Ionic liquid based pretreatment of lignocellulosic biomass for enhanced bioconversion

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Abstract

Lignocellulosic biomass is the most plentiful renewable biomolecule and an alternative bioresource for the production of biofuels and biochemicals in biorefineries. But biomass recalcitrance is a bottleneck in their usage, thus necessitating their pretreatment for hydrolysis. Most pretreatment technologies, result in toxic by-products or have lower yield. Ionic liquids (ILs) have successfully advanced as 'greener and recyclable' alternatives to volatile organic solvents for lignocellulosic biomass dissolution. This review covers recent developments made in usage of IL-based techniques with focus on biomass breakdown mechanism, process parameter design, impact of cation and anion groups, and the advantageous impact of ILs on the subsequent processing of the fractionated biomass. Progress and barriers for large-scale commercial usage of ILs in emerging biorefineries were critically evaluated using the principles of economies of scale and green chemistry in an environmentally sustainable way.

Keywords: Lignocellulosic biomass, Ionic liquids, Pretreatment, Enzymatic hydrolysis, Biorefinery

1   Introduction

The population of the world today is ~1900-times the size of what it was 12 thousand years ago when it was around 4 million – half of today's population of London. This rapid growth is creating tremendous usage of natural resources, energy and chemicals. In 2018, global energy requirement grew by 2.3%, its fastest speed in the past decade. The surge in the cost of fuel energy, need to reduce dependence on traditional chemicals that impact the environment, and the changing societal and cultural value of the world is challenging us as humanity to look towards efficient usage of renewable resources and to accelerate efforts to upcycle traditional organic wastes. Lignocellulosic biomass is a natural vessel for amassing solar energy and hence presents itself as an important renewable resource for raw material and energy (Bhatia et al., 2019a; Bhatia et al., 2019b). Plants convert approximately 4,500 Exa Joules (EJ) of solar energy annually (Ralph, 2014) and convert nearly 120 Giga Tonnes of carbon from the atmosphere into biomass - nearly eight times the global energy demand. Approximately 50% of the global biomass is made up of lignocellulose, making it the most available organic compound in the biosphere. Various industries such as food, pharmaceutical, and cosmetics exploit lignocellulose in their production chain. Lignocellulose also serves as a substrate in the synthesis of bioethanol (Naghshbandi et al., 2019), beauty masks, curative chows, fillers for thermoplastic composite materials and many other products (de Paula et al., 2019).

The physical properties of lignocellulosic material make it a biologically renewable and sustainable source of organic carbon and thus it is a possible raw material for renewable biofuel manufacture that can serve as an alternate to fossil fuels. Additionally, there has been a growing interest in the transfiguration of lignocellulosic biomass to manufacture green chemicals (Kang and Zhang, 2018; de Paula et al., 2019). However, usage of lignocellulosic biomass as feed material for biofuel production or synthesis of green platform chemicals is

not straightforward in its natural physical form. Thus, pretreatment becomes a vital step in the process of obtaining/producing useful end products from lignocellulosic biomass. Pretreatment ensures to decrease crystallinity and heighten the porosity of the lignocellulosic biomass, which makes it more susceptible to further chemical reactions and usage across multiple industries. A lot of processes have been developed over the years for lignocellulosic biomass pretreatment, each with its own merits under varying conditions. Ionic liquids (ILs) have gained significant traction in pretreatment process due to their unique and green properties combined with their potential to completely breakdown and dissolve lignocellulosic materials (Sun et al., 2017; Bhatia et al., 2019a).

The focus of this review is to explore the current undertakings in pretreatment of lignocellulosic biomass using ILs, highlighting their green nature, and advantageous impact in further alteration of lignocellulosic biomass components thus derived into value-added end products. While most available reviews focus on the pretreatment step using ILs, not many have brought forward the advantages that ILs bring when combined with other pretreatment materials, as well as the benefit that ILs bring to the subsequent processes after pretreatment step. Towards this the focus is to bring attention towards recent works published for using ILs in conjunction with alkali and acids and enhanced enzymatic hydrolysis via single-step hydrolysis studies performed on various lignocellulosic biomass feedstock once pretreated with ILs. The review also sheds light on cost-benefit analysis of usage of ILs through some of the techno-economic studies performed to highlight the feasibility of using ILs in large-scale pretreatment plants.

2   Lignocellulosic Biomass

Lignocellulosic biomass is a major component in agriculture, forestry, and fruit and vegetable waste. The lignocellulosic materials comprise of trees, stems, grass, and flowers along with quick growth high energy plants e.g., poplar, miscanthus and energetic willow. Additionally,

agricultural waste such as corncob, corn and cereal straw, sugar beets parts, potato haulms, rapeseed and sunflowers oil pressing residue, paper industry residue, sawmills, paper waste are the major supplies of lignocellulosic materials (Hassan et al., 2018; Hernandez-Beltran et al., 2019). Forestry wastes such as stems, stumps, branches, residues from wood industry are also a good supply of lignocellulosic biomass. Organic wastes such as municipal solid wastes (MSW), food wastes from restaurants, households, and food industry waste can be recycled and reused for energy generation.

2.1 Lignocellulosic Biomass Composition

Cellulose $(C_6H_{10}O_5)_n$, hemicellulose $(C_5H_{10}O_5)_m$, and lignin $(C_{10}H_{11}O_{3.5})$ are the three major components of lignocellulosic biomass along with small number of other organic compounds such as pectin, protein etc. (Hassan et al., 2018; Bhatia et al., 2018; Bhatia et al., 2019a). The spatial arrangement of these components is dependent on the source of the lignocellulosic biomass and can vary widely. The share of each component as a percentage of the dry matter generally is in the following range: cellulose (30-60%), hemicellulose (14-40%) and lignin (7-25%) (Dahadha et al., 2017). Though, depending on source the composition of these constituents varies as shown in Table 1. The different bond arrangement makes the carbohydrate configuration tough and unyielding to attack.

