 1.** Ionic liquids commonly used for the pretreatment of lignocellulosic biomass

| Name / abbreviation   | Structure   |
|---|---|
| 1-ethyl-3-methylimidazolium chloride<br>[EMIM]Cl                                      |  |
| 1-ethyl-3-methylimidazolium acetate<br>[EMIM][CH <sub>3</sub> COO]                    |   |
| 1-allyl-3-methylimidazolium chloride<br>[AMIM]Cl                                      |   |
| 1-ethyl-3-methylimidazolium diethylphosphate [EMIM][DEP]                              |   |
| 1-butyl-3-methylimidazolium chloride<br>[BMIM]Cl                                      |   |
| 1-butyl-3-methylimidazolium acetate<br>[BMIM][CH <sub>3</sub> COO]                    |   |
| 1-butyl-3-methylimidazolium methylsulfate<br>[BMIM][CH <sub>3</sub> SO <sub>4</sub> ] |  |

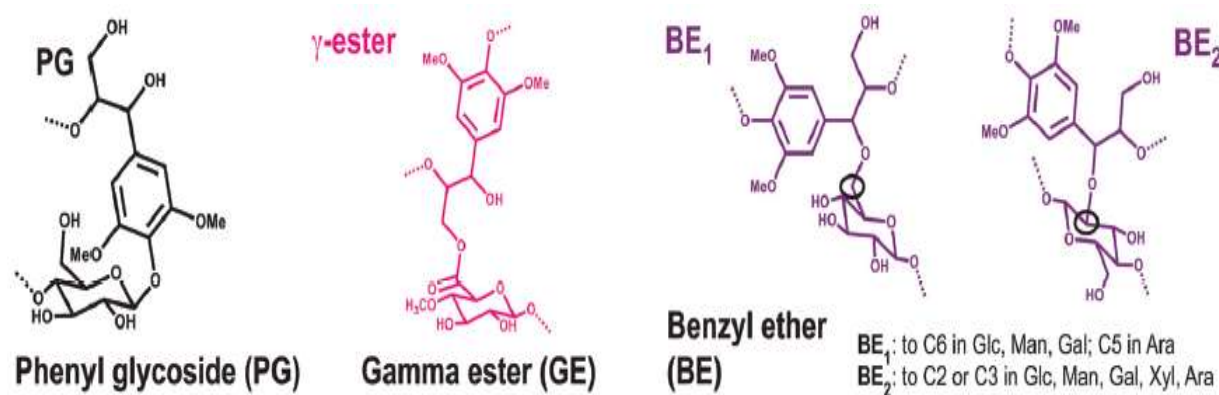


**Figure 6.** a) Lignin interunit linkages

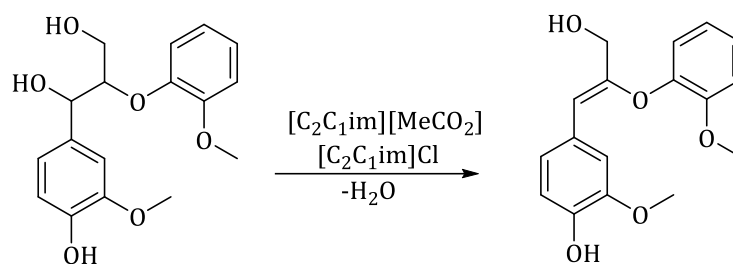
compound featuring a  $\beta$ -O-4 aryl ether linkage has been studied (Scheme 7) [94]. The compound was dissolved in [C<sub>2</sub>C<sub>1</sub>im]Cl or [C<sub>2</sub>C<sub>1</sub>im] [MeCO<sub>2</sub>] at 120 °C, a dehydration reaction was reported for both ionic liquids. The dehydration was significantly faster in [C<sub>2</sub>C<sub>1</sub>im][MeCO<sub>2</sub>] than in [C<sub>2</sub>C<sub>1</sub>im]Cl, possibly

reflecting the acetate's greater basicity and affinity towards water [95]. The occurrence of such dehydration reactions has also been suggested by George et al., more recently [96].

Transformation of solubilised lignin in ionic liquids has attracted limited attention so far. The oxidation of organosolv beech lignin in ionic liquids in the presence of transition metals and molecular oxygen has been demonstrated by Stärk et al. [96]. The main product was 2,6-dimethoxy-1,4-benzoquinone; vanillin, syringaldehyde and other less abundant oxidized aromatic fragments were also identified. The compounds were partially extracted into organic solvents. Since Ragauskas and co-workers [97] reported in 2007 that some ILs could serve as superior solvents for lignin, the use of ILs in separation of lignin has been studied intensively [98–111]. A recent review by Hossain and Aldous [112] provided a comprehensive summary of the multifunctional use of ILs in lignin processing. Rogers and co-workers developed a process for isolation of lignin using ILs. In this process, IL dissolves all major components of the biomass, and then the polysaccharides and lignin are stepwise precipitated by adding an antisolvent. However, this process is relatively time-, solvent-, and energy-intensive. To improve the efficiency, selective dissolving, and extraction of lignin, specialized ILs, such as dialkylimidazolium cations in combination with acetates [113] and alkylbenzene sulfonates [92], have been developed. Overall, the IL process is a tunable strategy that could be conducted under mild conditions. The obtained lignin has little structural change, larger average molar mass, and more uniform molar mass distribution as compared to those of Kraft lignin. The precise circumstances surrounding lignin dissolution in ILs have not yet been fully understood. Many parameters, including extraction conditions (Temperature, time, etc.), purity of IL, wood species, wood particle size, wood load, and both IL anion and cation species, influence the extraction efficiency [113]. Although pretreatment of lignin with ILs has shown promise in biorefinery processes, the problem of high IL cost and recyclability issues hampers the use at a commercial scale.



