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Archana Singh

Department of Biochemistry, G.
B. Pant University of
Agriculture and Technology,
Pantnagar, Uttarakhand, India

Ashutosh Dubey

Department of Biochemistry, G.
B. Pant University of
Agriculture and Technology,
Pantnagar, Uttarakhand, India

Vivek Chandra Verma

Department of Biochemistry, G.
B. Pant University of
Agriculture and Technology,
Pantnagar, Uttarakhand, India

AK Verma

Department of Biochemistry, G.
B. Pant University of
Agriculture and Technology,
Pantnagar, Uttarakhand, India

Corresponding Author:**Archana Singh**

Department of Biochemistry, G.
B. Pant University of
Agriculture and Technology,
Pantnagar, Uttarakhand, India

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Combine pretreatment of lignocellulosic biomass with ionic liquid and aqueous ammonia: Better approach for bioethanol production

Archana Singh, Ashutosh Dubey, Vivek Chandra Verma and AK Verma

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Abstract

Lignocellulosic biomass is the most suitable and renewable energy resource for bioethanol production which is considered as the most potential bioethanol which can change the dependency on the petroleum energy. The biomass constituents are cellulose, hemicellulose and aromatic polymer lignin. Cellulose is the major constituent and good source of bioethanol production. Despite of huge potential in bioethanol production, high cost of procedure departs its commercial viability impractical, since there are some technical and economic problems associated with the efficient degradation of cellulose. Bioethanol production process require pretreatment, enzymatic treatment and fermentable, where pretreatment and enzymatic treatment require high cost. Pretreatment is a prerequisite technology to facilitate the recovery of fermentable sugar from lignocellulosic biomass. There is various type of pretreatment methods available such as physical, chemical and Physio-chemical. Among them combine pretreatment with aqueous ammonia and ionic liquid pretreatment has gained attention as a potential pretreatment method for the degradation of lignocellulosic biomass. Pretreatment with aqueous ammonia and ionic liquid confers lots of attractive features in contrast to the conventional procedure. These consist of the potential for considerably lower temperature below or at 80 °C, no hazardous chemicals and conditions leading to ease of handling. Additionally, ionic liquid can be recycle and reused after reaction for further cost minimization and can easily serve to increase the enzymatic hydrolysis of lignocellulosic biomass.

Keywords: Ionic liquid, lignocellulosic biomass, pretreatment, saccharification, cellulose

Introduction

The imminent depletion of petroleum energy and its outcome on global economic and environment has strengthened the interest in development of an alternative non petroleum dependent source of energy. Lignocellulosic biomass has been considered as potentially sustainable feedstocks for bioethanol production (Knauf *et al.*, 2004) [37]. Production of bioethanol from a variety of lignocellulosic biomasses such as corn stalks, wheat straw, rice straw sugarcane leaves, bagasse etc. is now considered as the potential biofuel that can change the dependency of petroleum energy (Somerville *et al* 2010) [61]. Worldwide huge quantity of lignocellulosic biomass is produced, the majority of which is burn up as waste material and some quantity is used for silage and biofuel. There are different three types of energy can be generated from the agricultural waste with the help of chemical methods *viz.* fluid fuel like bioethanol, gaseous fuel like biogas and syngas and electrical energy (Menon *et al.*, 2012) [47]. According to the International Energy Agency (IEA) lignocellulosic materials are the major source for foodstuff, silage and a bioenergy resource provide approximately 10.2% or 50.3 EJ globally total bio-energy supply per year from the various lignocellulosic biomass (IEA 2010) [29]. Lignocellulosic bioethanol is also good for our environment, still related to the financial feasibility of procedure (Sorensen *et al.*, 2011) [62]. Despite of huge potential in bioethanol production, high cost of procedures departs commercial viability impractical. Since, there are many problems associated with using lignocellulosic materials as a source of alternative fuel, due to the crystallinity of cellulose and the existence of condensed lignin and the involvement of covalent cross-linkages between hemicelluloses and lignin in the plant cell wall that can potentially block the accessibility of enzyme for monomeric sugar production. These restrictions limit the degree to which competent enzymatic hydrolysis of biomass will change into fermentable sugars.