Cellulose is a linear homopolymer compound that is made up of amorphous and crystalline region. The share of crystalline fraction varies from 50 to 90%. Cellulose is formed by repeated D-glucose sub-units held together by β-1,4 glycosidic bonds (Kumar and Sharma, 2017). Cellulose exhibits beneficial characteristics e.g. hydrophilicity, biocompatibility, reactive hydroxyl groups and stereoregularity making it an important resource for derivative products such as chemicals, fibers, composites, films, and biofuels (Jedvert and Heinze, 2017). Hemicellulose is a highly branched heteropolymer structure made of pentose (α-L-Arabinose and β-D-xylose), hexose (β-D-mannose, α-D-galactose and β-D-glucose) sugars

and sugar acids (α-D-4-O-methyl-D-glucuronic, α-D-galacturonic and α-D-glucuronic) with small presence of other sugars like α-α-L-fucose and L-rhamnose. As opposed to cellulose, it can be easily broken down into monosaccharides due to non-crystalline nature and low degree of polymerization (usually <200) (Farhat et al., 2017). Lignin, the recalcitrant heteropolymer, is the generic name given to a diverse set of complex three-dimensional cross-linked polymers of aromatic alcohols that provide structural rigidity to vascular plants along with cellulose and hemicellulose. It is formed by different structural units of phenyl propane such as guaiacyl, syringyl, and p-hydroxyphenyl (Zhuang et al., 2016), and are linked to each other by carbon-carbon bonds such as 5-5, β-β and aryl ether linkages e.g., β-O-4, α-O-4, provided that aromatic rings contain methoxyl groups substitutes. Lignin is attached to hemicellulose by covalent bonds creating protection against microbial enzyme action, inhibiting usability of raw lignocellulosic biomass for production of bioethanol.

2.2 Pretreatment of lignocellulosic biomass

Multiple factors such as complexity of cell-wall constituents, structural heterogeneity, crystallinity of cellulose, and degree of lignification are responsible for the biomass recalcitrance making it resistant to biological and chemical breakdown. To overcome the recalcitrance of feedstock, pretreatment process becomes a significant step in utilizing lignocellulosic biomass for industrial applications. Throughout the pretreatment process, lignocellulosic biomass witnesses a breakdown in crystallinity of cellulose accompanied by reduced degree of polymerization, degradation of hemicellulose and breakage of lignin sheath, upsetting the recalcitrant structure of lignocellulose (Chen et al., 2017). Pretreatment is highly cost-intensive but critical step to enhance accessibility of enzymes during the saccharification step (Gupta et al., 2016; Srivastava et al., 2019). Pretreatment should also reduce chemical reactive consumption, costs and energy demand and enhance the production of monomers of sugar during hydrolysis (Abraham et al., 2020).

A variety of lignocellulosic biomass pretreatment techniques have been established and fall under four major categories: physical, chemical, physicochemical, and biological (Hassan et al., 2018; Singh et al., 2018; Tu and Hallett, 2019). The selection of the pretreatment processes is governed by the choice of lignocellulosic biomass used as there is variation in the hemicellulose, cellulose and lignin composition (Dahadha et al., 2017). Various pretreatment methods and their successful implementation are depicted in Table 2. While the focus of pretreatment is to break down lignocellulosic biomass into its components, it is also important to keep in view the resultant toxicity in the residual mass for further saccharification and conversion into usable products. Thus, focus is needed to develop and scale the methods that cause less or no toxicity. ILs have proven to be the greenest option in the chemical pretreatment of lignocellulosic biomass (Table 2). While other processes such as supercritical CO_2 explosion and steam explosion can also be considered green, ILs certainly have added advantage through their tailor-made nature in their choice of anion and cation making them usable across multiple sources of biomass feedstock. ILs were also found to enhance the production of end-products in various cases (Mohammadi et al., 2019).

3   Ionic Liquids

ILs are considered to be green alternatives to volatile organic solvents, as no hazardous chemicals are formed by their application and ~100% recovery of the IL used is possible (Brandt-Talbot et al., 2017). These salts are entirely organic in nature constituting both anionic and cationic species and possessing a melting point lower than 100°C (Alayoubi et al., 2020). At room temperature most of the ILs stay in liquid state, thus making these solvents easy to work with. ILs possess a modular nature and structural alterations can be introduced to the cation core, anion, or substituents. ILs exhibit interesting attributes such as high thermal stability, wide electrochemical window, and wide liquid regions (Jordan and Gathergood, 2015; Alayoubi et al., 2020). ILs can be tuned by altering the branching and

length of the alkyl chains which are attached to the cation. ILs can be designed accordingly to perform an impressive part in lignocellulosic biomass breakdown (Mai et al., 2014). These unusual characteristics have positioned them as favorable solvents for a variety of applications in environmental chemistry, medicine and nanotechnology. The ability to recycle and reuse ILs further improves the economic efficiency of their application.

3.1   Chemistry of Ionic liquids

ILs possess some internal characteristics such as non-flammability, very low vapor pressure, high viscosity, low conductivity, and high thermal and chemical stability (Bhatia et al., 2019a; Paul et al., 2020). These ILs are non-corrosive, economical, have good biodegradability and non-toxic. But few ILs having structures similar to ionic surfactants on releasing into the environment pose the problem of toxicity (Singh et al., 2018; Bhatia et al., 2019b). Several studies have been performed by the researchers focusing on the preparation of ILs using variety of anions and cations and their ability to pretreat lignocellulose under different conditions. The activity of ILs like 1-butyl-3-methylimidazolium chloride [Bmim][Cl], 1 allyl-3-methylimidazolium acetate [Amim][OAc] and 1-butyl-3-methylimidazolium hydrogen sulphate [Bmim][HSO$_4$] for saccharification of Norway spruce enzymatically was observed and [Bmim][HSO$_4$] dissolved lignin most effectively in high water content. Muhammad et al. (2013) performed a comparison of four nitrile constituting ILs like [C$_2$CNAim][Cl], [C$_2$CNBim][Cl], [C$_2$CNHEim][Cl] and 1-propyronitrile-3 benzyl imidazolium chloride [C$_2$CNBzim][Cl] for extraction of lignin from bamboo at a temperature of 120°C for 24 h. Maximum lignin extraction efficiency was observed with [C$_2$CNAim][Cl]. Acetate and chloride based ILs with methanol as anti-solvent were used for lignin extraction from *Eucalyptus globulus* and *Pinus radiata* from 140°C to 170°C for 1 h under microwave heating (Casas et al., 2012). Li et al. (2016) observed the use of 1-Butyl-3-methylimidazolium acetate [Bmim][OAc] for pretreatment of Eucalyptus followed by NaOH

resulted in separation of lignin and glucose production to 90.53%. It may be attributed to the release of better accessibility of IL to reactive surface area in the biomass feedstock.

