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Ionic liquids as potential pretreatment agent for bioconversion of biomass to biofuels

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Abstract: Ionic liquids (ILs) have been greatly exploited as a good solvent and/or reagent with various applications because of their "green" properties and also with their physiochemical and biological properties. One of the applications is pretreatment of biomass such as lignocellulosic biomass precedent to enzymatic hydrolysis for bioenergy production and other biomaterial production. Generally, the method collected of an IL pretreatment or recovery forwarded by hydrolysis of lignocellulosic biomass. Another approach came in vision in which simultaneously pretreatment process and saccharification of lignocellulosic biomass were used. However, the employment of ILs during this integrated process, within which enzymatic hydrolysis is finished within the presence of IL applied for biomass pretreatment, will simply inactivate the enzymes. Cellulases emerged as one of the important enzymes which are used to catalyze the polysaccharide from biomass and showed a higher level of stability in various ILs. Also, numerous approaches were created together with the synthesis of enzyme-compatible ILs, screening ILs-tolerant enzymes, and media engineering to boost cellulases performance. This review highlights the advancement and use of IL for the pretreatment or hydrolysis of lignocellulosic biomass. The structure of ILs and cellulase stabilization approaches are also discussed. From this review, this tends to powerfully believe that IL-compatible cellulase systems would eliminate the requirement to recover the regenerated biomass and cause simple, saccharification of cellulosic materials, which might be helpful in developing integrated bioprocesses.

Keywords: Biomass, Ionic liquids, Biofuels, Fermentation, Enzyme activity, Hydrolysis, Cellulose, Cellulase.

I. INTRODUCTION

The search for renewable feedstocks to supply good and cheap chemicals, materials that are associate with degreed fuels has become an important goal for supply, with the ever-growing energy demands and environmental considerations, at the side of the decreasing fuel reserves. Biomass such as lignocellulosic biomass could be a promising difference to fossil resources due to its abundance, renewability, and flexibility. Lignocellulosic biomass is one in every of the most-ample renewable resources on the planet and its utilization won't involve the increment of carbon emissions. It is anticipated that property and environmentally friendly organic trade using biomass as a significant feedstock can displace this inorganic or harmful trade that causes serious environmental problems.

In recent years, intensive analysis has established the conception and the basic framework of biorefinery through that biomass will be regenerate into a series of fuels and various chemicals. Based on the recently developed technologies biorefinery process will be categorized into 2 strategies. (1). One of the strategies is direct gasification and liquefaction of biomass mainly lignocellulose by pyrolysis. After these processes, the forms products, such as syngas, power biofuels, heat, fertilizer, and biochar, will be integrated into the corresponding industrial process, severally. Another strategy is, firstly fractionization of lignocellulosic biomass into cellulose, hemicellulose, and lignin and conversion of these three biopolymers into final products or various important intermediate products. The latter strategy is well designed in the line with the composition and structure of biomass, as it may reach additional complete utilization of biomass and supply an additional ample product than the former. Conventionally, cellulose has already been widely used for the assembly of paper and textiles. From the view of biorefinery, numerous added products will be obtained from cellulose. For example- bioethanol will be formed via fermentation of aldohexose, which is the building unit of cellulose. Hemicelluloses are composed of many simple sugar and monosaccharide sugars, including mannose, galactose, saccharide (predominantly), and arabinose. The dehydration product of the saccharide plant product has already been commercial with associate degree annual production near to three hundred kilotons. Lignin consists of 3 monomers- conifuyl, sinapyl, and pcoumoryl alcohols and it is a promising beginning material for the assembly of aromatic compounds and fuels. (2). Although many biomass conversion technologies with high potential were developed within a previous couple of decades, few processes are presently operating attributable to several economic and technical barriers. The direct conversion of lignocellulose and polyose typically ends up in a comparatively low yield and selectivity of product, and also the separation and purification of the product are additionally terribly energy-extensive. Pretreatment to beat the intractability of lignocellulosic biomass is incredibly vital for the economically viable utilization of lignocellulosic biomass. However, traditionally pretreatment strategies have many disadvantages, as well as low potency and high pollution, seriously preventive their large-scale application.

Recently, Ionic liquids (ILs) have emerged as efficient and promising solvents for lignocellulosic as they supply and efficient tools for the pretreatment of biomass. This article gives a summary of the potential activity of ionic liquids as a pretreatment agent of biomass and then to bioconversion to biofuels.

1. Biomass for biofuels

Lignocellulosic biomass from various source is widely distributed as residues from major agricultural and biology industries like corn fodder, little grain straw, grasses, and woody crops and used as a potential sustainable source of sugar for bioconversion into biofuels and other high-value products. Lignocellulosic categories have several chemical compositions and structure variables from one to a different which will have an effect on the cooperativeness of the deconstruction method, inflicting the strategies to be assessed during a slim vary of feedstock. Lignocellulose is technically a material that makes up the cell walls of most woody plants and comprises of 3 polymers: cellulose at 38-50% (w/w), hemicelluloses 23-32% (w/w), and lignin 12-25% (w/w), where the ratios vary depending on the source of biomass, making up appropriately 90-92% of the dry matter. (3). Cellulose consists of glucopyranose subunits coupled with extremely resistant B-1,4- glycosidic bonds, that may reach many thousand glucose units long.

To enhance the cellulose accessibility by cellulase enzymes, an efficient treatment approach to weaken those bonds is needed, so creating the extraction of lignin and hemicellulose and isolation of glucose within the preparation step as a standard follow. (4). Lignin carbohydrate complex is known when together with lignin, hemicellulose forms a covalent bond with each other.