Structure of lignocellulose

Generally, lignocellulose biomass composed of cellulose, hemicellulose, lignin and other components (Hassan *et al.*, 2018) [24]. Cellulose is a linear chain of glucose connected with β -1, 4 glycosidic bonds while hemicelluloses are non-linear branched polymer of L-arabinose, D-xylose, D-glucose, D-mannose, D-glucuronic acid and D-galactose. Lignin structure is made up of three main phenolic compounds *viz.* coniferyl alcohol, p-coumaryl alcohol and sinapyl alcohol. The cellulose fibers are packed into the microfibrils which are stabilized by hydrogen bond (Fig.1). In cellulose polymer, each glucan chain consists of 25,000 glucose unit. At the microscopic level each microfibril is made up of 15-45 glucan chain organizes in the crystalline fashion. A group of these microfibrils aggregate to form a cellulose fiber, organize in a Para crystalline manner with alternative crystalline and amorphous part (Heredia *et al.*, 1995) [26]. The crystalline part of cellulose designed as firmly that not enzyme and even any tiny molecule such as water also not able to go into the composite structure. Amorphous part of cellulose is less ordered and non-crystalline. Complex tertiary structure and

high molecular weight made cellulosic structure not soluble in water. Crystalline parts of celluloses are further resistant to enzymatic hydrolysis or biodegradation than the non-crystalline or amorphous parts (Arantes *et al.*, 2010; Hallac *et al.*, 2011; Menon *et al.*, 2012) [1, 23, 47]. Generally, plant cell walls are further divided into primary cell wall (PW) and the secondary cell (SW) wall.

The allocation of cellulose, hemicelluloses and lignin varies greatly between these cell wall layers. The secondary wall is composed of secondary cell wall 1, 2, and 3 where secondary cell wall 2 is generally thicker than others cell walls and hold the large fraction of the cellulose. The middle lamella, that binds the neighboring cells, is about totally composed of lignin (Pandey *et al.*, 2011) [51]. The major obstruction in making cost-effective and feasible technique for degradation of the complex cellulosic structure is the organization of cellulose with hemicelluloses and lignin, crystallinity and level of organization. Thus, cellulose is unsuitable for bioconversion unless effective and economic pretreatment are developed to remove or modify the crystallinity and lignin structure (Arantes *et al.*, 2011; Menon *et al.*, 2012) [2, 47].