3.2 Ionic Liquids in pretreatment of lignocellulosic biomass

ILs have strong hydrogen bonding coordination making them unique in their ability to dissolve the complete biomass rather than individual subcomponents (Bhatia et al., 2019a), or selectively dissolve components that may not be soluble in conventional solvents, while maintaining the biopolymers intact. Other biomaterials also have been observed to dissolve in ILs, for example lignin from lignocelluloses (Carrozza et al., 2019). The cations in ILs are generally organic e.g. imidazolium ($[(C_3N_2)X_n]^+$), ammonium-based $[NX_4]^+$, pyrrolidinium based ($[C_4N)X_n]^+$, pyridinium ($[(C_5N)X_n]^+$), sulfonium-based $[SO_3]^+$, phosphonium-based $[PX_4]^+$, and few more such as choline, while the anions can be both inorganic and organic (Yoo et al., 2017). Although, all aforementioned variety of ILs have been used, most attention has been given to imidazolium-based ILs (Zhang et al., 2017). Dissolution of cellulose and lignin during the pretreatment process is impacted by both anions and cations.

3.2.1 Mechanism of dissolution of biomass

An eventual realization of a predictive tool to recognize new combinations of anions and cations can provide significant breakthroughs in every aspect of the IL pretreatment or sugar production process. Mechanism through which ILs interact with biomass is based on the specific combination of anions and cations along with specific constituent of biomass (hemicelluloses, lignin and cellulose) of interest. Lignocellulosic biomass structure is formed by a mix of seven bond types viz. α-O-4, β-O-4, β-1, β-β, β-5, 5-5 and 4-O-5 of which β-O-4 forms the majority (~50%). The splitting of β-O-4 bond results during pretreatment of biomass, is followed by formation of ion-dipole bonds resulting in the breakdown of lignin structure (Zhang et al., 2019). The splitting of inter-unit bonds diminishes crystallinity and heightens porosity. Several semi-empirical and empirical parameters such as Hansen

parameters for solubility, COSMO-RS and the Kamlet-Taft parameters for polarity have been used to explain and simulate the solubility of biomass and other biomolecules in ILs. These parameters have served as a good measure to understand the interaction between biomass and ILs resulting in their solubility (Li et al., 2015). Theoretical lignin recovery ability of any IL may be calculated via solvation parameters such as hydrogen bond acidity (α), polarizability (π*) and hydrogen bond basicity (β). Muhammad et al. (2011) concluded that extent of biomass deconstruction is directly proportional to hydrogen bond basicity of aromatic cations and anions constituents of ILs. Higher hydrogen bonding basicity (β=1) of 1-ethyl-3-methylimidazolium glycine [Emim][Gly] rendered it a better solvent for precipitation of lignin when compared with 1-Ethyl-3-methylimidazolium trifluoroacetate [Emim][TFA]. This is because of weaker electron withdrawing capability of NH_2 group present in [Emim][TFA] restricting its effect on biomass deconstruction. Observing the solubility of cellulose and lignin in various ILs as a function of the Kamlet-Taft Basicity (β) value of the IL reveals that higher β value is an indirect measure of their solubility (Fig. 1). The data is mined from various research works conducted (Table 3). Although the maximum solubility is a function of operating parameters such as temperature, dosing, residence time, degree of polymerisation, water content, it is apparent that higher β value (>0.8) is important for better solubilization/yield (Minnick et al., 2016; Tomimatsu et al., 2019).

3.2.1.1 Dissolution Mechanism of Cellulose by ILs

Various studies use the empirical solvatichromic parameters to derive a relationship between ILs and their cellulose dissolving capability (Mao et al., 2016), which may be attributed to the type of anion and its affinity to H-bond. The breakdown of cellulose by [Bmim][Cl] can be attributed to the formation of electron donor-electron acceptor (EDA) complex via the interaction of O and H atoms of cellulose-hydroxyl with the IL. Hydrogen atoms act as electron acceptors and cellulose molecules as electron pair donors. Similarly, the anion in IL

functions as the electron pair donor and cation as the acceptor. Under optimal conditions the proximity of these acceptors and donors results in the EDA complex formation. Computational studies have brought forward the interactions between cellulose construct and anion which clearly demonstrated the destruction of cellulose-cellulose linkages resulting in faster dissolution of cellulose (Rabideau et al., 2014). Raj et al. (2016) observed a strong correlation hydrogen bond accepting behavior of imidazolium based ILs and structural transformation of cellulose by measuring various solvation parameters. They concluded that IL pretreatment increases the porosity of biomass consequently increasing the surface area for subsequent hydrolysis process. This effect is further proven by a study where Torr et al. (2016) used 1-Ethyl-3-methylimidazolium Chloride [Emim][Cl] and 1-Ethyl-3-methylimidazolium Acetate [Emim][OAc] on pine wood at a temperature of 80-120°C. They were able to demonstrate that IL pretreatment resulted in higher reactional surface area in the wood sample, along with changes in cellulose and lignin crystallinity. Further elucidation of the impact of H-bonding capability of IL with cellulose was demonstrated by Liu et al. (2016). They selected a combination of 21 anions and 17 cations and used COSMO-RS parameters as an indirect measure to determine their ability to breakdown cellulose. They found that cellulose dissolution to be anion-dependent and excess enthalpy calculations pointed out that H-bonding between cellulose and the IL was the prime force driving this.