2. Pretreatment process for biomass

On the whole, processing of lignocellulose to biofuels like bioethanol, four steps are required: Pretreatment, Enzymatic hydrolysis, Fermentation, and at last Ethanol separation. Within the initial stage of the pretreatment method, the primary obstacle that has to be solved is the efficient removal of lignin and hemicellulose through thought of low price and economical method to boost up the cellulose hydrolysis. Operative conditions should be taken into consideration, making them not be severe or extremely toxic. Pretreatment involves the alteration of biomass thus that enzymatic hydrolysis of hemicellulose and cellulose can be rapidly achieved and with higher yields. This includes the removal of lignin that later on increase the surface area and scale back the crystallinity of cellulose. (5). From the various lignocellulosic components, lignin is only the most resistant to dissolution and it is due to the presence of strong covalent bonds. The natural lignin in wood is way harder to be dissolved than pure lignin by reason of advanced structure and strong intramolecular interactions of lignocellulose. Regardless, it is necessary to develop a strong solvent for the dissolution of natural lignin in order to enhance the application of lignocellulose. (6).

Recently, the utilization of ionic liquids (ILs) has been providing a well-organized treatment whereas hemicellulose and lignin could be removed and reduction of crystallinity of cellulose. ILs can be used to dissolves a wide range of substrates together with soft and hardwood. This article will review the efforts that are introduced to attain the pretreatment, dissolution as well as hydrolysis of biomass so as to provide fermentable sugars using ILs. The recent development showed that the integrated enzymatic hydrolysis of polysaccharides within the presence of ILs may be verified as a possible route to utilize the lignocellulose within the biofuel production. (7).

3. Ionic Liquids

The rise of the recognition of ionic liquids (ILs) is traced back to the advancement of green chemistry as a legitimate scientific field and sparked a surge of interest in ILs wherever these fluids when used as an appropriate replacement for volatile organic solvents. Ionic liquids are also known as liquid salts that have a melting point below the boiling point of water.

"Ionic liquids" is a very broad term, and various forms of structure can be converted into IL form by introducing complexity and diversity to IL structure and properties. Indeed, IL includes both organic and/or inorganic ions, (8) and contain more than one anion or cation. There are unit electrostatic and dispersive interactions at totally different length scales among liquids, which ends in its extremely non-isotopic character. There is massive structural diversity of ions that vary from inorganic to organic, simple to complex, chiral or achiral, as well as absolutely or partly ionizing acid or base, charged bridging ligands, metallate coordination polymers, organic polymeric metal ions, etc. These contain the recognized cations as azolium, phosphonium, pyridinium, pyrolidinium, alkylammonium, etc. cations, and also include many new classes of cations. Anions include various form of inorganic anions, e.g.- halide, nitrate, perchlorate, sulfate, azide, etc. and a large number of organic ions e.g.- trifate, benzoate, alkylsulfates, alkylcarbonates, organic carboxylates, etc. (9). Such intrinsic quality of the ILs and variety of ions is exacerbated by the shortcoming to attribute one common characteristic to all or any ILs except melting point (mp) and there's no single model that might be comprehensive enough to explain the entire family of ILs.