**Figure 6.** b) Lignin carbohydrate complexes (LCCs)



**Scheme 7.** Dehydration of the lignin model compound guaiacylglycerol- $\beta$ -guaiacyl ether in ionic liquids

## Conclusion

There are a number of key features that need to be considered for the effective pretreatment of lignocellulosic biomass. The pretreatment process should have a low capital and operational cost. It should be effective on a wide range and loading of lignocellulosic biomass and should help in the recovery of most the lignocellulosic components in a useable form. Moreover, it should not be a difficult task in separate fractions. Many pretreatment methods have been studied, and are still in development. It is difficult to evaluate and compare pretreatment technologies because they involve upstream and downstream processing cost, capital investment, chemical recycling and waste treatment systems. However, as an integrated part of an industrial system or biorefinery, mass balance analysis can be used to validate the pretreatment efficacy of a process with any given feedstock. Today, ionic liquids still have a higher cost as compared to the traditional catalysts. However, it should be taken into account that the higher the number of reuses of these catalysts is, the lower the cost of the process. Therefore, studies that focus on the reduction of the production costs of these ionic liquids and their reuse would increase the feasibility of using this system. An increased use of biofuels would contribute to sustainable development by reducing greenhouse gas emissions, the use of non-renewable resources and also reduce dependency on other countries for the supply thereby improving nation's economy while getting their supply from available renewable sources within. To conclude, it can be said that the field of ionic liquid catalysis holds enormous possibilities that still need to be explored.

## Disclosure statement

No potential conflict of interest was reported by the authors.

## Abbreviations

SD

Steam distillation

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|                                   |   |
|-----------------------------------|---|
| <i>HAD</i>                        | <i>Hydro-distillation adsorption</i>                    |
| <i>SFE</i>                        | <i>Supercritical fluid extraction</i>                   |
| <i>DIC</i>                        | <i>Instantaneous controlled pressure drop process</i>   |
| <i>MASE</i>                       | <i>Microwave-assisted solvent extraction</i>            |
| <i>SCO<sub>2</sub></i>            | <i>Supercritical carbon dioxide</i>                     |
| <i>MAE</i>                        | <i>Microwaves assisted extraction</i>                   |
| <i>MASD</i>                       | <i>Microwave-accelerated steam distillation</i>         |
| <i>CO<sub>2</sub></i>             | <i>Carbon dioxide</i>                                   |
| <i>MILT-MHD</i>                   | <i>Hydro-distillation</i>                               |
| <i>CAMD</i>                       | <i>Compressed air microwave distillation</i>            |
| <i>SFEM</i>                       | <i>Solvent-free microwave extraction</i>                |
| <i>MHG</i>                        | <i>Microwave hydrodiffusion and gravity</i>             |
| <i>VMHD</i>                       | <i>Vacuum microwave hydro-distillation</i>              |
| <i>CSFME</i>                      | <i>Conventional solvent-free microwave extraction</i>   |
| <i>ISFME</i>                      | <i>Improved solvent-free microwave extraction</i>       |
| <i>MAHD</i>                       | <i>Microwave assisted hydro-distillation</i>            |
| <i>HD</i>                         | <i>Hydro-distillation</i>                               |
| <i>USAE</i>                       | <i>Ultra-sound assisted extraction</i>                  |
| <i>%</i>                          | <i>Percentage</i>                                       |
| <i>USWE</i>                       | <i>Ultrasound-enhanced subcritical water extraction</i> |
| <i>SLE</i>                        | <i>Super-heated liquid extraction</i>                   |
| <i>SE-SD</i>                      | <i>Solvent extraction and steam distillation</i>        |
| <i>MSD</i>                        | <i>Microwave steam distillation</i>                     |
| <i>MSDF</i>                       | <i>Microwave steam diffusion</i>                        |
| <i>OAHD</i>                       | <i>Ohmic-assisted hydro-distillation</i>                |
| <i>AFNOR</i>                      | <i>Association française de normalisation</i>           |
| <i>cm</i>                         | <i>Centimetre</i>                                       |
| <i>mm</i>                         | <i>Millimetre</i>                                       |
| <i>°C</i>                         | <i>Centigrade</i>                                       |
| <i>mL</i>                         | <i>Milliliter</i>                                       |
| <i>Anhydrous MgSO<sub>4</sub></i> | <i>Anhydrous magnesium sulphate</i>                     |
| <i>EO</i>                         | <i>Essential oil</i>                                    |
| <i>Tc</i>                         | <i>Critical temperature</i>                             |



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|              |  |
|--------------|--|
| $g/cm^3$     | Gram per cubic centimetre  |
| $\alpha$     | This is a significant difference of 5%, which means we have a 5% chance of being wrong |
| $Y$          | Yield of extrcation  |
| $P$          | Pressure   |
| $Q_{CO_2}$   | Flow rate of $CO_2$  |
| $kg\ h^{-1}$ | Kilogram per hour conversion chart   |
| Kilo Pascal  | KPa  |
| kWh          | kilowatt hour  |
| s            | Second   |
| Kg           | kilogram   |

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