3.2.1.2 Dissolution Mechanism of Lignin by ILs

The mechanism of lignin dissolution is attained by cleavage of the H-bonds in lignin and merging the aliphatic chain with aromatic nucleus (Xue et al., 2016). Hart et al. (2015) performed a comparative study on solubility of lignin in [Emim]$^+$ with different anions, weak coordinating ions tetrafluoroborate ([BF$_4$]$^-$ and [N(SO$_2$CF$_3$)$_2$]) and coordinating ions ([OAc]$^-$, [O$_2$PCOCH$_2$ CH$_3$)$_2$]$^-$, [CF$_3$ CO$_2$]$^-$, [CH$_3$SO$_3$]$^-$ [NCS]$^-$, [CF$_3$ SO$_3$]$^-$ and [SO$_2$CF$_3$)$_2$N]$^-$) and observed that the latter dissolved considerable amounts of lignin. Financie et al. (2016)

reported about [Emim][O$_2$P(OCH$_2$CH$_3$)$_2$] and Perez-Pimienta et al. (2016) reported about [Emim][OAc] ability to readily dissolve lignin. The authors also compared the lignin solubility in ILs to similar anion trifluoromethanesulfonate [CF$_3$SO$_3$]$^-$ but with various other cations ([Emin]$^+$, [Bmin]$^+$, [N^{4448}]$^+$, 1-butyl-2,3-dimethylimidazolium [Bm$_2$im]$^+$, and [Bpyr]$^+$), and observed their lignin dissolution capability in the order: [Emin]$^+$>[Bmin]$^+$>[Bpyr]$^+$>[Bm$_2$im]$^+$>[N^{4448}]$^+$. [N^{4448}]$^+$ lacks aromatic structures and [Bm$_2$im]$^+$ has its C2 carbon methylated resulting in reduction of lignin solubility, confirming that interactions among the aromatic component of lignin and cations impacts lignin solubility in ILs.

3.3 Lignocellulosic biomass pretreatment using Imidazolium-based ILs

Raj et al. (2018) observed the influence of pretreatment on mustard stalk using imidazolium-based ILs at different operating temperatures subsequently conducting enzymatic hydrolysis. They concluded that ILs that contain acetate ions enhance porosity and specific surface area accessible to enzymes thus significantly improving the output of reducing sugar. At 130°C/2h, the analysis of differential scanning calorimetry exhibited an increased porosity of 108.9 mg/g as opposed to a porosity of 107.8 mg/g at 100°C/5h which on subsequent hydrolysis resulted in production of 97.7% and 78.7% glucose. Stanton et al. (2018) also investigated the impact of various imidazolium-based ILs on the properties and structure of biocomposite films blended with silk, and concluded that the anion structure of the ILs affect the intermolecular interactions in the films. Smuga-Kogut et al. (2017) leveraged response surface methodology to study the impact of [Emim][Cl] pretreatment on rye straw under operating conditions of 2h, 120°C and 1 ml/g of dry matter rye. They found that enzymatic hydrolysis of pre-treated rye straw yielded almost three times reducing sugars when compared with untreated rye straw. Li et al. (2018) studied the factors affecting biomass dissolution in ILs and found that source of feedstock, anions, cations, temperature, and time

are key parameters that impact solubility. A significant effort has been underway to study the usage of ILs in dissolution of lignocellulosic biomasses e.g. wheat straw (Lavarda et al., 2019), bagasse (Vieiraa et al., 2019), and corn stover (Papa et al., 2017) have gained traction. Table 3 gives an overview of solubility of lignocellulosic biomass in ILs/co-solvent mixtures. It has been established that higher anion density coupled with the existence of electron-affinity groups in the alkyl chains of IL cation enhances disintegration of lignocellulosic biomass in ILs (Yoo et al., 2017). Further to this, Yavir et al. (2018) suggested that IL cations exhibit π-π interactions with aromatic compounds of lignin. This observation is further established by the breakdown of lignin obtained with [Amim][Cl], which is considered to be an excellent solvent for a variety of woody biomass as it is the only IL that has p-electrons on the side-chain. 1-butyl-3-methylimidazolium chloride [Bmim][Cl] and 1 allyl-3-methylimidazolium chloride [Amim][Cl] can be used to effectively dissolve cellulose at temperatures below 100ºC (Cai et al., 2014). Under the operating temperature of 50-100ºC, [Amim][Cl] can dissolve up to 10% (w/w) concentration of cellulose. The cellulose component of lignocellulosic biomass may be salvaged by the addition of antisolvents such as water, acetone or ethanol to ILs. In fact, crystallinity and digestibility of cellulose are significantly impacted during the regeneration of ILs. Fig. 2 gives an overview of treatment of lignocellulosic biomass using ILs and subsequent regeneration of ILs. Cellulose, recovered using this method, has reduced crystallinity and improved porosity while maintaining same degree of polymerization as untreated cellulose. This makes pre-treated cellulose susceptible to degradation by cellulose, significantly improving glucose output. Microcrystalline cellulose (MCC) can be regenerated using [Bmim][Cl]. Within 4 hours of regeneration, more than 90% of the MCC recovered using water and acetone, can be converted into glucose. The conversion ratio stands at 90% after 40h for MCC regenerated from water and freeze dried,

whereas it is 48.5% after 96h (Cao et al., 2014). ILs can be recovered and reused after each cycle using various methods such as reverse osmosis, ion exchange or salting out.

Hossain et al., 2019 exposed woody biomass (pine wood) to several ILs to extract lignin under various conditions. [Emim][OAc] was able to segregate lignin from woody biomass when pretreated for 18 hours at 115°C. The lignin thus recovered after pretreatment using ILs is depolymerized and contains the highest molecular mass molecules without forming any new condensed structures. Pretreatment using [Emim][OAc] is a better choice over [Bmim][Cl], for enhanced enzymatic delignification of woody biomass, possibly because of compatibility with enzymes and its capability to dissolve wood. Application of N-methylpyrrolidinium-2-one chloride [Hnmp][Cl] and N-methyl-2-pyrrolidonium methylsulfonate [Hnmp][CH_3SO_3] ILs on maize stalks at a temperature of 90°C for 30 min, resulted in a peak lignin recovery of 85.94% (Ma et al., 2016). Hamada et al. (2013) used temperature variance to selectively fractionate lignocellulosic biomass into its components. Usage of Pyrolidin-1-ium 2,6-diaminohexanoate [P1ME][Lys] proved to be a good lignin solvent at a temperature below 60°C, while temperatures above 80°C resulted in cellulose solubility. They further found that the lignin yield remained the same even after recycling and reusing the IL for five times.

3.4 Lignocellulosic biomass pretreatment using non-Imidazolium-based ILs

Recently there has been progress on the usage of ILs apart from Imidazolium based ones for effectively treating lignocellulosic biomass. When compared to imidazolium-based ILs, cholinium based ones are found to be greener and more economical because their source is natural and renewable (Hou et al. 2012). When compared with untreated bagasse powder, choline acetate (ChOAc) pre-treated bagasse powder produces better propionylated bagasse composites with improved modulus of elasticity from 2.0 giga pascal (GPa) to 2.6 GPa and increased tensile strength from 35 Mega Pascal (MPa) to 40 MPa (Ninomiya et al., 2017).