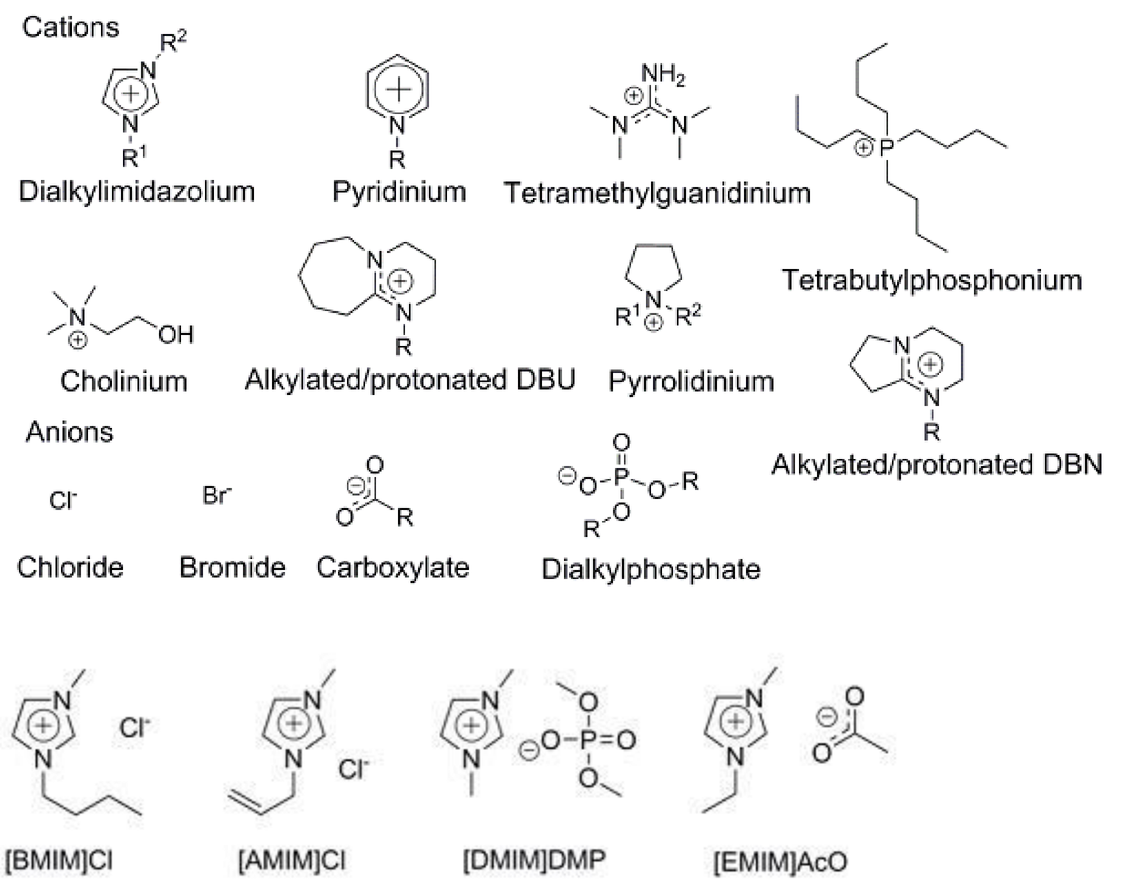

Fig. 1 Common cations and anions used in ionic liquids. (BEJ 6393)

3.1. Basic concepts on synthesis

Ionic liquids can be synthesized from various types of different cations or anions precursor providing a variety of interactions, diversity of properties, and structure. Whereas a high quantity of ions can be used for ILs, as they are primarily synthesized by quaternization reaction of a phosphine, pyridine, amine, or azole like- alkyl halides, sulfates, or triflates forming corresponding ILs. Other techniques such as anion exchange or metathesis and acid-base neutralization methods, conducted either beneath neat conditions or in binary compounds solutions or volatile organic solvents. (10).

In metathesis, ILs are synthesized from ammonium, halide, silver, and metal salts and ion exchange finally leads to the formation of solid by-products. Despite the simplicity of the synthetic approach and straight forward removal of solid by-product by filtration, halide ions still would possibly stay in synthesized ILs as impurities. These drawbacks may be overcome by acid-base neutralization or quaternization ways. In addition, ILs from bioactive compound cannot be synthesized by metathesis because of use of transition metals being capable of complicated formation with amino acids and proteins upon use. The acid-base neutralization is extremely efficient for reactions between amines and organic acids, whereas the quaternization reaction does not turn out any by-product. It is worth notice, that ILs synthesis isn't restricted to solely combining single anion/cation pair; ILs with distinctive chemical science properties can also be synthesized by a combination of 3 or a lot of distinctive ions in their compatible vary to make therefore known as "double salts ILs”. (11).

4. Ionic liquids for biomass dissolution

There are many criteria to be thought of so as to use the ILs for dissolution and enzymatic hydrolysis. Recently, ILs are getting a breakthrough in green technology. These molten or liquified organic salts are composed of ions and exist within the liquid state, usually melt below 100°C and exhibit low vapour pressure. ILs give many enticing options additionally to power to dissolve lignin and carbohydrates. Mild conditions can be applied for these reactions and can be reused after the processing. They provide straight forward recovery of the polysaccharide as well as ILs with no harmful or odour emissions. They get additional interest due to the possibility to distant the physical or chemical properties according to the process. It is a proven fact that the dissolution could be physical solvent-solute interaction which may be dominant by the character of each element of ILs and physical factors. There are two crucial stages for enzyme-catalyzed hydrolysis of cellulose are the enzyme adsorption on the cellulosic particle and enzyme-substrate complexes (ES) formation. These stages associated with various enzymes and substrate related factor. (12). Enzyme related factors embrace inhibition by cellobiose and D-glucose products, thermal stability, synergism, and adsorption. Substrate related factors embrace the presence of hemicellulose and lignin, the crystallinity of cellulose, and polymerization degree as well as internal and external surfaces of cellulose. Since celluloses regenerated from ILs are abundant less crystalline than untreated ones and are liable to faster enzymatic hydrolysis. It is reasonable to postulate that regenerated celluloses are additionally accessible by celluloses. (13). Within the valorization processes of lignocellulosic biomass, celluloses and hemicelluloses are largely hydrolyzed to sugar monomers and afterward regenerate into alcohols, hydrogen, or methane by the fermentation process.

In a study of testing applicable IL to dissolve sugarcane bagasse, six IL were investigated: 1-Butyl-3-methylimidazolium chloride, 1-Ethyl-3-methylimidazolium acetate, 1-Allyl-3-methylimidazolium chloride, N-methylimidazolium Dimethyl phosphate, 1-Butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide, and 1-Ethyl-3-(hydroxymethyl) pyridine ethyl sulfate. Among all, 1-ethyl-3-methylimidazolium acetate was chosen because it considerably enhanced enzymatic saccharification of sugarcane bagasse and yielded 99.7% of glucose after pretreatment of 60 min at 120°C. (14). 1-Ethyl-3-methylimidazolium is the most well-known IL for biomass pretreatment. The Avicel, poplar, and switchgrass were fully dissolved after 30 min at 120°C. After 24 hours of hydrolysis yielded 85% for poplar, 91% of switchgrass, and approx. of 100% of Avicel, of glucose. 1-Ethyl-3-methylimidazolium acetate is used due to its enzyme compatible nature. Wood chips delignification was performed with IL following laccase enzymatic hydrolysis. This approach recommends the separation of cellulose fibers in IL from the wood biomass- aqueous buffering system. Subsequently, the lignification potency of IL treated wood was improved within the presence of 2.5 WT%. IL in an aqueous system wherever cellulose didn't endure structural changes. Swelling of wood cell walls happens throughput IL treatment, due to the breaking of a number of bonds between major biopolymers within the wood matrix. A little portion of the hemicellulose and lignin was solubilized, leading to the decrease of their content within the wood material when treatment. Therefore, IL treatment of wood fibers had higher cellulose content, compared to untreated sample because of the removal of hemicellulose, lignin, and water throughout the pretreatment method. Fibers from the cellulose content were approximately 73% and the lignin content was 9.8%, abundant under the lignin content (29.3%) of untreated wood cellulose crystallinity, and thermal stability of treated cellulose fibers is much higher compared to untreated wood material. (15).

