Review Article
pISSN: 2288-9744, eISSN: 2288-9752
Journal of Forest and Environmental Science
Vol. 36, No. 2, pp. 69-77, June, 2020
https://doi.org/10.7747/JFES.2020.36.2.69

JFES
Journal of Forest and
Environmental Science

Ionic Liquid Pretreatment of Lignocellulosic Biomass

Song-Yi Han[1], Chan-Woo Park[1,2], Gu-Joong Kwon[1,4], Nam-Hun Kim[1,2], Jin-Chul Kim[1,3] and Seung-Hwan Lee[1,2,5,*]

[1] *Institute of Forest Science, Kangwon National University, Chuncheon 24341, Republic of Korea*
[2] *Department of Forest Biomaterials and Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon 24341, Republic of Korea*
[3] *Department of Medical Biomaterials Engineering, College of Biomedical Science and Institute of Bioscience and Biotechnology, Kangwon Nationa University, Chuncheon 24341, Republic of Korea*
[4] *Kangwon Institute of Inclusive Technology, Kangwon National University, Chuncheon 24341, Republic of Korea*
[5] *Institute of Fermentation and Brewing, Kangwon National University, Chuncheon 24341, Republic of Korea*

Abstract

Lignocellulosic biomass has recalcitrant characteristics against chemical and biological conversion due to its structural heterogeneity and complexity. The pretreatment process to overcome these recalcitrant properties is essential, especially for the biochemical conversion of lignocellulosic biomass. In recent years, pretreatment methods using ionic liquids (ILs) and deep eutectic solvents (DESs) as the green solvent has attracted great attention because of their advantages such as easy recovery, chemical stability, temperature stability, nonflammability, low vapor pressure, and wide liquids range. However, there are some limitations such as high viscosity, poor economical feasibility, etc. to be solved for practical use. This paper reviewed the research activities on the pretreatment effect of various ILs including DESs and their co-solvents with organic solvents on the enzymatic saccharification efficiency of lignocellulosic biomass and the nanocellulose preparation from the pretreated products.

Key Words: ionic liquid, deep eutectic solvent, pretreatment, enzymatic saccharification, nanocellulose

Introduction

The pretreatment of lignocellulosic biomass is a critical step in the biochemical process. The criteria for the ideal pretreatment of lignocellulosic biomass for biochemical process include; the increase of the accessible surface area and the decrystallization of cellulose, partial or complete depolymerization and solubilization of components, maximization of the enzymatic digestibility of the pretreated material, minimization of the loss of sugars, capital, and operating costs, and minimization of the formation of inhibitors or excess sugar degradation (Canilha et al. 2012; Kumar and Sharma 2017). In recent years, pretreatment of lignocellulosic biomass using ILs and DESs as green solvents has attracted substantial attention due to their advantages such as; easy recovery, chemical stability, temperature stability, nonflammability, low vapor pressure, and wide liquidus range. The ILs are a potential application for lignocellulosic biomass pretreatment because they can dissolve biomass at low temperatures, possess low viscosity, are

Received: April 23, 2020. Revised: May 8, 2020. Accepted: May 8, 2020.

Corresponding author: Seung-Hwan Lee

Department of Forest Biomaterials and Engineering, College of Forest and Environmental Sciences, Kangwon National University, Chuncheon 24341, Republic of Korea
Tel: +82-33-250-8323, Fax: +82-33-259-5621, E-mail: lshyhk@kangwon.ac.kr

chemically stable, do not decompose biomass, are easy to regenerate and recycle, are cost-effective, are easy to process, and are non-toxic to enzymatic and microbial fermentation (Weerachanchai and Lee 2013). Several studies on ILs and DESs pretreatments have been published. Among them, representative research mainly related to this review are summarized in the following four categories. The first category deals with pretreatment using ILs and DESs; the second focuses on the recycling and reusing of ILs; the third introduces the combined method that is ILs-based and other pretreatment methods, and; the forth emphasizes the preparation of value-added products such as nanocellulose and high molecular lignin.

Pretreatment Using ILs and DESs

A number of pretreatment methods have been developed (Kumar and Sharma 2017). Among these, the pretreatment using various ILs and DESs is known to be environmentally friendly and more effective than conventional pretreatment methods such as dilute sulfuric acid pretreatment (Dadi et al. 2007; Han et al. 2020).

da Silva et al. (2011) investigated the effect of pretreatment using six ILs on the rate and yield of enzymatic saccharification of sugarcane bagasse. These ILs were 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium acetate ([EMIM]Ac), 1-allyl-3-methylimidazolium chloride, 1,3-dimethylimidazolium dimethyl phosphate, 1-butyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide, and 1-ethyl-3-(hydroxymethyl) pyridine ethyl sulfate. They reported that [EMIM]Ac was the most powerful IL among the used ILs, resulting in 80% glucose yield within 6 h and greater than 90% glucose yield within 24 h of saccharification. It was possible to obtain fibrillated materials as small as 100 nm after pretreatment, exhibiting 100 times more specific surface area in comparison to untreated bagasse. The ability of [EMIM]Ac to simultaneously increase the specific surface area and decrease the biomass crystallinity is responsible for the improved bagasse enzymatic saccharification rates and yields obtained in this work.