Corn stalk when treated with a range of pyrrolidonium-based ILs at 90ºC for 30 minutes, was witnessed to undergo 85.94% lignin removal and subsequent enzymatic hydrolysis yielded 91.81% reducing sugar (Ma et al., 2016). Sun et al. (2014) compared the sugar yields post pretreatment of switchgrass with imidazolium-based and amino acid-based ILs and found the latter to produce better yield of glucose and xylose (96.5 and 95.7% as opposed to 95.8 and 93.3%).

3.5   Enhanced enzymatic hydrolysis of lignocellulosic biomass in ILs

Typically, the enzymes associated with the successful saccharification of cellulose into reducing sugars are endo-1,4-β- glucanases, exo-1,4-β- glucanases, cellobiases, cellobiohydrolase, and β-glucosidases. Though ILs are categorized as 'green solvents', they still pose toxicity towards microorganisms. The enzymes get denatured due to the strong hydrogen bonds formed by anions. The selection of IL for pretreatment of biomass should be considered in synergism with the IL biocompatibility with the enzymes. Moreover, ILs are highly viscous which poses an unfavorable effect on the in-situ biocatalytic transformations. Thus, ILs possessing both enzyme compatibility and cellulose dissolving ability are more studied for research purposes in order to conduct one-step hydrolysis of biomass with enzymes in the presence of the solvent ILs. This is important in order to decrease the cost associated with the IL based pretreatment of biomass and converting them into useful products like bioethanol. Kassaye et al. (2017) examined the acidic hydrolysis of bamboo biomass pretreated in alkaline medium followed by treatment with [Bmim][Cl]. They found that lignin recovery improved with the concentration of sodium hydroxide while biomass recovery reduced owing to the partial loss of lignin and hemicellulose. Moreover, [Bmim][Cl] reduced the recalcitrance of bamboo making it more susceptible to further acidic hydrolysis. Alkaline treatment alone increased the yield of total reducing sugars to 64% as opposed to only 30% for untreated bamboo sample. Further pre-treatment with IL, increased

the yield of reducing sugar to 80%. Tiong et al. (2017) performed hydrolysis of cellulose (oil palm) at 160 °C for 5 h post pretreatment with Bronsted Lewis acidic IL resulting in the formation of glucose. Further dehydration of the glucose results in the formation of 5-Hydroxymethylfurfural (5-HMF). They also observed that higher IL loading resulted in decrease in 5-HMF production, which may be attributed to 5-HMF's high instability and its ease of condensation.

Nargotra et al. (2018) found that alkali (NaOH) pretreatment combined with IL [Bmim][Cl] resulted in 69.14% increase in reducing sugar yield from sunflower stalk with a saccharification efficiency of 26.51%. Ma et al. (2016) pretreated corn stalk pretreated with [Hnmp]Cl and [Hnmp]CH$_3$SO$_3$ at 90 °C for 30 minutes achieving a lignin recovery of 85.94% and 56.02% respectively. This resulted in the production of 91.81% and 73.59% of reducing sugar respectively post enzymatic hydrolysis. Hou et al. (2012) conducted a similar experiment on rice straw for lignin removal using Cholinium lysine [Ch][Lys] and found the maximum yield of glucose (87.7%) was obtained when the biomass was pre-treated at 90°C for 24 hours, while further increasing the temperature actually reduces the output. Hashmi et al. (2017), studied the effect of 1-butyl-3-methylimidazolium acetate [Bmim][OAc] on autohydrolysis of sugarcane bagasse. Their study found that pretreatment using [Bmim][OAc] at 110°C for 30 minutes caused a significant reduction in the amount of present lignin and crystallinity of cellulose and improved the digestibility of xylan and glucan (98.6% and 97.4% respectively). Xylan and glucan exhibited enhanced autohydrolysis rate of 57.5% and 62.1% respectively at 205°C. Rigual et al. (2017) studied the effect of microwave IL [Emim][OAc] and autohydrolysis pretreatment on Eucalyptus followed by enzymatic hydrolysis. Autohydrolysis enhanced the enzymatic digestibility in eucalyptus and microwave IL enhanced the lignin removal resulting in better recovery of cellulose. The highest glucan digestibilities of 84.4 and 85.5% were obtained for autohydrolysis at 175°C,

IL pretreatment at 80°C, and autohydrolysis at 175°C, IL pretreatment at 120°C respectively. The autohydrolysis at 175°C, IL pretreatment at 120°C resulted in maximum glucan output of 39.6 g/100 g of untreated wood. ILs along with solid phase acid catalysts can be used for cellulose hydrolysis. Xiong et al. (2014) studied hydrolysis of cellulose using [Bmim][Cl] as the IL and $Fe_3O_4@SiO_2$-SO_3H acid catalyst for hydrolysis. They treated Avicel® cellulose for 8h at 130°C and found a fair yield of 73% of reducing sugars. An important point to note is the reusability of the catalyst $Fe_3O_4@SiO_2$–SO_3H due to easy recovery from reaction mixtures using a permanent magnet, and high stability during the hydrolysis without any noticeable loss in activity. Zhang et al. (2015) used various ILs with acid catalysts under microwave radiation to study their impact on the hydrolysis of straw. They found the combination of [Bmim][Cl] with H_2SO_4 at 150°C under microwave heating to yield the maximum amount of reducing sugar 35.5 wt% upon hydrolysis as opposed to 19.8 wt% when using water as a solvent and conventional heating.

3.6 Enhanced bioconversion of lignocellulosic biomass using ILs

ILs based pretreatment can increase enzymatic digestibility and biofuel yield. Saha et al. (2018) used [Emim][OAc] to pretreat sugarcane bagasse for 2h at 140°C and use X-Ray diffraction and SEM to study the structure of resultant biomass. They observed a reduction in the crystallinity index by 14.7% resulting in enhanced bioconversion of pretreated bagasse into reducing sugars. Mohammadi et al. (2019), pre-treated spruce (softwood) and birch (hardwood) with IL 1-H-3-methylmorpholinium chloride [HMMorph][Cl]. The subsequent hydrolysis under optimum conditions of 140°C for 3 h yielded more than 3.3 times output than the untreated substrate. Ethanol production, via fermentation of the resultant hydrolysates, increased by more than 34.8%. Yang et al. (2016) performed a study using three different ILs [Amim][Cl], [Bmim][Cl] and 1-Ethyl-3-methylimidazolium chloride [Emim][Cl] on triploid poplar under the reaction conditions of 130°C for 2h followed by

enzymatic hydrolysis at 50°C for 48h. They observed the conversion of cellulose I to cellulose II which inherently resulted in 1.3 times yield of fermentable sugars, thereby resulting in enhance production of bioethanol from biomass.