5. Ionic liquids- cellulose compatible system

There are several reports on the multistep method applying pretreatment of various sorts of lignocellulosic biomass by varied ILs followed by enzymatic hydrolysis after recovery of cellulose which makes this wholesome process costly. However, researches forwarding for one-pot hydrolysis wherever combining ILs. Pretreatment of lignocellulosic biomass and enzymatic hydrolysis in a very single-step method for biofuel production. It generally accepted that 3 sorts of enzymes are needed to hydrolyze cellulose into glucose monomers, particularly exo-1,4-β-glucanases, endo-1,4-β-glucanases, and β-glucosidases. Ends of cellulose chains attacked by cellobiohydrolases whereas endo-glucanases cleave cellulosic chain within the middle and decrease the degree of polymerization. Reducing or non-reducing ends of cellulosic chain attacks may be preferred by cello-biohydrolases. The elimination step of regenerated cellulose ought to be a cause a straight forward, in place of saccharification of cellulosic material which might be helpful in the integrated process like bioethanol production. Although ILs with chloride or bromide were finalized with enzyme deactivation, it was also emphasized that the composition of ILs includes a vital impact on cellulose dissolution. (16).

It has been denoted that the anionic element of ILs play a vital role in enzyme catalysis and it is established that ILs within alkyl phosphate anions are proficient in dissolving cellulose. Many studies concerning compatibilities show promising results. Early reports on the compatible system of IL and cellulase were earned by using 1-ethyl-3-methylimidazolium diethyl phosphate. By the studies, it has been reported that polarity and viscosity are two vital or important factors affecting the stability of IL and enzyme activity. Cellulase activity belittled with the increase in viscosity and therefore the decrease in polarity of IL. In order to overcome the enzyme insolubility, ILs can be outlined by introducing functional groups like amide, hydroxyl, and ether with a high affinity to protein molecules. The viscosity of longer alkyl chains is much more than shorter chains in ILs. In addition, ILs with smaller anions are also less viscous. (17).

The use of ILs with cellulases during a combined system needed careful choice of the components further because of the conditions to regulate the reaction. There is some common feature showed by enzyme compatible ILs:

a. Having a large molecular structure so as to reduce the fundamental nature of the H- bonding as well as nucleophilicity.
b. Contain multiple hydroxyl groups and/or ether groups to improve the viscosity, water affinity, and hydrogen bond basicity for interaction with the enzyme.

ILs can be designed for a selected reaction that was not possible in typical organic solvents. In addition, the enzyme's thermal stability in ILs provides the chance of conducting the process at high temperatures. To overcome the negative impact of the ILs on enzymatic hydrolysis researches going on to regenerate the cellulose from IL biomass before enzymatic enzyme hydrolysis.

Studies on one-pot process victimization an aqueous IL mixture, 1,3-dimthylimidazolium dimethyl phosphate at totally different concentrations with citrate buffer and cellulose loading, and whole these results showed that rate of hydrolysis process was higher in a two-step process with respect to one process after 96 hr. (18). 1-ethyl-3-methylimidazolium acetate or alternative acetate base imidazolium ILs might be helpful in improving the stability and activity of cellulases in aqueous IL mixtures. Recently some reports showed that cellulases from the Thermatoga maritma and Pyrococcus horikoshi preserved high activity in 15% 1-ethyl-3-methylimidazolium acetate. At 40℃ aqueous IL, the mixture enhanced the activity of enzyme cellulase in cellulose hydrolysis. After 24h, 70% of cellulose was converted which was two-fold more than an aqueous system. At IL/water ratio of 3:2, cellulase activity was dropped which revealed that phosphobased ILs are often a good candidate for in situ hydrolysis of biomass.

It was investigated that the impact of reaction condition on cornstalk enzymatic degradation within the system of aqueous 1-ethyl-3-methylimidazolium acetate. Cellulase was used in absence of a recovery step and therefore the reaction was nearly completely in 30h. investigators suggested that the victimization IL system increased the reaction rate reportedly to 96.6% whereas it was only 46.1% in the E buffer system. Cellulase activity in ILs exhibited a small amount of deactivation impact whereas the activity of cellulase was reduced in chloride based ILs. 1-butyl-3-methylimidazolium acetate was better IL for lignocellulosic residues pretreatment. Hydrolysis yields of biomass by ILs are higher than dilute acid.

A study was conducted that proved the rigidity of commercial recombinant cellulase from T.reesei at 75°C and has the ability to hydrolyze cellulose within the presence of pure 1-butyl-3-methylimidazoliumchloride throughout the entire reaction. After 24h of incubation in 30% of 1-ethyl-3-3methylimidazolim acetate, a commercial mixture of cellulase preserved over 70% of the original activity. The cellulose retained 75% to 85% of activity within the presence of 5% to 10% IL, severally proving that at higher concentrations of IL cellulases tend to lose some activity. It was also observed that the hydrolysis of cellulose might be influenced by treatment even though the content of lignin is 60% of treated lignocellulose.