Sun et al. (2014) also investigated the pretreatment efficiency of four ILs: cholinium lysinate, cholinium acetate, 1-ethyl-3-methylimidazolium lysinate, and 1-ethyl-3-methylimidazolium acetate for switchgrass in terms of lignin content, cellulose crystallinity, and enzymatic digestibility. Pretreatment with ILs containing lysinate anions resulted in higher lignin removal (70-80%) and glucose yields (78-96%) than ILs containing acetate anions (16-50% of lignin removal; 56-90% of glucose yield).

Mood et al. (2014) compared the effects of five different ILs, namely [EMIM]Ac, [BMIM]Cl, 1-ethyl-3-methyl imidazolium diethyl phosphate, 1-allyl-3-methylimidazolium chloride, and 1-ethyl-3-methylimidazolium hydrogen sulfate, on the pretreatment of corn stover in terms of the chemical structure change, crystallinity index, cellulose digestibility, and glucose release. The [EMIM]Ac pretreatment was found to be the most efficient in terms of altering the physical structure of corn stover, followed by pretreatments using 1-ethyl-3-methyl imidazolium diethyl phosphate and 1-allyl-3-methylimidazolium chloride. Among the ILs, [EMIM]Ac-pretreated corn stover led to significantly higher saccharification, with cellulose digestibility reaching 69% after 72 h, whereas the digestibility of untreated barley straw was measured at only 21%.

da Cunha-Pereira et al. (2016) utilized 1-butyl-3-methylimidazolium acetate to pretreat soybean hull and investigated the optimal parameters required to maximize sugar yields in the subsequent enzymatic hydrolysis. Optimal pretreatment conditions were found to be 75°C for 165 min, 57% (mass fraction) of 1-butyl-3-methylimidazolium acetate, and 12.5% solid loading, resulting in 91.7% of glucose yields by an enzyme complex from *Penicillium echinulatum*. The hydrolysate was free of toxic compounds such as furfural and 5-(hydroxymethyl) furfural.

Trinh et al. (2018) also investigated the feasibility of producing bioethanol from mixed softwood pretreated with 1-butyl-3-methylimidazolium acetate ([BMIM]Ac). The optimal pretreatment conditions were at 100°C for 15 h, producing a fermentable sugar yield of 92.5%. Efficient pretreatment of softwood was maintained even after reutilizing [BMIM]Ac up to four times. Bioethanol yield was 0.42 g/g with 0.24 g/L/h of productivity after the enzymatic saccharification and subsequent fermentation.

Chang et al. (2016) reported that the use of [BMIM]Cl assisted by surfactants (e.g., sodium dodecyl sulfate and cetyl trimethyl ammonium bromide) as a pretreatment method for rice straw increased delignification efficiency and cellulose conversion during subsequent enzymatic hydrolysis compared with pretreatment without surfactants. The optimal pretreatment conditions were [BMIM]Cl + 1% sodium dodecyl sulfate at 110°C for 60 min, yielding a maximum of 5.17 mg/mL total reducing sugar by enzymatic saccharification. The pretreated products showed a lower cellulose crystallinity index and a porous structure.

Parthasarathi et al. (2016) used an inexpensive IL comprised of tetrabutylammonium hydroxides ions to pretreat switchgrass under very mild processing conditions (50°C), generating > 90% glucose yields. The tetrabutylammonium hydroxides was effective in the pretreatment of lignocellulosic biomass at much lower temperatures at similar efficiency as top-performing conventional ILs such as [EMIM]Ac. The authors insisted that this biomass pretreatment approach at lower temperatures could substantially enhance the affordability and energy efficiency of lignocellulosic biorefineries.

Recently, ILs derived from lignocellulosic biomass have been developed to replace expensive imidazolium-based ILs, which limits their large-scale industrial deployment. Socha et al. (2014) prepared a series of tertiary amine-based ILs using vanillin, p-anisaldehyde, and furfurals such as N-ethyl-N-(furan-2-ylmethyl) ethanamine, phosphoric acid salt, 4-(diethylamino) methyl-2-methoxyphenol, phosphoric acid salt, and N-ethyl-N-(4-methoxybenzyl) ethanamine, phosphoric acid salt derived from hemicellulose and lignin, the major by-products of lignocellulosic biofuel production. Their pretreatment effect on switchgrass was compared to that of [EMIM]Ac. The N-ethyl-N-(furan-2-ylmethyl) ethanamine, phosphoric acid salt and N-ethyl-N-(4-methoxybenzyl) ethanamine, phosphoric acid salt showed excellent performance in biomass pretreatment, providing 90% and 96% of total possible glucose and 70% and 76% of total possible xylose, respectively, after enzymatic saccharification. Although the lignin removal efficiency of these ILs was lower than [EMIM]Ac, the final sugar yields were comparable to those by other conventional ILs. This result shows significant potential for the realization of a ‘closed-loop’ process for future lignocellulosic biorefineries and has far-reaching economic implications for other IL-based process technology currently using ILs synthesized from petroleum sources.