4 Commercialization of IL based pretreatment on lignocellulosic biomass

For efficient utilization of biomass, it is important to fractionate the biomass into its constituents via pretreatment process. Inspite of the fact that a lot of research is going on lignocellulosic biomass conversion into biomaterials, the pretreatment process stills holds to be very expensive presenting 11-27% of the total costs (Madanayake et al., 2017). The method involving pretreatment generally have elevated costs, long reaction time, higher consumption of energy, lower degradation of sugar, environmental pollution and high requirement for corrosion resistance of the equipment. Pretreatment process depends on various factors (a) value of the by-products (b) kind of biomass. To ensure the efficiency and economic viability of the pretreatment process, it should have following characteristics: (a) lower concentration of fermentation step inhibitors (b) higher yields of sugar from fermentation (c) hemicellulose and lignin recovery for production of valuable by-products (iv) minimal energy, water and chemicals (Mussatto and Bikaki, 2016).

4.1 Modeling and simulation of large-scale pretreatment process using ILs

Developing an efficient design of processing units and optimizing the process parameters are the criterion for large scale pretreatment of lignocellulosic biomass using ILs. Baral and Shah (2016) proposed a full-scale pretreatment plant for pretreatment of biomass using Super Pro Designer software. The model operates with a comprehensive process design involving feedstock grinding and milling, pretreatment of biomass, enzymatic hydrolysis and recovery of ILs. Though, it lacked the logistics behind the feedstock. Oleskowicz-Popiel et al. (2014) also developed a plant for IL-mediated pretreatment of lignocellulosic biomass into ethanol by Super Pro Designer. The same software was used to develop a model including various

parameters such as reactor design and energy intensity of IL by Parthasarathi et al. (2016). A reduction in 75% of the pretreatment energy cost was observed through this model implementation. Brandt-Talbot et al. (2017) observed the fractionation of Miscanthus using triethylammonium hydrogen sulphate ($[Et_3NH][HSO_4]$) and also explored the economic routes for fractionation of IonoSolv. Delignification of 85%, 80% recovery of lignin and 80% yield of glucose was obtained in this process. They further reported that increase in the recycling rate of IL unusually decreases the high cost of glucose production which in turn results in an economically viable process. Sen et al. (2012) established a process model for pretreatment of corn stover using ILs resulting in the production of sugar. Their modelling studies were based on experiments and simulated moving bed separation technique. They designed the decrystallization unit having the first hydrolysis for 150 mins and second hydrolysis for 180 mins. 98% recovery of IL was obtained by simulated moving bed separation technology. To reduce the consumption of IL, authors recommended hydrolysis by dilute acid first and subsequently followed by IL. In 2017, the process parameters were optimized by Gogoi and Hazarika for lignin recovery from IL-pretreated lignocellulosic biomass using nanofiltration membranes. Anugwom et al. (2016) derived a mathematical model for three different reactors used in dissolution of lignin by alkanol amine based switchable ILs. They further analyzed and optimized the model by Modest™ software and observed that rotating bed reactor was an efficient reactor with respect to dissolution of lignin on comparing to loop reactor and non-stirring batch reactor. However, these computer-based models should be more developed with respect to solid loading, quantity of feedstock supply, agitation level and heat and mass transfer.

4.2 Cost Analysis of IL based pretreatment

ILs are costly solvents, which is detrimental to their large-scale application in industry. Thus, their recycle and reuse in biomass pretreatment can be an effective tool to reduce cost

coverage (Perez-pimienta et al., 2016). Various recycling methods have been developed and studied at laboratory scale (Mai et al., 2014). Hou et al. (2012) conducted a study on the regeneration and reapplication of eight ILs concocted using amino acids anions and cholinium cation ([Ch][AA]). They concluded that repeated use of recycled IL (five times) resulted in a marginal reduction in lignin recovery from 58.8% to 52.5%. While IL reuse definitely reduces the overall processing cost, it was observed that recycling of [Bmim] [OAc] and [Amim][Cl] slightly decreases the digestibility of cellulose (Xu et al., 2017).

A cost-revenue analysis was performed by Sen et al. (2012) for a 10 tonne/hour biomass pretreatment plant. They were able to create a model that could bring down total cost (operational, setup and fixed costs) to achieve mean selling price of \$1.14/kg of sugar. This process accounted for reusability of ILs with 95-99% recovery, multi-step hydrolysis with first step being dilute acid hydrolysis followed by IL-based hydrolysis. Their model accounted for Capex (setup cost) and Opex (feed material, upkeep and waste removal cost). Total plant cost C_{Total} can be calculated as:

$$C_{Total} = C_{Capex} + C_{Opex} \qquad (1)$$

A model developed by Wright and Brown, (2007) to calculate the optimal cost of biorefineries established the following equations to estimate cost of a large-scale IL based pretreatment plant.

$$C_{Capex} = C_o \ (M/M_o)^a \qquad (2)$$

$$C_{Opex} = C_o \ (M/M_o)^a + C_P + C_F + C_D = C_{Po} \ (M/M_o)^b + C_{Do} \ (M/M_o)^c + C_{Fo} \ (M/M_o) \quad (3)$$

Here, C_P is total operational cost of the plant, C_F is the cost price of biomass produced at farm, C_D is the cost of biomass delivery, M is the installed capacity of the plant, M_o is the capacity of base plant, and o subscripted cost components are costs at capacity M_o. The range of values for dimensionless scale factors a, b and c are taken as 0.6-0.8, 0.9-1 and 1.5, respectively.