In many cases, it is discovered that ILs with hydrophobic nature, chosmotropic anion, chaotropic cation, and less viscosity, increases the stability and activity of the enzyme. However, the correlation could not be generalized because of variations in results. Therefore, search for an acceptable combination and optimum concentration of ILs would be useful for the hydrolysis process efficiently.

5.1. Effect of IL composition

In General, cellulose dissolving ILs are hydrophilic and are supported by imidazolium, cholinium, pyrrolidinium, pyridinium, tetrabutylammonium, tetrabutylphosphonium, and alkylalkyloxyammonium cations. Mainly, anions were phosphates, sulfates, imides, amides, halogens, carboxylates, sulphonate, and dichloro aluminates. Evidently, chloride anion was the most effective alternative thus far in dissolving lignocellulosic biomass and it has a good dissolution capability but it ends up in enzyme deactivation. Due to the restrictive effect of ILs, they are typically employed in the pretreatment step forwarded by washing out to remove residual ILs. The inhibition is accepted to be associated with the high salinity of the ILs that mess with the protein folding and results in the inactivation of the enzyme. Therefore, to lower the melting point and viscosities carboxylic acid anions were introduced to ILs. Moreover, all this improves the ability of ILs to react with cellulose hydroxyl groups and enhance dissolution power. In studies of the effect of anions and performance of ILs, uniform cation with various anions: trifluoromethanesulfonate, methylsulfate, dimethylphosphate, dicyanamide, chloride, and acetate were used.

The anions showed to have an impact on both dissolution and swelling of biomass. Anions basicity was recommended to be related with the capability to expand and dissolve lignocelluloses. Cellulose solubility rises with the rise of hydrogen bond acceptive ability of anions which might be formed a systematic hydrogen bond between cellulose hydroxyl protons and the anions. (19). Studies proved acetate to be a good choice as compare to chloride. On the other hand, the large size of anion results in reduction of dissolution, therefore, contributes to the low efficiency of H-bonds formation.

Structures of cations play a vital role in determining the melting point of ILs. Alkyl radial groups on imidazole lower the melting point and encourage wood dissolution. A higher amount of cation and anions with delocalized charge and unsymmetrical contribute to ILs low melting point. Extra functional group on cation side chain like-m OH-group would additionally weaken the H-bonds among cellulose fibers leading to amorphous regions that may increase the dissolution potency. Moreover, the introduction of allyl groups to cation results in an increase in polarity and higher dissolution. The OH-group in alkyl side chain affects cellulose solubilization because of the competitiveness to H-bonding with the cellulose.

Investigators approached interesting treatment as they have treated bamboo powder with choline acetate which remains solid by the use of a low amount of IL to reduce the wastewater and cost. (20). Furthermore, 1-butyl-3-methylpyridinium chloride was used for bagasse and Encalyptus pretreatment which results in an increase of 8-fold of cellulose conversion. This IL served for enhanced enzymatic saccharification with comparison to 1-ethyl-3-methylimidazolium acetate.

At last, the small size of aromatic heterocyclic cation and small alkyl side chain accelerate the cellulose dissolution. All inclusively, both cation and anion increase cellulose solubility and are vitally equal and involved in the dissolution mechanism. Basicity of IL controlled by selection of anion associate degree is crucial for getting an IL that is capable of dissolving of cellulose.

5.2. Effect of pretreatment temperature and time

The temperature of pretreatment is a vital issue that influences the yield of the reducing sugars discharged from the biomass, that is that the main concern within the idea of turning biomass into biofuels. There are many factors to be thought-about once selecting the optimal temperature: (i) low temperature at that IL is in liquid state (ii) potency in solubilization (iii) maintaining the enzyme activity over long periods (iv) the working temperature should be below the decomposition temperature of the IL so as to avoid IL decomposition which may end up in unwanted cellulose derivatization at high temperature. According, ILs dissolve a large amount of polysaccharide at a high temperature however this may well be littered with the IL type. As for 1-ethyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium acetate systems, reducing sugar yield was double larger in an exceeding two-step method. An increase in temperature reduces the viscosity of the acetate/formate based ILs a lot of quickly than chloride-based ILs as chloride-based ILs are a lot of viscous. Variation in temperatures was used to take a look at the result on the potency of the enzymatic hydrolysis of pulp within the presence of 1-ethyl-3-methylimidazolium dimethyl phosphate. IL employment within the method enhanced the potency of hydrolysis of an enzyme. However, the yield reduced with any increases in IL concentration (above 10%) as a result of cellulase was partly inactivated. Range of temperature between 20℃ to 60℃, high amount of yield was obtained between 50℃ to 60℃ after 1h pretreatment. However, to scale back the energy consumption, the pretreatment process was conducted at 50℃, which resulted in a hydrolysis yield of 54.94%. These studies prompt that time and temperature affected the hydrolysis compared to the result of the ILs composition.

According to theories, utilization of extremophilic enzymes may be helpful to the saccharification of the biomass to liberate reducing sugar, in terms of the use of high temperatures. the production of the enzyme by the extremophiles is purposeful and catalytically active under intense conditions and perform the reaction consequently. It was declared that the category thermophiles is one in all the opposite sorts that are thought of to be best suited to pretreatment applications due to the actual fact that the method itself is commonly performed below this condition. (21). However, it still must be explored whether or not these kinds of enzymes are compatible with the ILs at a one-stage pretreatment method.