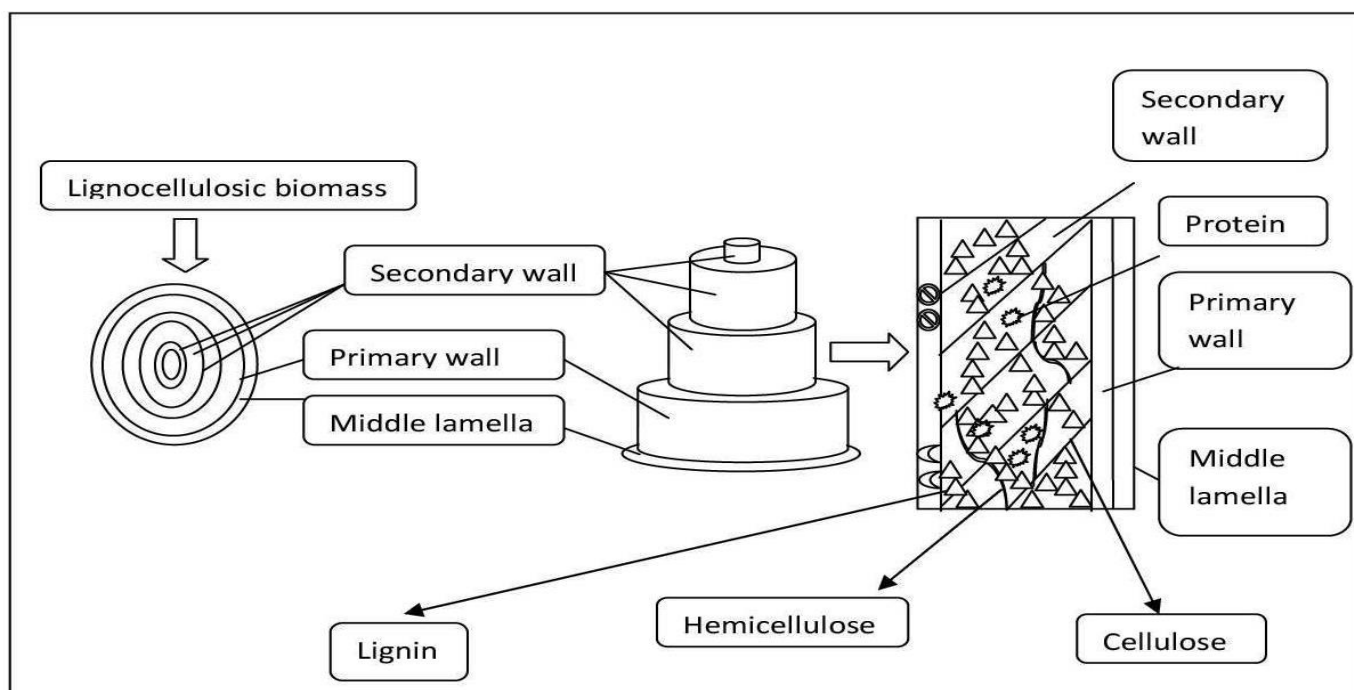


Fig 1: Structure of lignocellulosic biomass

Therefore, lignocellulosic biomasses should be first pretreated, for conversion of recalcitrant lignocellulose biomasses into reactive cellulosic intermediates prior to enzymatic hydrolysis to increase accessibility, efficiency of enzyme and improve the yield of fermentable sugars. The monomer sugar undergoes fermentation to produce bioethanol and whole process is summarized in the fig. 2. Extensive world-wide research has investigated the transformation of lignocellulosic materials into simple, fermentable sugars by different pretreatment methods (Chandra *et al.* 2009) [7].

Pretreatment of lignocellulosic biomass

The lignocellulosic biomass has to pretreated prior to enzymatic hydrolysis to make the complex arrangement of cellulose into reactive intermediates of cellulose. Pretreatment is done for the separation or solubilization of the main components of lignocellulosic materials which is hemicelluloses, lignin and cellulose and thus provides the

digestibility of biomass. Steps of the pretreatment should be simple, environmental friendly, commercial and economically reasonable (Hassan *et al.*, 2018; Ravindran *et al.*, 2018) [24, 54]. An efficient pretreatment approach includes: (1) disrupting and eliminating the cross-linked structure of hemicelluloses and lignin that embed the cellulose structure, (2) disrupting hydrogen bond of crystalline cellulose and (3) increasing the porosity as well as surface area of cellulose for successive enzymatic hydrolysis (Li *et al.*, 2010) [44]. Globally, extensive study has done for transforming the complex lignocellulosic materials into simple fermentable sugar by a variety of pretreatment methods (Mosier *et al.*, 2005; Chandra *et al.*, 2007; Chen *et al.*, 2017) [48, 8, 9]. The type of pretreatment should consider the overall compatibility of biomass. The traditional pretreatment methods are physical and chemical methods. Various methods include both methods together (Nguyen *et al.*, 2010; Kumar and Sharma 2017) [49, 16].