Konda et al. (2014) established a simulative functional model for a one-pot biofuel production from IL pretreated biomass and were able to achieve a competitively low production cost of $3/gallon. They were able to achieve this by lignin valorization and few other advancements. They took into account the operational costs of production such as raw material, power and infrastructure. Another model developed by Baral and Shah (2016) for a commercial-scale study using SuperPro Designer software brought forward the techno-economic practicability of IL pre-treatment. They utilized poplar, corn stover and switchgrass as feedstock for a 113 million liter/year plant for the base case. The key process parameters observed during their feasibility study were recovery of IL, its cost, and heat recovery. Total investment costs (including initial setup cost, total fixed costs, and working capital) for corn stover, switchgrass and poplar were evaluated to be $873, $1002 and $941/t of total sugars respectively. Baral and Shah (2017) also stated that the total cost of biofuel production via fermentation of lignocellulosic biomass could be reduced by wastewater management in the process. Fermentable sugars are the main constituent of wastewaters from biorefineries with 74.1-79.0 wt % lignin in the biomass. Lignin can be utilized for producing high value products like biochar, bio-oil and biogas production. Klein-Marcuschamer et al. (2011) validated that IL cost, IL recovery and IL loading have direct impact on the minimum selling price of ethanol. They also found that sale of residual lignin combined with the reduction in cost of IL can bring down the net selling price of ethanol to $1.50/gallon. Settani et al. (2016) suggested that focus should be shifted from effective recycling to usage of inexpensive ILs synthesized from cheap raw materials in order to make their usage cost-efficient. They demonstrated that production cost of 1-methylmidazole hydrogen sulfate ([Mmim][HSO_4]) and [Et_3NH][HSO_4] can hit a competitive price of $2.96-5.88/kg and $1.24/kg respectively, which is comparable to the prices of organic solvents. But their commercial application in pretreatment plants will need some more analysis of their delignification performance.

As most applications of ILs in biomass pretreatment have been limited to laboratory scale, there is a need for further research to make application of ILs commercially viable. Nonetheless, there is a need for further commercial scale studies keeping in mind various operational parameters to create a low-cost methodology utilizing ILs for the pretreatment process to accelerate industrial-scale adoption.

5   Advantages and drawbacks of ILs based pre-treatment

The green nature of ILs makes them an excellent choice in the pretreatment process when compared to more hazardous chemicals that are currently in use while maintaining comparable sugar yields. Brandt-Talbot et al. (2017) pioneered the use of Triethylammonium hydrogen sulfate [N_{2220}][HSO_4], a low-cost IL for pre-treating *Miscanthus* x *giganteus* grass. This IL exhibited solubilization levels of up to 100% hemicellulose and 75% lignin. Further enzymatic saccharification yielded around 77% glucose. This IL was also reused with 99% recovery for four times. Despite of their unique chemical properties and greenness, usage of ILs in pretreatment of lignocellulosic biomass present certain shortcomings - (i) the recovery and reuse of ILs is challenging, (ii) usage of ILs is cost-intensive despite some progress in making it cheaper, (iii) post-cellulose extraction the recovery of hemicellulose and lignin from the ILs poses some difficulty (iv) they may be toxic to microorganisms and enzymes. The solutions become viscous and tough to handle post cellulose extraction making it difficult to recover hemicellulose and lignin. Usage of water-ILs mixture can be a solution to avoid this problem. Some ILs can cause an irreversible inactivation of enzymes impacting the cellulase activity negatively (Pedersen et al., 2019). Thus, to enhance the sugar yields and preserve cellulase activity, removal of IL residues precedes enzymatic hydrolysis.

5.1   Toxicity and Biodegradability

From the initial research related to chloride constituting ILs concentrating only on lignocellulosic biomass pretreatment, the focus shifted towards ILs with lower toxicities. Mai

et al. (2014) used [Emim][DMP]-DMSO (1:1) and [Emim][OAc]-DMA (1:1) in their study as IL formulations for rice straw for cellulose dissolution. Generally, ILs constituting chlorides pose toxicity and have corrosive properties, which might not be suitable to be used in biorefinery projects. Researchers are now promoting the use of biological agents, which are exposed to ILs during biocatalytic conversions or fermentation. In such cases, ILs can act as a media for microbial processes. ILs biocompatibility is a crucial factor to counterbalance the complex processes and surplus cost of efficient purification of biomass for further microbiological processes. Non-toxic ILs opens more opportunities for enhancing the applications of ILs for eg. the use of food grade chemicals. Concerns related to impacts of residual quantities of impurities produced from IL synthesis (Francesco et al., 2017) were also observed. This would involve huge costs for purification procedures.

ILs exhibiting biodegradability properties are preferred for lignocellulosic biomass dissolution to promote the use of environmentally sustainable ILs and to live up to their role of 'green solvents'. Hou et al. (2012) reported that cholinium constituting ILs possess low toxicity and are readily biodegradable. ILs generation from renewable materials along with its biodegradability are essential factors with respect to biorefinery model. Hou et al. (2013) prepared several ILs like choline glycine, choline alanine and choline lysine for pretreatment of sugarcane bagasse. Choline lysine showed the best results yielding 84% xylose and 80% glucose from enzymatic hydrolysis of the residue.

5.2 Recyclability and Recovery of ILs

Recycling property of ILs is enabled due to their near-zero volatility under ambient conditions. As ILs are considered to be as expensive solvents, it is important to recover ILs after extraction of cellulose and lignin in order to develop an economical and energy saving protocol (Zhang et al., 2017; Hossain et al., 2019). The solution comprises of acetone, lignin, IL and water after extraction of cellulose. Evaporation of acetone followed by lignin

precipitation, leaves behind IL in aqueous solution. Evaporation of water using a rotary evaporator under reduced pressure, recovers the ILs. The ILs after recovery are vacuum dried at a temperature of 80°C. This process can lead to 90% recovery of IL. The ILs, constituting dimethylamine with CO_2 in the ratio 2:1 to produce dimethyl carbamate anion and dimethylammonium cation are distillable at low temperatures of 45°C thus enhancing the options for applications and IL recycling. Hou et al. (2013) demonstrated the recovery and reuse of 50% [Ch][Lys]-water mixture directly (without lignin filtration) in bagasse pretreatment for three batches. However, due to repeated use of ILs, the yields of xylose and glucose decreased to 73.0% and 62.7% respectively. It may be due to reduction in delignification capacity of the solvent mixture owing to amassing lignin. In a study performed by Brandt-Talbot et al., (2017), triethylammonium hydrogen sulfate (an economic IL), was used for pretreatment of *Miscanthus* x *giganteus* grass. They observed 100% dissolution of hemicellulose and 75% lignin solubilization using the IL solution. They re-used the same IL four times obtaining a recovery of 99% at each time. Thus, IL recovery is an integral part of lignocellulosic biomass pretreatment process. This way the integrity of IL can be preserved by a fairly simple regeneration process.