Bernardo et al. (2019) investigated the effect of lignocellulosic biomass types on the efficiency of ILs pretreatment and subsequent enzymatic saccharification. Two very distinct types of biomasses, herbaceous (wheat straw) and hardwood (eucalyptus), were pretreated with hydrogen-bond basic ([EMIM]Ac) and hydrogen-bond acidic (1-ethyl-3-methylimidazolium hydrogen sulphate) ILs. The use of the acetate-based IL enhanced the glucan to glucose yield to 93.1±4.1 mol% and 82.9±1.2 mol% for wheat straw and eucalyptus, respectively. However, for the hydrogen sulfate IL, the same enzymatic hydrolysis yields were 61.6±0.2 mol% for wheat straw and only 7.9±0.3 mol% for eucalyptus residues. These results highlight the importance of both IL characteristics and biomass type for efficient biomass processing.

Rigual et al. (2019) reported a side-by-side comparison of softwood (pine) versus hardwood (eucalyptus) pretreatment using three protic ILs (2-hydroxyethylammonium formate, 2-hydroxyethylammonium acetate, 1-methylimidazolium chloride), three aprotic ILs ([EMIM]Ac, 1-ethyl-3-methylimidazolium dimethyl phosphate, 1-allyl-3-methylimidazolium chloride), and three cholinium-derived ILs (cholinium acetate, cholinium lysinate, and cholinium serinate). The 2-hydroxyethylammonium formate led to alkali lignin dissolution at 30°C after 1 h, however, interactions with the whole-cell wall were insufficient, which limited biomass disruption. The protic IL (1-methylimidazolium chloride) produces a catalytic effect that almost entirely extracts the hemicelluloses and partially extracts the lignin. A remarkable digestibility (69%) of eucalyptus was obtained with cholinium acetate, whereas the digestibility of pine by protic and choline-derived ILs was lower than 55%, which was considerably lower compared to that obtained with [EMIM]Ac (84%).

Even though ILs are effective for lignocellulosic biomass pretreatment, several properties of ILs should be considered for further improvement of their pretreatment capability. Notably, the viscosity of ILs is an important factor for practical utilization. For example, the viscosity of [BMIM]Cl is high (142 mPa·s) at 80°C and occurs in a solid-state at room temperature; thus, its dissolution capability is achieved at high temperatures. This high reaction temperature could lead to unstable IL properties, unwanted side reactions, and loss of treated biomass.

Weerachanchai et al. (2012) reported that a significant loss of biomass yield resulted from the pretreatment with ILs at high temperatures (150 and 180°C) due to the excessive degradation of carbohydrates into the water-soluble fraction, including monosaccharides, oligosaccharides, furfural, and 5-(hydroxymethyl) furfural at high temperatures. To avoid these problems, Weerachanchai et al. (2012; 2013), Wu et al. (2013), Han et al. (2017) used the co-solvent of ILs and organic solvents to provide lower viscosity of the pretreatment solvent, higher biomass loading, and ease of operation.

Hou et al. (2017) recently reviewed the pretreatment of lignocellulosic biomass with ILs and IL-based solvent systems with the focus of the efficient dissolution and fractionation of biomass components and the emphasis of enzymatic saccharification after pretreatment with ILs and IL-based solvent systems. It was reported that a reasonable design of ILs and the use of IL-based solvent systems can be effective to improve the dissolution, pretreatment, and fractionation efficiency, reducing the cost of ILs, and improving their compatibility with enzymes.

Weerachanchai and Lee (2013) attempted to lower the viscosity of ILs ([BMIM]Cl and [EMIM]Ac) by mixing organic solvents with high Hildebrand solubility parameters for pretreatment of corncob and rice straw. The used organic solvents were N,N-dimethylacetamide, N,N-dimethylmethanamide, dimethyl sulfoxide, and ethanolamine. The co-solvent system consisting of [EMIM]Ac with 40-60 vol% N,N-dimethylacetamide provided similar pretreatment ability (sugar conversion yield, extracted lignin content, and yield of regenerated biomass), compared with those of [EMIM]Ac. In contrast, the pretreatment ability of the co-solvent system of both ILs with 40 vol% ethanolamine was remarkably higher than that of the corresponding ILs. After pretreatment with [BMIM]Cl/ethanolamine (60/40 vol%), the sugar conversion yield exceeded 90 wt%, which was 25-39% higher than that obtained with pure [BMIM]Cl.

Moreover, Wu et al. (2013) attempted to use a co-solvent system of [EMIM]Ac and dimethyl sulfoxide with different mixing ratios for the pretreatment of eucalyptus wood to improve the saccharification yield. They found that the appropriate ratio of [EMIM]Ac and dimethyl sulfoxide could help minimize [EMIM]Ac consumption without impairing the pretreatment performance and contribute to the improvement in pretreatment efficiency due to the viscosity reduction effect on the pretreatment liquor.