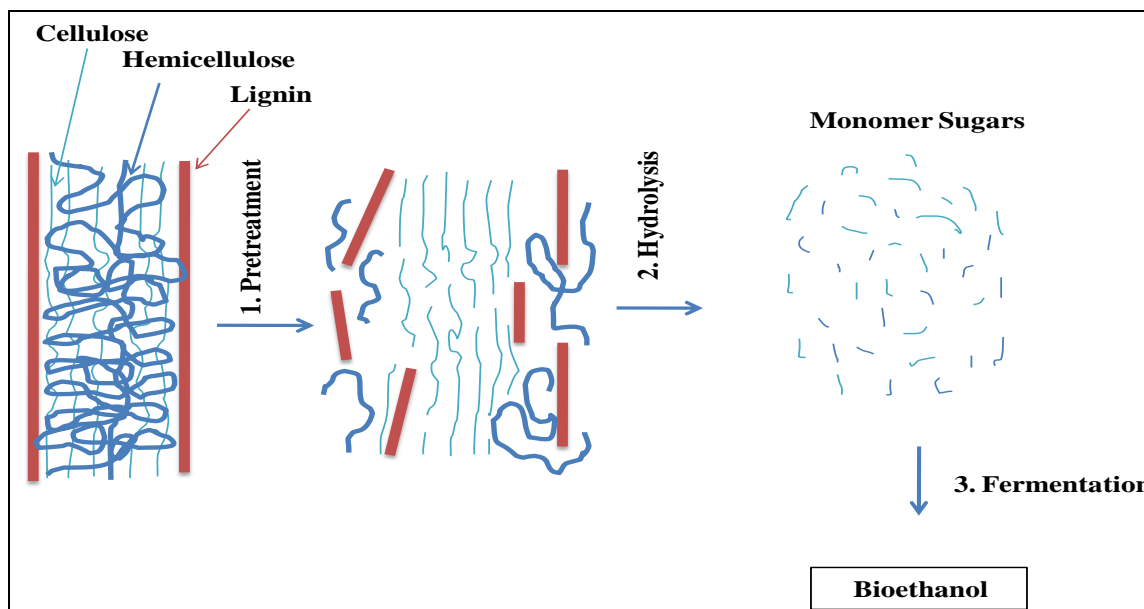


Fig 2: Process of Bioethanol production from lignocellulosic biomass

Physical methods of pretreatment

Mostly lignocellulosic materials necessitate a number of mechanical progressions for reducing the size of biomass. Various pretreatment processes like milling, irradiation by using electron beam, gamma rays and microwave radiation are generally required to enhance the enzymatic degradation of lignocellulosic materials. Enhanced degradation will happen with the help in reduction of complexity and to get better results qualities from reducing dimension of the particles. The required cost in the physical pretreatment is based on the dimension of the particles and reduction in the complexity of the biomass. These procedures are costly, time consuming and not fit for complete degradation of biomass (Mosier *et al.*, 2005; Menon *et al.*, 2012) [48, 47].

Chemical pretreatment

Chemical pretreatment was initially developed and has been widely utilized in the paper industry for removal of lignin from cellulosic biomass to make good quality of paper products. Chemical pretreatment techniques that have been considered as a major objective of enhancing the biodigestibility of biomass by removing crystallinity of the cellulose and eliminating lignin and hemicelluloses (Menon *et al.*, 2012) [47]. Pretreatment with chemical is the most studied among pretreatment methods. The various commonly used chemical pretreatment include: acid, alkali and ionic liquids.

(a) Acid pretreatment

Pretreatment with acid uses concentrated or diluted acids to crack the dense organization of the lignocellulosic biomass. The most widely used acid is diluted sulphuric acid (H_2SO_4), that has been profitably used for a various type of biomass such as switchgrass (Digman *et al.*, 2010) [14], corn Stover (Du *et al.*, 2010), spruce or softwood (Shuai *et al.*, 2010) [59], and poplar (Wyman *et al.* 2009) [69]. Other acids also have been used like phosphoric acid (H_3PO_4) (Zhang *et al.*, 2007) [72] hydrochloric acid (HCl) (Wang *et al.*, 2010) [67] and nitric acid (HNO_3) (Himmel *et al.*, 2007) [27]. Due to its capacity to remove hemicellulose, acid pretreatment has been used as parts of overall process in fractionating the component of lignocellulosic material (Zhang *et al.*, 2007) [72]. Pretreatment with acid (removal of hemicelluloses) followed by the pretreatment with alkali (removal of lignin) consequences in

relatively digestible cellulose. This chemical pretreatment generally consists of addition of diluted or concentrated acid (generally between 0.2% to 2.5% w/w) to the biomass, followed by continuous mixing at temperature between 130°C to 210°C . Depending on the condition of pretreatment, the hydrolysis of the cellulose could take from a few minutes to hour (Saha *et al.*, 2005; Esteghlalian *et al.*, 1997) [57, 17]. However, there are several disadvantages of acid pretreatment such as involvement of hazardous, toxic and corrosive chemicals, several neutralization steps are required and high cost (Menon *et al.*, 2012) [47].