Generally, increasing dissolution times incorporates a similar result to increasing temperatures. Increasing the dissolution time from 5 min to 15 min ends up in lower lignin yield and lower carbohydrate content. Longer dissolution times lead to a lot of supermolecule degradation however facilitates the separation of a polymer. De-alkylation would possibly occur upon heating and a lot of at higher temperatures even for shorter periods of time. Moreover, mistreatment higher temperatures, even at shorter times seems to guide to a lot of IL decomposition. this implies care within the final choice of temperature likewise because of the time used for treatment. (22).

5.3. Effect of water content

The deactivation impact of the ILs on the cellulase isn't that important that gave promising basics for additional investigations. It was said that the IL water mixture could be used to decline the cost and viscosity of IL. This gradually reduces the effect of ILs on cellulose. It was noticed that few ratios tested, 1:4 (IL: water v/v) was designated as best for conversion. After 24 hr, 70% of cellulose is fully converted by hydrolysis by cellulase wherever the increment in ratio 2:3 deactivates the enzyme. An investigation reported that in a mixture of grading pulp as microcrystalline cellulose with 1-ethyl-3-methylimidazolium and water shows that at lower water content, gave high conversion in a two-step process. It was reported that dissolution, additionally as conversion and there was inhibition at water content above 10% to 15%.

On the other hand, it was founded that water content at 15% with IL has a low dissolution rate. It was shown that low water concentration below 25 wt% was studied as cellulose can not fully be dissolved in 1-ethyl-3-methylimidazolim acetate – water mixture where water content higher than 20wt%. it was also reported that only 1% of water can also able to interrupt the dissolution process, as water content participates with IL anion for H-bond formation. Another study stated that 10% of water content was tolerated by acetate anions for biomass dissolution. It is evidenced that some water is important for the dissolution of biomass. (23).

5.4. Effect of substrate loading

Substrate loading is another issue that influences the pretreatment process, with the hydrolysis process. An experiment in which 1.6% of cellulose loads for in situ reaction within the presence of 1-ethyl-3-methylimidazoilium acetate. After the pretreatment process by highly pure IL, the whole mixture diluted to 15%, and enzymes hydrolysis reached approx. of 91% of conversion. On the other side, by the addition of 4% of poplar to the same concentration, then the rate of hydrolysis reached approx. of 45%. It was reported that loading of solid oil palm frond at 6 wt% with a low pretreatment time. At a fixed retention time of 38 min with 10 wt% of solid loading, the recovery of glucose multiplied well with the process temperature up to 100℃ succeeded by enzyme hydrolysis after regeneration. Another trend observed by lower solid loading at 2 wt% was used. All of the this-compiled results reported that an increase in IL/biomass ratio increases the final glucose yield, but reduces the recovery of glucose.

High loading may reverse the impact of pretreatment that will increase the protein accessibility of biomass as higher solid loading ends up in intermixture issues and more causes heat and mass transfer limitation within the system. Moreover, high loading also can cause the formation of repressive compounds, like furfural, that inhibits protein chemical reaction. However, the viscousness of IL affects the blending and mass diffusion throughout pretreatment. Therefore, a better biomass concentration underneath agitation permits additional frequent contact and collision between the biomass particles, caused striking on the biomass surface, inadvertently advancing cellulose dissolution from the matrix. it's ended that increasing the loading is another promising approach to boost the pretreatment potency. On the opposite, it was reported that biomass loading at 5 wt% in 1-ethyl-3-methylimidazolium acetate to a two-step process. (24). In the other study, it was implied that al lower biomass concentration the higher dissolution rate attained to the diffusion of IL in the biomass pores. (Y. Wang, M. Radosevich, D. Hayes, N. Labbé,2011). In an exceeding dissolution investigation, 1-butyl-3-methylimidazolium acetate may dissolve the maximum amount as 25% of cellulose below 100°C with dimethyl sulfoxide (DMSO), as a co-solvent. it had been ascertained that it improved the dissolution power of the IL by decreasing the time needed, even at low temperatures. DMSO reduced the viscousness and will increase the conductive phenomenon of the mixtures.

1-ethyl-3-methylimidazolium acetate pretreated biomass by two-step hydrolysis results in sugar yield of 80% of glucose and 50% of xylose where substrate loading ranges to 33% (w/w). when biomass loading ranges to 50% (w/w) the yields results to 55% and 34% for glucose and xylose, which ultimately shows that with the increase in biomass loading there is a decrease in yield. (25). According to research, cotton stalks pretreatment at 30% (w/w) showed the incapability of 1-ethyl-3-methylimidazolium acetate at high biomass loading to effectively extract lignin by multi-step hydrolysis process. In contrast, at biomass loading of 10% with 1-ethyl-3-methylimidazolium acetate 45% of lignin was achieved from cotton stalks. It was terminated that the methodological conversion of pretreated cotton stalks to glucose at uplifted substrate loadings as high as 15% (w/w) was coupled to the disordered crystalline structure of biomass that plays an important role in enzyme hydrolysis than to biomass delignification which is regardless of biomass loading used.