Mai et al. (2014) proposed a microwave-assisted pretreatment method of rice straw using the co-solvent of ILs and polar organic solvents. They expected that the combined use of appropriate ILs and organic solvents would enhance the solubility of lignocellulosic biomass due to its lower viscosity compared to those of pure ILs while the hydrogen bond basicity was maintained. The microwave-assisted pretreatment using [EMIM]Ac/dimethyl sulfoxide (1:1 volume ratio) co-solvent provided at least 22 times faster enzymatic hydrolysis than that of untreated-rice straw due to more efficient lignin extraction, less crystalline cellulose, and lower residual ILs in treated-rice straw. Furthermore, it was reported that the co-solvents could be recycled and reused at least five times without significant loss in pretreatment efficiency. They suggested that this method might be beneficial for large-scale biomass pretreatment.

Procentese et al. (2015) analyzed the effect of DES treatment on the saccharification yield of the corncob. The used DESs were cholinium chloride/glycerol, cholinium chloride/urea, and cholinium chloride/imidazole. Pretreatment with DES enhanced enzymatic saccharification resulting from lignin removal and a reduction in the crystallinity of cellulose. The researchers obtained 27 g of glucose and 14 g of xylose from 100 g of corncob, representing 86% and 63% of the initially available carbohydrates.

Xu et al. (2016) conducted DES (cholinium chloride/formic acid) pretreatment of corn stover for enzymatic saccharification. They reported that the pretreatment increased cellulose accessibility due to the removal of hemicellulose and lignin. Following pretreatment optimization, the glucose released from the pretreated product reached 17.0 g/L, and a yield of 99% from the hydrolysate was achieved.

The kind of lignocellulosic biomass, particle size, and solid loading could also greatly influence the pretreatment effect for enzymatic saccharification. Additionally, the yield of monosaccharides obtained after IL treatments is strongly dependent on the treatment time, temperature, biomass species, and position applied, because different species and positions of lignocellulosic biomass (e.g., hardwood, softwood, heartwood, sapwood, transition wood, knots, and bark) possess different properties and are chemically different.

Aid et al. (2016) investigated the effect of woody biomass such as spruce, birch, and pine on the pretreatment efficiency of ILs ([BMIM]Ac and 1-ethyl-3-methylimidazolium chloride). The highest yields of glucose and arabinose were 12.1 and 7.7 mmol/L from the pretreated spruce and pine, respectively.

Bağder Elmacı and Özçelik (2018) investigated the effect of particle size of yellow pine wood (<2.5 mm, 500-850 μm, 363-500 μm, and <363 μm) prior to pretreatment and pretreatment time (15, 30, and 45 min) on the structural properties and enzymatic saccharification yield of a [EMIM]Ac-pretreated product. In general, [EMIM]Ac was more effective on large particle sizes than small ones. The dissolution of solids and the lignin extraction, as well as biomass to glucose yield, became excessive with increasing pretreatment time. The conversion of biomass to glucose was 56% under the selected optimum conditions, i.e., 500-850 μm particle size, 5% biomass concentration, for 15 min at 140°C.

Recycling of ILs

Even though significant developments have been achieved for the direct utilization of ILs during the lignocellulosic pretreatment process, the high cost limits the commercial use of IL-based pretreatment technology for biorefinery (George et al. 2015; Chang et al. 2016; Zhang et al. 2016; Xu et al. 2017). To combat this limitation, ILs could be reused as they can be readily recovered (Elgharbawy et al. 2016; Perez-Pimienta et al. 2017).

Sangian et al. (2015) investigated the enzymatic saccharification efficiency of coconut coir dust pretreated by twice-recycled IL (1,3-dimethylimidazolium dimethyl phosphate) and its combination with an alkaline agent (sodium hydroxide). Sugar yields after pretreatment using fresh IL and once-and twice-recycled IL, were 0.19, 0.15, and 0.15 g sugar/g cellulose + hemicellulose, respectively. When a sodium hydroxide solution was combined with the twice-recycled ILs in the pretreatment, the sugar yields were similar to those obtained using pure IL and the alkaline agent. Pretreatment with the alkaline agent, or the combination of alkaline and twice-recycled IL, resulted in sugar yields of 0.25 and 0.28 g/g, respectively. When alkali was combined with the recycled ILs in the pretreatment, sugar yields were similar to those obtained using an alkaline agent followed by pure IL. The authors thus suggested that the recycled IL pretreatment for lignocellulosic biomass presents a new prospect for the economical manufacture of fermentable sugars and biofuel in the coming years.

Ding et al. (2016) reported the pretreatment of corn stover using a pure and recycled IL ([BMIM]Cl). The glucose concentration from the product pretreated by the 10-times recycled IL was 18.7 g/L after 12 h of enzymatic hydrolysis, which was 5.5 g/L lower than the 24.2 g/L glucose concentration in the product pretreated using pure [BMIM]Cl.

Cheenkachorn et al. (2016) investigated the effect of [EMIM]Ac pretreatment on rice straw saccharification and tested different types of anti-solvents to recover the used IL and make it reusable for pretreatment. Enzymatic saccharification of IL-pretreated rice straw increased significantly compared to that of untreated rice straw and had a glucose yield of approximately 90%. The recyclability of [EMIM]Ac using methanol as an anti-solvent was found to retain $>90\%$ efficiency for five cycles, without any modification in the pretreatment process.