(b) Alkaline pretreatment

Pretreatment with alkaline involves the bases, such as potassium, calcium, sodium and ammonium hydroxide for the pretreatment of cellulosic biomass. The involvement of an alkali causes the degradation of glycosidic side chains resulting structural changes in cellulose, hemicellulose and lignin like partial de-crystallization of cellulose (Cheng *et al.*, 2010) [10] and partial solvation of hemicellulose (McIntosh *et al.*, 2010). Sodium hydroxide has been widely studied, it has been exposed to disorder the structure of lignin, enhancing the accessibility of enzyme toward cellulose and hemicelluloses (MacDonald *et al.*, 1983) [45]. Though, the above methods are useful in degradation of some lignocellulosic biomass and necessitate several neutralization steps, expensive machinery and participation of elevated energy. The drawbacks of these methods, these are dangerous and do not able to remove lignin completely. Furthermore, include several anti-corrosion chemicals and require added recovery procedures. Pretreatment with ammonia fiber explosion, steam explosion and liquid hot water can hold a high efficiency. However, involvement of high temperature and high pressure is necessary in these methods. Besides, these methods require high expenses in comparison to the worth of the result which is glucose. These are mainly responsible for the major drawbacks in processing of these methods (Hendriks *et al.*, 2009; Nguyen *et al.*, 2010) [25, 49].

(c) Ionic liquid pretreatment

Modern research demonstrates that, ionic liquids (ILs) are useful to degrade the lignocellulosic structure like corn stalk, sugarcane residue, rice straw, wheat straw and wood as shown

in fig. 3. The pretreatment of lignocellulosic materials with ionic liquids confers a number of attractive features in comparison to the traditional methods. These involve considerably lower temperature less than 80°C and do not require any harmful chemicals and procedure. In addition, ionic liquids can be recycled and reuse after the reaction and

without any difficulty it can increase the accessibility of enzyme toward the substrate and proficiently can gather the fermentable sugars like glucose and xylose from lignocellulosic materials. Though the pretreatment by ionic liquids