5.5. Effect of particle size

Milling or grinding is an essential step to get smaller particles that facilitate the dissolution of biomass and therefore the sort of biomass plays an important role in energy consumption units. for example, grasses need less energy than woody biomass. On dissolution, it was founded that according to temperature and time reduction once the particle size of Miscanthus was reduced. for example, it needed 6-8h at 120˚C for the particle size of 1.0 mm to be dissolved whereas over 15h were required for 4.0 mm at 130℃. In research, wheat straw was dissolved in 1-ethyl-3-methylimidazolium diethyl phosphate that yielded 54.8% of reducing sugar in 1hr of pretreatment and regenerated wheat straw in 12h batch hydrolysis. (26). Smaller particle size attributes to the fracturing of the inner advanced structure throughout mechanical grinding and milling and will increase area which might facilitate the diffusion of IL within the pores of biomass material. It was also reported that various different ILs favors particle size. For example, lower glucose was acquired upon pretreatment of cotton stalks (<0.15) millimeter in 1-ethyl-3-methylimidazolium acetate whereas larger particle sizes gave higher aldohexose yields once the application of protein reaction of the regenerated material. On the opposite hand, 1-ethyl-3-methylimidazolium chloride functioned additional with efficiency with cotton stalks with smaller particle sizes (<0.15 millimetre and zero.15–0.5 mm) wherever increment in the particle size resulted in glucose yields reduction.

6. Researches for improved IL pretreatment

6.1. Use of new IL

The acidic and hydrophobic ILs with multiple functions may be synthesized for organizing biphasic system therefore the cellulose hydrolysis, glucose recovery and fermentation substance removal may be achieved in one step with water and one IL. 1-ethyl-3-methylimidazolium hydrogen sulfate was planned to be capable of not solely aiding hydrolysis of biomass however additionally executing saccharification reaction of amylum hampas, sugarcane pulp, and rice husk. Restated, the presence of saccharifying anions will create the ILs reach biomass process with increased efficiencies.

There is no need for high temperature and long operational time for pretreatment by IL. In an experimentation process, there was compared the pretreatment results on corn stalks at 90°C for 30 min with various forms of pyrrodilinium based ILs and resulted that 1-butyl-1-methylpyrrolidinium chloride deceased 85.94% lignin from the test on corn stalks in only 30 min treatment. (27). Various new ILs, tetrabutylphosphonium-based ILs, where amino acids as anions, were made to dissolve cellulose at 30°C in IL with dimethyl sulfoxide mixtures.

To decrease the IL usage in lignocellulosic biomass pretreatment, it was investigated the consequences of amount of 1-butyl-3-methylimidazolium chloride applied for pretreat Eucalyptus dunnii bark and noted that the minimal IL merely enough to wet the sample however not dissolve the biomass is adequate to reinforce potency of ulterior saccharification method.

To minimize water usage throughout biorefinery, it was utilised saltwater as cosolvent to make cholinium-based IL with seawater mixture for agricultural residues pretreatment. This was noted that there's no adverse result on pretreatments within the presence of saltwater.

To reduce the price for chemical reaction catalysts, it was planned the utilization of carboniferous solid acid catalyst derived from black liquor for hydrolysis on 1-butyl-3-methylimidazolium chloride pretreated rice straw. The carbon residues were generated by direct thermal shift beneath N2 atmosphere at 400°C victimisation black liquor solids. In another study, it was planned the utilization of chitosan immobilized catalyst metals (Fe3+) for chemical reaction in IL-containing pretreated bamboo biomass. The solid catalysts were recycled for fourfold with sufficient activities and recovery. Use of well-designed novel ILs brings the potential to developing new generation IL-based biorefinery.

6.2. Water tolerant ILs

Water is bestowed altogether biomass. If water and IL mixtures will effectively pretreat lignocellulosic biomass, the chemical prices are considerably reduced. However, trace quantity of water will inhibit cellulose dissolution in standard ILs. Some tests disclosed that among 100 percent water content the 1-ethyl-3-methylimidazolium acetate will still cut back crystallinity of polysaccharide, whereas alternative tests showed that at elevated temperatures (160°C) up to eightieth water content is allowed for 1-ethyl-3-methylimidazolium acetate to dissolve switchgrass polysaccharide. It was noted that up to 8.6% w/w water is allowed for 1-ethyl-3-methylimidazolium chloride to effectively pretreat beech wood. (28). All these studies projected that the ILs initial removed deliquescent polymers from polysaccharide microfibrils, then the regionally “concentrated” 1-ethyl-3-methylimidazolium acetate dissolved xyloglucan and polysaccharide to swell the microfibrils for sequent catalyst attacks.

Addition to lithium chloride was noted to considerably improve the tolerance of 1-butyl-3-methylimidazolium chloride on water; especially, the 45 w/w 1-butyl-3-methylimidazolium chloride and 55 w/w lithium chloride 2H2O dissolve 96 polymer and 92 hemicellulose of bamboo substrates. Molecular dynamics simulations disclosed the breakdown of ordering structures of focused ILs once water contents exceeded twenty-fifth. Similar analyses might give info on however totally different additives will improve tolerance of ILs within the presence of water.

6.3. ILs tolerant enzymes

The high H-bond basicity of ILs is correlating with the high potency for lignocellulosic biomass pretreatment; whereas the high H-bond basicity can even move with the inner H-bonds in cellulase. The anions of ILs will coordinate with the positive-charged sites of enzymes, therefore, succinylation and acetylation of amine group of enzymes will for the most part scale back the coordination effects by the ILs to retain most cellulase activities in 15% 1-butyl-3-methylimidazolium. In addition, the ILs were projected to interfere with the hydrophobic interactions between the hydrophobic residues of cellulase and therefore the polyose, therefore inhibiting the activities of the catalyst. In molecular simulation studies, it was showed that the deactivation of GH5 catalysts by ILs could also be induced by deformation of binding pockets of enzyme or by loss of secondary structure of enzymes. (29). These studies showed that the water-like enzymes don't lose activities within the presence of ILs, that ought to be a target for future analysis on ILs-tolerant enzymes.