Kuroda et al. (2016) reported cellulose hydrolysis using a novel biphasic system consisting of water and an acidic and hydrophobic IL. The glucose yield in cellulose hydrolysis was 12.9% at 190°C. The acidic and hydrophobic ILs did not decompose during the cellulose hydrolysis and could be recycled up to four times.

Xu et al. (2017) assessed the effects of the reuse of 1-allyl-3-methylimidazolium chloride and [BMIM]Ac on the pretreatment of eucalyptus for enzymatic hydrolysis. Enzymatic digestibility slightly decreased as the number of recycles increased. Glucose yield by ILs that were recycled four times was 54.3% for 1-allyl-3-methylimidazolium chloride and 72.8% for [BMIM]Ac, which were 5.0 and 6.7-fold higher than that of untreated eucalyptus, respectively. Deteriorations of the pretreatment effects of the recycled ILs were observed after four cycles, showing relatively lower sugar conversion and lignin removal. They finally suggested that pretreatment using the recycled ILs was a potential alternative for low-cost biorefinery operation.

Combination of ILs and Other Pretreatment Methods

To improve the economic feasibility of large-scale IL-mediated pretreatment, a feasible recycling process and large biomass loading in ILs are required. To accelerate the pretreatment effect of ILs, there are some research studies on the combination pretreatments of ILs and other methods, especially extrusion processes.

Sriariyanun et al. (2015) investigated the effect of combining screw press pretreatment with four different types of ILs on the saccharification efficiency of rice straw. Of the four types of ILs tested, [EMIM]Ac was found to yield the highest percentage of recovered sugar. Compared to the conventional chemical pretreatment (i.e., diluted alkaline or acid), the combination of screw press and IL pretreatment had a much higher efficiency and a shorter reaction time (Brodeur et al. 2011; Guragain et al. 2011).

da Silva et al. (2013) carried out the extrusion process at 140°C with a 15 rpm screw speed in the presence of [EMIM]Ac with different sugarcane bagasse loadings in IL. They reported that the twin-screw extruder, which is capable of continuous processing of the extrusion process, can increase the solid loading in IL and reduce the operating torque through the addition of IL, thereby improving the flow performance in the barrel and the processing efficiency. In general, the solid loading of lignocellulosic biomass in ILs is approximately 5.0 wt%. In the present study, a twin-screw extruder with high shearing force was used to pretreat sugarcane bagasse at high loadings (25 wt%) in IL. The glucose yield was $>$90% after 24 h of enzymatic saccharification from the pretreated bagasse at 140°C for 8 min. This value is comparable to that of the 4.8 wt% bagasse loading that was pretreated for 120 min at 120°C in a stirring reactor and enzymatically hydrolyzed under the same conditions.

Yue et al. (2012) investigated the dissolution of holocellulose isolated from bagasse with the pretreatment of [BMIM]Cl assisted by ball-milling and ultrasound irradiation. Ball-milling pretreatment, ultrasonic irradiation assistance, and their combination effectively reduced the dissolution time of holocellulose in [BMIM]Cl. The crystallinity decreased after the dissolution process and regeneration assisted by ball-milling pretreatment and ultrasound irradiation.

Normark et al. (2015) explored pretreatment using [BMIM]Ac and the torrefaction of Norway spruce. Pretreatment using the [BMIM]Ac overcame the additional recalcitrance caused by torrefaction, and the glucose yields after 72 h of enzymatic hydrolysis of wood torrefied at 260°C for 8 min and at 285°C for 16.5 min were as high as those of IL-pretreated non-torrefied wood. Compared to IL-pretreated non-torrefied reference wood, the glucose production rates after 2 h of enzymatic hydrolysis of IL-pretreated wood torrefied at 260°C for 8 min and at 285°C for 16.5 min were 63% and 40% higher, respectively.

Isolation of Nanocellulose and Lignin by Pretreatment Using IL

Pretreatment using IL can also facilitate mechanical defibrillation efficiency of lignocellulosic biomass by partially or completely removing lignin and weakening the hydrogen bonding between cellulose microfibrils, thus resulting in disruption of the cell wall structure of lignocellulosic biomass.

Nanocellulose exist as either cellulose nanocrystals or cellulose nanofibrils and have applications in various fields owing to its non-immunogenicity, biocompatibility, high specific area, good mechanical properties, and variability for chemical modification (Lee et al. 2019).

Abushammala et al. (2015) reported for the first time the direct extraction method of cellulose nanocrystal from wood by [EMIM]Ac pretreatment. A native cellulosic product could be recovered at a 44% yield with respect to the wood cellulose content. They were the partially acetylated cellulose nanocrystals with native cellulose I microstructure, a crystallinity index of approximately 75% and an aspect ratio of 65. The pretreated product contained 60% of cellulose nanocrystals, which were easily extracted upon dispersion in water and were partially acetylated. The authors suggested that cellulose nanocrystals could be obtained through the simultaneous capacity of [EMIM]Ac to dissolve lignin while only swelling cellulose, to decrease intermolecular cohesion via acetylation and catalyze cellulose hydrolysis.