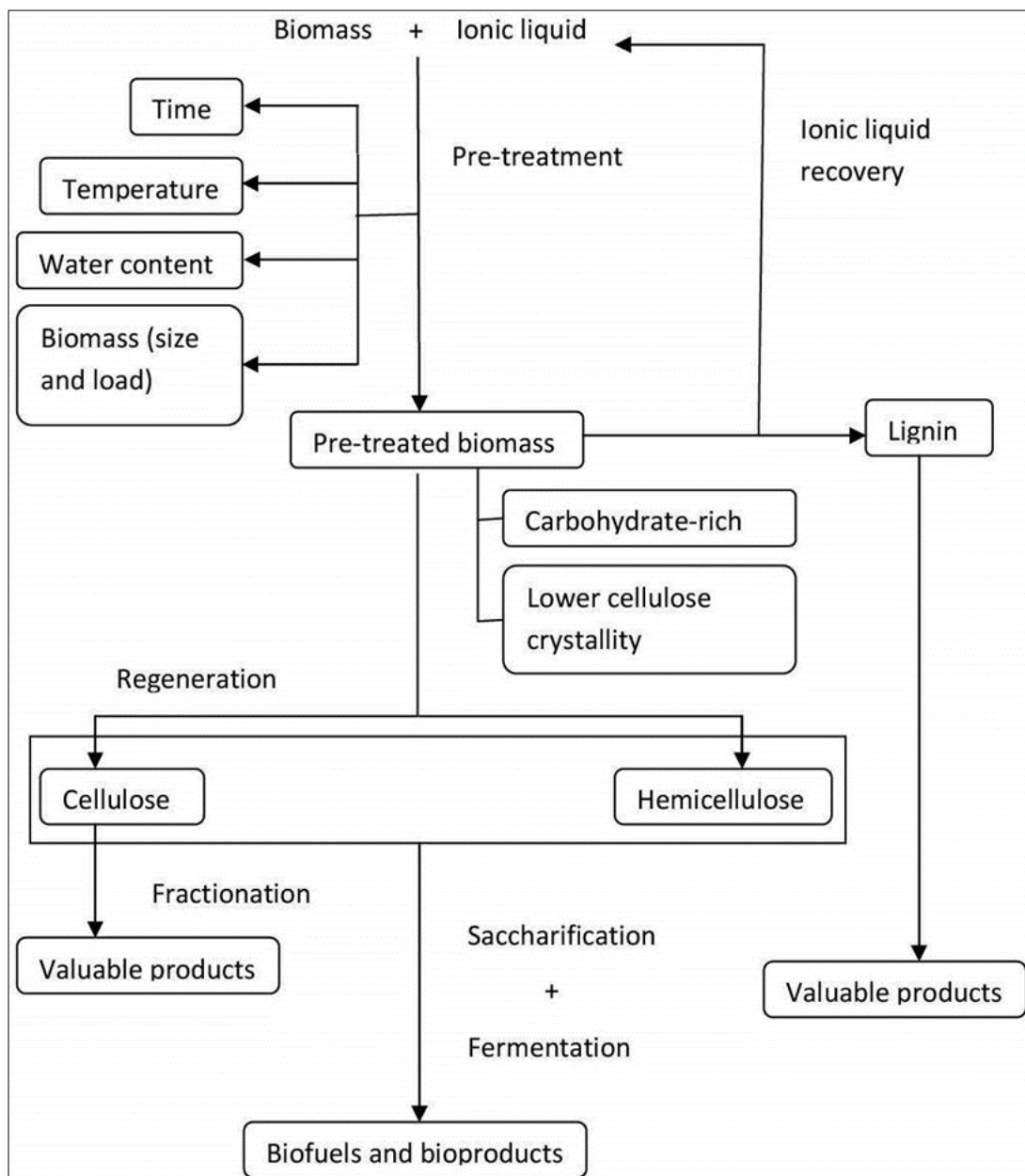


Fig 3: Pretreatment with ionic liquid.

has been increase the interest as a novel method from few years ago, at present this method has been very costly for the pretreatment of lignocellulosic materials because of high price of ionic liquid. Consequently, refined methods are required by using ionic liquid to make the procedure further proficient with the minimum cost (Lee *et al.*, 2009; Nguyen *et al.*, 2010) [49, 42]. There are several types of ionic liquids (ILs) are utilized for the pretreatment of lignocellulosic materials as mentioned in Table 1. These are 1-ethyl-3-methylimidazolium chloride EmimCl, 1-butyl-3methyl-imidazolium chloride BmimCl, 1-ethyl-3methylimidazolium hydrogen sulfate EmimSu and 1-ethyl-3methylimidazolium acetate EmimAc. These ionic liquids are the most efficient for the pretreatment of the biomass with the maximum competence of the cellulose solubilization. Furthermore, mostly ionic

liquids are non-hazardous, do not having any corrosive properties and easy to handling at low temperature (Hassan *et al.*, 2018; Nguyen *et al.*, 2010) [24, 49].

The pretreatment of lignocellulosic biomass relies on a relatively small number of ionic liquids, containing highly hydrogen-bond basic anions which are required for solubility of cellulose. The most widely used solvent being 1-ethyl-3methylimidazolium acetate or EmimAc. The lignocellulose dissolving ionic liquid disrupts the hydrogen-bonding network structure, including the hydrogen bonds in highly crystalline fibrils of cellulose. The materials regenerated after the pretreatment with EmimAc exhibit high yield after enzymatic hydrolysis due to low cellulose crystallinity, consequently increased accessibility of enzymes Brandt-Talbot *et al.*, (2017) [4].

Table 1: Ionic liquid used for degradation of lignocellulosic biomass subcomponents

Ionic liquids	Structure	Uses	References
1-ethyl-3-methylimidazolium acetate [EMIM]OAc		Dissolution of a variety of carbohydrates such as sugar, starch and cellulose, extraction of lignin from maple wood flour	Zhao <i>et al.</i> , 2008 ^[73] ; Vitz <i>et al.</i> , 2009 ^[66] ; Lee <i>et al.</i> , 2009 ^[42] ; Reddy <i>et al.</i> , 2015 ^[55]
1-ethyl-3-methylimidazolium chloride [EMIM]Cl		Dissolution of cellulose	Kosan <i>et al.</i> , 2008 ^[38] ; Vitz <i>et al.</i> , 2009 ^[66] ; Nguyen <i>et al.</i> , 2010 ^[49]
1-butyl-3-methylimidazolium chloride (BMIM)Cl		Dissolution of cellulose, dissolution of hard and softwood, dissolution of lignin from maple wood flour	Kosan <i>et al.</i> , 2008 ^[38] ; Zavrel <i>et al.</i> , 2009 ^[71] ; Lee <i>et al.</i> , 2009 ^[42]
1-allyl-3-methylimidazolium chloride		Dissolution of cellulose, dissolution of hard and softwood, dissolution of lignin from maple wood flour	Kilpelainen <i>et al.</i> , 2007; Fukaya <i>et al.</i> , 2008 ^[20]
1-butyl-3-methylimidazolium bromide (BMIM)Br		Degradation of cellulose and lignin	Pu <i>et al.</i> , 2007
1-butyl-3-methylimidazolium acetate (BMIM)OAc		Removal of lignin from flour of wood	Doherty <i>et al.</i> , 2010 ^[15]
1-butyl-3-methylimidazolium tetrafluoroborate [BMIM]BF ₄		Degradation and dissolution of cellulose, extraction of lignin from the flour of wood	Zavrel <i>et al.</i> , 2009 ^[71] ; Lee <i>et al.</i> , 2009 ^[42]
1-butyl-3-methylimidazolium methyl sulphate [BMIM]MeSO ₄		Dissolution of lignin from maple wood flour	Pu <i>et al.</i> , 2007
1-butyl-3-methylimidazolium hexafluorophosphate [BMIM]PF ₆		Degradation of cellulose, extraction of lignin from the flour of wood	Lee <i>et al.</i> , 2009 ^[42] ; Zavrel <i>et al.</i> , 2009 ^[71]
1-octyl-3-methylimidazolium chloride [OMIM]Cl		Dissolution of cellulose	Vitz <i>et al.</i> , 2009 ^[66] ; Zavrel <i>et al.</i> , 2009 ^[71]