Since the anions of ILs largely correspond to the inactivation of the enzymes, the ILs with anions of huge mass will improve IL tolerance. as an example, the acetate-based ILs with a protracted alkyloxyalkyl chain on the anions has low inhibition effects on the enzymes. Various studies added polyethylene glycol chains onto cations to enlarge their sizes thus to scale back the effective ionic concentrations of the ILs with reduced inhibition to enzymes. Another attention-grabbing study is that the finding that presence of excess aldohexose, the top product of polysaccharide reaction, will type advanced with an accelerator to stabilize the activity of β-glucosidase in ILs.

7. Recyclability of ILs

The high price of ILs remains one among the most obstacles for his or her large-scale application within the pretreatment of lignocellulose. as luck would have it, ILs could have superb recyclability and may be reused so as to scale back the value of the treatment method. Furthermore, the priority regarding the setting and therefore the disposal of the ILs considering biodegradation and toxicity makes it a matter of attention. Studies highlighted the necessity to resolve few problems so as to use ILs at industrial scale: (i) to possess complete recovery of regenerated product, (ii) to eliminate impurities (side-products), and (iii) to maintain the soundness of the IL for next economical usage. Distillation of volatile solutes is always being the primary option to recover the ILs because of their low force per unit area. different strategies such as extraction n with organic solvents or critical greenhouse gas and membrane separation processes area unit utilized. ILs are re-obtained below reduced pressure to get rid of water. For example, it was reported that the structure of the recycled 1-ethyl-3-methylimidazolium chloride remained basically unchanged. moreover, similar biomass edibleness and accelerator potency of the regenerated cellulose fractions were determined. (30). In an experiment, the researcher used molecular distillation to recover 1-ethyl-3-methylimidazolium chloride. They succeeded to recycle and use the IL for five times with a purity of 99.56% with no structural changes. Surprisingly, investigator recovered 1-ethyl-3-methylimidazolium acetate using neutralization with NaOH followed by evaporation below reduced pressure. The same IL was utilized in seven pretreatment cycles of wheat straw. In further studies, investigators reused 1-butyl-3-methylimidazolium chloride catalytic system for many times despite the slight loss of its activity. Novel ILs that consisted of amino acids were reused for several cycles and recovered by evaporation while not purification in the treatment method of rice straw with high aldohexose yields (>80%) and sugar yields (52.2%). Moreover, 1-ethyl-3-methylimidazolium diethyl phosphate was reused to pretreat the wheat straw for 5 times, and therefore the yield of reducing sugars wasn't but 52.8%. As an alternative, a lot of thermally stable ILs and a lot of efficient heating strategies can be thought-about.

8. Fermentation for biofuel production

As the replacement of fossil fuels takes place that ignoring these issues, the way to avoid the negative effects of manufacturing biofuels from food provides is to create lignocellulosic derived fuels out there at intervals the shortest potential time (i.e., second generation biofuels). Generally, production of bioethanol or renewable product from lignocellulosic biomass involves 3 steps as pretreatment process, enzymatic hydrolysis, and fermentation. A primary obstacle featured within the production of biofuel from lignocelluloses biomass is that the issue to hydrolyse the cellulose attributable to the advanced structure. Various ILs are used for the degradation of lignocellulosic biomass and with the different processes.

Taking into consideration the multi-disciplinary nature of the complete method of bioethanol production, a deep understanding of the characteristics of lignocellulosic biomass, innovations for developing additional economical cellulases, and microbic strains for increased rates, yields and process integration and improvement for reducing energy consumption needs persistent effort. Moreover, the event of a biomass-based biorefinery to utilize the feedstock additional comprehensively, and within the in the meantime add additionally added coproducts like bio-based materials from the lignin element into the assembly train, would offset the price of biofuel and build it additional economically competitive. (31). However, the fermentation potency is directly associated with the pretreatment and chemical reaction steps, and achieving high yields of possible sugars as a result of the optimized method can cause economical fermentation while keeping in mind the improvement of the fermentation itself in terms of media elements, conditions, and germ choice.

9. Conclusion

In conclusion, ILs have proceeded as potential solvents and/or reagents within the field of lignocellulosic biomass pretreatment underneath "green" conditions that are well-proved over the last decade. IL pretreatment provides a replacement powerful platform to boost enzyme hydrolysis of biomass. Of specific importance has been found that some researchers have found impressive results on the look and development of IL-tolerant cellulases further as accelerator compatible ILs. On the full, there square measure several opportunities to boost any catalyst hydrolysis of biomass when IL pretreatment. The most necessary challenges within the use of ILs in lignocellulosic biomass pretreatment for bioenergy and biomaterials production from biomass square measure economical solutions to IL use. In fact, it's required to search out a lot of innovative methodologies during which the application and recycle of ILs as well as cellulases may be performed in a good means. The analysis in such a direction is simply starting. though cellulases are used extensively for biomass reaction in ILs, the use of other hydrolytic enzymes or mixers of enzymes is extremely restricted.

10. Future prospects

Pretreatment of biomass from ILs becomes a suitable process as it is effective and cost-efficient. ILs are also used for the pretreatment as well as saccharification of biomass and the efficiency of IL to processes these two-steps together will be used later to reduce the cost of the process and also used to reduce the processing period. Recyclability of the ILs will be beneficial for the regular and long run of treatment of biomass for faster conversion of biofuel. ILs are compatible with various emerging so that they will be used for different types of bioconversion.

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