Berglund et al. (2017) demonstrated the high commercial potential of switchable IL processing for wood pulping prior to mechanical fibrillation using ultrafine grinding into cellulose nanofibrils. The switchable IL treatment drastically reduced the energy demand to achieve high strength cellulose nanofibrils with diameters below 15 nm and intact crystalline structures. The switchable IL-pretreated pulp was fibrillated more efficiently than traditional pulp since cellulose nanofibrils were produced using > 30% less energy compared to the reference pulp.

Pretreatment with IL is also sufficiently powerful to extract lignin with high molecular weight and without chemical modification from lignocellulosic biomass. Strehmel et al. (2017) isolated lignin from birch using four different ILs: [BMIM]Cl, [BMIM]Ac, 1-ethyl-3-methylimidazolium mesylate, and 1-ethyl-3-methylimidazolium tosylate. The molecular weight of lignin was different from that of the samples obtained by [BMIM]Ac and 1-ethyl-3-methylimidazolium tosylate; [BMIM]Ac was the most efficient IL among ILs investigated for the extraction of lignin from birch bark. This high efficiency may be attributable to a high IL catalytic function.

Tan et al. (2009) investigated the yield of lignin extraction from sugarcane bagasse using 1-ethyl-3-methylimidazolium xylenesulfonate in the temperature range of 170-190°C. The yield of lignin extraction was > 93% and the extracted lignin had a uniform molecular weight of 2,220 g/mol after acetylation.

da Costa Lopes et al. (2013) reviewed the fractionation of lignin from lignocellulosic biomass using ILs (1-allyl-3-methylimidazolium chloride, [BMIM]Ac, [BMIM]Cl, and [EMIM]Ac). Pinkert et al. (2011) reported that lignin extracted by ILs has a higher and more uniform molecular weight than kraft lignin that was mostly obtained during the pulping process Moreover, the ILs have a molecular structure that is similar to proto lignin. The ILs can not only isolate lignin with good characteristics but can also contribute to the homogenization of its characteristics.

An et al. (2017) investigated the effect of residual lignin on the subsequent enzymatic hydrolysis of rice straw treated by three cholinium-based ILs: (cholinium glycinate, cholinium acetate, and cholinium glycolate). Of the three residual lignins examined, lignin isolated from cholinium glycinate-pretreated rice straw had the highest carboxylic acid content (1.27 mmol/g) and the lowest phenolic hydroxyl content (0.72 mmol/g), resulting in the weakest non-productive enzyme adsorption. The strongest enzyme adsorption was found for cholinium glycolate-pretreated rice straw as it exhibited the lowest carboxylic acid content (0.14 mmol/g) and the highest phenolic hydroxyl content (1.19 mmol/g).

Concluding Remarks

In current review, the research activities on the pretreatment of lignocellulosic biomass using ILs and DESs as green solvents for enzymatic saccharification and nanocellulose production are summarized. Both solvents have many advantages such as easy recovery, chemical stability, temperature stability, nonflammability, low vapor pressure, and wide liquidus range. In addition, they also can dissolve biomass at low temperatures, possess low viscosity, do not severely decompose biomass, are easy to regenerate and recycle, are cost-effective, are easy to process, and are non-toxic to enzymatic and microbial fermentation for biochemical conversion. These research will be highlightened with a magnificent importance today and in the future of biorefinery process, including bioenergy and nanocellulose production.

Acknowledgements

This study was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (No. 2018R1A6A1A03025582).

References

Abushammala H, Krossing I, Laborie MP. 2015. Ionic liquid-mediated technology to produce cellulose nanocrystals directly from wood. Carbohydr Polym 134: 609-616.

Aid T, Hyvärinen S, Vaher M, Koel M, Mikkola JP. 2016. Saccharification of lignocellulosic biomasses via ionic liquid pretreatment. Ind Crops Prod 92: 336-341.

An YX, Zong MH, Hu SQ, Li N. 2017. Effect of residual lignins present in cholinium ionic liquid-pretreated rice straw on the enzymatic hydrolysis of cellulose. Chem Eng Sci 161: 48-56.

Bağder Elmacı S, Özçelik F. 2018. Ionic liquid pretreatment of yellow pine followed by enzymatic hydrolysis and fermentation. Biotechnol Prog 34: 1242-1250.

Berglund L, Anugwom I, Hedenström M, Aitomäki Y, Mikkola JP, Oksman K. 2017. Switchable ionic liquids enable efficient nanofibrillation of wood pulp. Cellulose 24: 3265-3279.

Bernardo JR, Gírio FM, Łukasik RM. 2019. The effect of the chemical character of ionic liquids on biomass pre-treatment and posterior enzymatic hydrolysis. Molecules 24: E808.

Brodeur G, Yau E, Badal K, Collier J, Ramachandran KB, Ramakrishnan S. 2011. Chemical and physicochemical pretreatment of lignocellulosic biomass: a review. Enzyme Res 2011: 787532.

Canilha L, Kumar Chandel A, dos Santos Milessi TS, Fernandes Antunes FA, da Costa Freitas WL, das Graças Almeida Felipe M, da Silva SS. 2012. Bioconversion of sugarcane biomass into ethanol: an overview about composition, pretreatment methods, detoxification of hydrolysates, enzymatic saccharification, and ethanol fermentation. J Biomed Biotechnol 2012: 989572.