Recycling of Ionic liquid

Another benefit of using Ionic liquid is that it can be recycle and reuses very efficiently after the process (Nguyen *et al.*, 2010) [49]. Due to their high-cost recycling and reuse of ILs is required for their commercial use in lignocellulosic biomass pretreatment. The cellulosic content of biomass can be recovered from the ionic liquid solution by the addition of the antisolvent such as water or ethanol. The antisolvent precipitates cellulose from the solution and cellulose can be recovered by the centrifugation or filtration and wash to remove excess IL or by evaporating the ethanol (Sun *et al.*, 2009) [63]. An alternative for recovery of ILs is provided by their ability to form a biphasic system by addition of an aqueous solution containing kosmotropic anion such as sulfate, carbonate or phosphate. Gutowski *et al.*, (2003) [22] reported that the formation of an aqueous biphasic system based on BmimCl, water and K₃PO₄. Subsequently phase diagram for a variety of IL/water/salt systems have been described, most of which are based on ionic liquid containing imidazolium cation and chloride anion (Wu *et al.*, 2008; Deng *et al.*, 2009; Shill *et al.*, 2011) [68, 13, 58].

Physio-chemical pretreatment

Procedure that combines both physical and chemical methods is called Physio-chemical pretreatment. These includes: steam explosion, microwave chemical pretreatment, ammonia fiber explosion (AFEX), ammonia recycling percolation (ARP) and liquid hot water treatment (Brodeur *et al.*, 2011; Menon *et al.*, 2012) [5, 47].

(a) Steam explosion

During the steam explosion method, the biomass is pretreated with elevated force of steam, after that the pressure is rapidly condensed and allow the biomass to go through a volatile compression. Generally, steam explosion process, initiate between temperatures 160°-260° (pressure 0.69-4.83 Mpa) for few seconds to few minutes prior to biomass screening for the atmosphere pressure. The biomass is kept for a period of time to promote hydrolysis and the method is ended with an explosive decompression. This procedure can cause the dissolution of lignocellulosic structure by using high temperature. Hence it can enhance the efficiency of the hydrolysis of cellulose structure. This method is widely used for pretreatment of different biomass (Focher *et al.*, 1991; Verga *et al.*, 2004; Menon *et al.*, 2012) [18, 47].

(b) Ammonia fiber explosion (AFEX)

In this method biomass is mix with liquid ammonia at elevated pressure and temperature for a short time of period after that pressure is rapidly condensed. The ammonia fiber explosion method is related to the steam explosion method. During this procedure, 1-2 kg of ammonia/kg of dry lignocellulosic biomass is used at 90°C temperature for 30 min. AFEX pretreatment can considerably enhance the rate of fermentation of a variety of crops and grasses (Zheng *et al.*, 2009; Menon *et al.*, 2012) [75, 47]. The ammonia fiber explosion method is used for various lignocellulosic biomass pretreatment. Consequence of ammonia fiber explosion pretreatment is the removal of crystallinity of the cellulose, degradation of hemicelluloses structure, elimination of the acetyl group which is mostly present in the hemicelluloses, breakdown of lignin and carbohydrate complex structure by breaking the bonding between lignin and carbohydrates and increasing the available exterior region due to disordering in

the structure in pretreated lignocellulosic biomass (Kumar *et al.*, 2009; Menon *et al.*, 2012) [40, 47].