5.3 SWOT Analysis

5.3.1 Strengths

Their unusual physico-chemical properties such as high thermal stability, melting point, and low vapor pressure are an asset for dissolution of biomass. ILs also possess high selectivity homogeneous phase derivatization. ILs have high extraction properties and binary mixtures (IL+ organic solvents) can be applied to the mixture for better extraction. ILs have proven to be very beneficial in extraction of food additives, cosmetics and nutraceuticals. Dissolution extraction selectivity and capacity can be adjusted by the structural design of the ILs. The advantages of completely liquefying the biomass as one of the first steps in a biorefinery may

lie in a lower waste fraction, a reduction in the number of required processing steps, a higher selectivity, lower energy demand, or greater flexibility in feed variety for the IL-based dissolution compared to heterogeneous processes.

5.3.2 Weaknesses

ILs are quite expensive with little information on cradle to grave life cycle assessment. Side reactions or strong adsorption on polar surfaces leads to loss in ILs. ILs are viscous solvents which in turn affects the processing costs. Conventional recovery and purification steps of ILs are also costly. ILs are composed of ions on and hence feature a low vapour pressure. Therefore, distillation is not in general an adequate means of removing impurities from ILs (as is conventionally done for the purification of organic solvents). Furthermore, their high dissolution capacity for polar molecules, an advantage for homogenizing biomass, can also turn into a disadvantage, as many polar compounds, such as water, inorganic salts, acids, monosaccharides and their decomposition products, accumulate and in turn affect the properties. It is difficult to remove moisture from ILs due to absorption of moisture from the feed and drying of ILs is time and energy consuming. There is a lack of data for specific ILs, including chemical engineering data on biorefinery-relevant mixtures of ILs and bio-based chemicals (required for modelling purposes), material compatibility, occupational safety and health (HSE), biodegradability and toxicity data.

5.3.3 Opportunities

The opportunities for the deployment of IL based pretreatment are immense due to the multitude of benefits that ILs bring forth. Their green nature, recyclability and highly tuneable characteristics being major drivers for their acceptance. While there is plethora of ILs being explored, the real opportunity is replacing conventional solvents with ILs at large scale pretreatment plants. Another key opportunity is the development of bio-based ILs that can be created in the same pretreatment plants from similar feedstock as the ones being used

in biorefinery. The shift in regulatory norms and drive towards a circular bioeconomy is also a major push for the development of IL based pretreatment technologies.

5.3.4 Threats

When comparing ILs against the mainstream solvents and other pretreatment techniques there is little information. In case of large-scale process like biomass fractionation and hydrolysis to fermentable sugars, IL technologies face competition with novel techniques like AFEX, Ultrasound and Microwave processes. Although the most likely approach to integrated biorefineries is to add further feed streams and product streams onto a dedicated biorefinery (e.g. sugar or pulp/paper mill), rather than building an integrated biorefinery from scratch, large investments are required, and the technical as well as bio-based product resilience needs to be overcome. Clearly, the risk currently is very high as no example for an integrated biorefinery, let alone one involving IL processes, is in operation as proof of principle.

6 Gaps in Knowledge

Ionic liquids are an efficient means for pretreatment of lignocellulose but still there are certain research gaps which needs to be addressed. Economic production of ILs in volumes, improvement in recyclability regeneration and reactivation of used IL, and identifying applications of used ILs are few gaps which needs to be discussed further. Developing an efficient recycling and reuse technique for handling the large volumes of lignocellulosic biomass. The process of using ILs for lignocellulosic pretreatment also requires integration of the process to reduce the cost and energy requirement. Proper design of the reactors and establishing the scale-up rules for lignocellulosic pre-treatment along with appropriate reaction kinetics and modelling of mass and heat transfers should be studied. Proper studies related to rheology in order to determine distortion in flow of ILs, any changes in thermal, chemical and structural properties during pretreatment of biomass should be promoted to successfully implement its large-scale application.

7   Future Research Directions

Most of the studies conducted on lignocellulosic pretreatment using ILs were laboratory scale. Thus, to scale and increase the adoption of this technique there is a need to conduct bench scale and pilot implementations in order to identify and overcome the challenges encountered during commercial use of IL in biomass pretreatment. Establishing reaction kinetics at commercial scale would need bringing together the knowledge attained during lab and bench scale experiments. Although some work has happened on bio-based ILs and their usage, there is a need for further progress to be made in synthesis of low-cost bio-based ILs. Research is needed to understand in detail the combinatory effect of ILs when used with water other co-solvent mixtures for delignification studies. While there is ongoing research on various operating conditions and parameters, viz. temperature, pressure, external stimuli, stirring speed, residence time, further exploration is needed to arrive at repeatable and standard operating conditions. There is a need to create a standard database of various feedstock, their pretreatment using various ILs, parameters used, reactor design and configurations, so that techno-economic assessments can be performed using simulations in ASPEN to build case for pilot deployments. Furthermore, conventional heating using oil bath may be replaced with microwave and ultrasound in IL based pretreatment. Current works have only scratched the surface of applications of IL-biomass interaction, which means that there is untapped potential requiring further exploration of these beneficial salts.

Conclusion

Utilization of lignocellulosic biomass is a useful way for clean energy generation along with organic wastes reduction. Overcoming the recalcitrance posed by lignocellulosic biomass through pretreatment is vital for any type of biological and chemical treatment to result in the production of biofuels and bioproducts. ILs as dissolution media present a wide array of advantages due to their greenness and customizability. ILs have also been proven to

significantly impact the output of end products such as xylan, glucan and other reducing sugars. Regardless, their high cost and viscous nature inhibits large-scale adoption and requires further research for effective commercialization.

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Conflict of Interest

The authors declare no conflict of interest.

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Figure Captions

Fig. 1. Correlation of Lignin and Cellulose solubilization with Kamlet-Taft Basicity

Fig. 2. Ionic liquid-based pre-treatment pathways of lignocellulosic biomass