Chang KL, Chen XM, Han YJ, Wang XQ, Potprommanee L, Ning XA, Liu JY, Sun J, Peng YP, Sun SY, Lin YC. 2016. Synergistic effects of surfactant-assisted ionic liquid pretreatment rice straw. Bioresour Technol 214: 371-375.

Cheenkachorn K, Douzou T, Roddecha S, Tantayotai P, Sriariyanun M. 2016. Enzymatic Saccharification of Rice Straw under Influence of Recycled Ionic Liquid Pretreatments. Energy Procedia 100: 160-165.

da Costa Lopes AM, João KG, Morais ARC, Bogel-Łukasik E, Bogel-Łukasik R. 2013. Ionic liquids as a tool for lignocellulosic biomass fractionation. Sustain Chem Process 1: 3.

da Cunha-Pereira F, Rech R, Záchia Ayub MA, Pinheiro Dillon A, Dupont J. 2016. Liberation of fermentable sugars from soybean hull biomass using ionic liquid 1-butyl-3-methylimidazolium acetate and their bioconversion to ethanol. Biotechnol Prog 32: 312-320.

Dadi AP, Schall CA, Varanasi S. 2007. Mitigation of cellulose recalcitrance to enzymatic hydrolysis by ionic liquid pretreatment. Appl Biochem Biotechnol 137: 407-421.

da Silva AS, Teixeira RSS, Endo T, Bon EPS, Lee SH. 2013. Continuous pretreatment of sugarcane bagasse at high loading in an ionic liquid using a twin-screw extruder. Green Chem 15: 1991-2001.

Ding JC, Xu GC, Han RZ, Ni Y. 2016. Biobutanol production from corn stover hydrolysate pretreated with recycled ionic liquid by *Clostridium saccharobutylicum* DSM 13864. Bioresour Technol 199: 228-234.

Elgharbawy AA, Alam MZ, Moniruzzaman M, Goto M. 2016. Ionic liquid pretreatment as emerging approaches for enhanced enzymatic hydrolysis of lignocellulosic biomass. Biochem Eng J 109: 252-267.

George A, Brandt A, Tran K, Zahari SMSNS, Klein- Marcuschamer D, Sun N, Sathitsuksanoh N, Shi J, Stavila V, Parthasarathi R, Singh S, Holmes BM, Welton T, Simmons BA, Hallett JP. 2015. Design of low-cost ionic liquids for lignocellulosic biomass pretreatment. Green Chem 17: 1728-1734.

Guragain YN, De Coninck J, Husson F, Durand A, Rakshit SK. 2011. Comparison of some new pretreatment methods for second generation bioethanol production from wheat straw and water hyacinth. Bioresour Technol 102: 4416-4424.

Han SY, Park CW, Kim NH, Lee SH. 2017. Co-solvent system of [EMIM]Ac and DMF to improve the enzymatic saccharification of pussy willow (*Salix gracilistyla* Miq.). Holzforschung 71: 43-50.

Han SY, Park CW, Park JB, Ha SJ, Kim NH, Lee SH. 2020. Ethanol Fermentation of the Enzymatic Hydrolysates from the Products Pretreated using [EMIM]Ac and Its Co-Solvents with DMF. J For Environ Sci 36: 62-66.

Hou Q, Ju M, Li W, Liu L, Chen Y, Yang Q. 2017. Pretreatment of Lignocellulosic Biomass with Ionic Liquids and Ionic Liquid-Based Solvent Systems. Molecules 22: E490.

Kumar AK, Sharma S. 2017. Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. Bioresour Bioprocess 4: 7.

Kuroda K, Miyamura K, Satria H, Takada K, Ninomiya K, Takahashi K. 2016. Hydrolysis of Cellulose Using an Acidic and Hydrophobic Ionic Liquid and Subsequent Separation of Glucose Aqueous Solution from the Ionic Liquid and 5- (Hydroxymethyl)furfural. ACS Sustain Chem Eng 4: 3352-3356.

Lee SH, Kim HJ, Kim JC. 2019. Nanocellulose applications for drug delivery: a review. J For Environ Sci 35: 141-149.

Mai NL, Ha SH, Koo YM. 2014. Efficient pretreatment of lignocellulose in ionic liquids/co-solvent for enzymatic hydrolysis enhancement into fermentable sugars. Process Biochem 49: 1144-1151.

Mood SH, Golfeshan AH, Tabatabaei M, Abbasalizadeh S, Ardjmand M, Jouzani GS. 2014. Comparison of different ionic liquids pretreatment for corn stover enzymatic saccharification. Prep Biochem Biotechnol 44: 451-463.

Normark M, Pommer L, Gräsvik J, Hedenström M, Gorzsás A, Winestrand S, Jönsson LJ. 2015. Biochemical Conversion of Torrefied Norway Spruce After Pretreatment with Acid or Ionic Liquid. Bioenerg Res 9: 355-368.

Parthasarathi R, Sun J, Dutta T, Sun N, Pattathil S, Murthy Konda NV, Peralta AG, Simmons BA, Singh S. 2016. Activation of lignocellulosic biomass for higher sugar yields using aqueous ionic liquid at low severity process conditions. Biotechnol Biofuels 9: 160.

Perez-Pimienta JA, Sathitsuksanoh N, Thompson VS, Tran K, Ponce-Noyola T, Stavila V, Singh S, Simmons BA. 2017. Ternary ionic liquid-water pretreatment systems of an agave bagasse and municipal solid waste blend. Biotechnol Biofuels 10: 72.

Pinkert A, Goeke DF, Marsh KN, Pang S. 2011. Extracting wood lignin without dissolving or degrading cellulose: investigations on the use of food additive-derived ionic liquids. Green Chem 13: 3124-3136.

Procentese A, Johnson E, Orr V, Garruto Campanile A, Wood JA, Marzocchella A, Rehmann L. 2015. Deep eutectic solvent pretreatment and subsequent saccharification of corncob. Bioresour

Technol 192: 31-36.

Rigual V, Ovejero-Pérez A, Rivas S, Domínguez JC, Alonso MV, Oliet M, Rodriguez F. 2019. Protic, Aprotic, and Choline-Derived Ionic Liquids: Toward Enhancing the Accessibility of Hardwood and Softwood. ACS Sustain Chem Eng 8: 1362-1370.

Sangian HF, Kristian J, Rahma S, Dewi HK, Puspasari DA, Agnesty SY, Gunawan S, Widjaja A. 2015. Preparation of Reducing Sugar Hydrolyzed from High-Lignin Coconut Coir Dust Pretreated by the Recycled Ionic Liquid [mmim] [dmp] and Combination with Alkaline. Bull Chem React Eng Catal 10: 8-22.

Sant'Ana da Silva A, Lee SH, Endo T, Bon EP. 2011. Major improvement in the rate and yield of enzymatic saccharification of sugarcane bagasse via pretreatment with the ionic liquid 1-ethyl-3-methylimidazolium acetate ([Emim] [Ac]). Bioresour Technol 102: 10505-10509.

Socha AM, Parthasarathi R, Shi J, Pattathil S, Whyte D, Bergeron M, George A, Tran K, Stavila V, Venkatachalam S, Hahn MG, Simmons BA, Singh S. 2014. Efficient biomass pretreatment using ionic liquids derived from lignin and hemicellulose. Proc Natl Acad Sci U S A 111: E3587-E3595.

Sriariyanun M, Yan Q, Nowik I, Cheenkachorn K, Phusantisampan T, Modigell M. 2015. Efficient Pretreatment of Rice Straw by Combination of Screw-Press and Ionic Liquid to Enhance Enzymatic Hydrolysis. Kasetsart J (Nat Sci) 49: 146-154.

Strehmel V, Strunk D, Wetzel H, Strehmel N. 2017. Investigation of lignin obtained by processing of *Betula pendula* with ionic liquids. Sustain Chem Pharm 6: 107-113.

Sun N, Parthasarathi R, Socha AM, Shi J, Zhang S, Stavila V, Sale KL, Simmons BA, Singh S. 2014. Understanding pretreatment efficacy of four cholinium and imidazolium ionic liquids by chemistry and computation. Green Chem 16: 2546-2557.

Tan SSY, MacFarlane DR, Upfal J, Edye LA, Doherty WOS, Patti AF, Pringle JM, Scott JL. 2009. Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. Green Chem 11: 339-345.

Trinh LTP, Lee YJ, Lee JW, Lee WH. 2018. Optimization of Ionic Liquid Pretreatment of Mixed Softwood by Response Surface Methodology and Reutilization of Ionic Liquid from Hydrolysate. Biotechnol Bioprocess Eng 23: 228-237.

Weerachanchai P, Leong SS, Chang MW, Ching CB, Lee JM. 2012. Improvement of biomass properties by pretreatment with ionic liquids for bioconversion process. Bioresour Technol 111: 453-459.

Weerachanchai P, Lee JM. 2013. Effect of Organic Solvent in Ionic Liquid on Biomass Pretreatment. ACS Sustain Chem Eng 1: 894-902.

Wu L, Lee SH, Endo T. 2013. Effect of dimethyl sulfoxide on ionic liquid 1-ethyl-3-methylimidazolium acetate pretreatment of eucalyptus wood for enzymatic hydrolysis. Bioresour Technol 140: 90-96.

Xu GC, Ding JC, Han RZ, Dong JJ, Ni Y. 2016. Enhancing cellulose accessibility of corn stover by deep eutectic solvent pretreatment for butanol fermentation. Bioresour Technol 203: 364-369

Xu J, Liu B, Hou H, Hu J. 2017. Pretreatment of eucalyptus with recycled ionic liquids for low-cost biorefinery. Bioresour Technol 234: 406-414.

Yue F, Lan W, Zhang A, Liu C, Sun R, Ye J. 2012. Dissolution of holocellulose in ionic liquid assisted with ball-milling pretreatment and ultrasound irradiation. BioRes 7: 2199-2208.

Zhang X, Zhao W, Li Y, Li C, Yuan Q, Cheng G. 2016. Synergistic effect of pretreatment with dimethyl sulfoxide and an ionic liquid on enzymatic digestibility of white poplar and pine. RSC Adv 6: 62278-62285.