(c) Ammonia recycling percolation (ARP)

In process of this method, aqueous ammonia goes from the biomass at high temperature between 150°-170° C with fluid speed 1cm/min for 14-15 min, after that ammonia is recovered from the process. Under these situations' ammonia can respond to the lignin and responsible for disruption of lignin structure by the breaking carbohydrate and lignin bonds (Jorgensen *et al.*, 2007; Galbe *et al.*, 2007) [21]. Difference between ammonia fiber explosion (AFEX) and ammonia recycling percolation (ARP) methods is that AFEX is done with liquid form of ammonia and ARP is operating by using aqueous ammonia (10-15%) (Sun *et al.*, 2002; Menon *et al.*, 2012) [64, 47].

(c) Microwave-assisted chemical pretreatment

The microwave-assisted pretreatment is a more efficient pretreatment than any other traditional pretreatment method like just heating of biomass with chemical and speeding up the reaction during pretreatment progression (Zhu *et al.*, 2006) [77]. Further, the microwave uniformly alters the ultra-structure of cellulose in a short span of time without generating any waste product. Menon *et al.*, (2012) [47] reported that there are three microwave and chemical dependent procedures for the pretreatment of biomass which is (1) microwave and alkali (2) microwave, acid and alkali (3) microwave, acid, alkali and H₂O₂ for the enzymatic hydrolysis followed by recovery of fermentable sugars from the pretreated biomass. They reported that fermentable sugars could not be recovered from the microwave and alkali pretreatment method, but it could be recovered as a crystalline structure in the microwave, acid, alkali and H₂O₂ method and microwave, acid and alkali methods. Hydrolysis with enzymes of pretreated biomass proved that the pretreatment with microwave, acid, alkali and H₂O₂ showed the maximum hydrolysis speed and fermentable sugar contents. Singh *et al.*, (2014) [60] reported that the application of microwave-assisted sodium hydroxide (NaOH) pretreatment on rice straw produced a maximum amount of reducing sugars (1334.79 mg/mL) under optimal condition which enhanced its enzymatic digestibility for production of bioethanol. Jin *et al.*, (2016) [31] used microwave-water, microwave-NaOH and microwave-Ca(OH)₂ pretreatment to enhance the enzymatic digestibility of catalpa sawdust which is promising for biofuel production. They concluded that microwave-Ca (OH)₂ pretreatment of catalpa sawdust is promising for enzymatic hydrolysis and it causes rapid hydrolysis of lignin and hemicelluloses.

(d) Liquid-hot water (LHW) pretreatment

In this method, pressure is used to maintain water in liquid state at higher temperature (Yu *et al.*, 2010) [70]. Biomass goes through the baking through the elevated temperature with water and high pressure. Liquid hot water pretreatment has been reported to have the capability to increase digestibility of cellulosic structure, recovery of pentoses and producing pre-hydrolyzates (Kim *et al.*, 2009) [36]. Sugar containing pre-hydrolyzates can be directly fermented into ethanol (Mosier *et al.*, 2005) [48].

There are several advantages and disadvantages of these techniques in pretreatment of lignocellulosic biomass mentioned in Table 2.

Table 2: Advantages and disadvantages of various pretreatment method

Method of Pretreatment	Effect	Advantages	Disadvantages	Reference
Mechanical disruption or milling	Reducing the dimension of the particle and complexity of lignocellulosic material	Cost effective for herbaceous and agricultural residues	Energy requirement is high for hardwoods	Sousa <i>et al.</i> , 2009; Datta <i>et al.</i> , 2010 ^[12] ; Li <i>et al.</i> , 2010; Hassan <i>et al.</i> , 2018 ^[24]
Extrusions	decreasing the fibers size and de-fibrillation	Work at high solid loadings, lower release of inhibitory compound, takes short time	More energy required; effects are limited	Hassan <i>et al.</i> , 2018 ^[24]
Steam explosion	Softening of lignin and reduction in particle size	Cost-effective for hardwoods	Hemicelluloses portion is partly degraded; inhibitory product can be produced due to release of acetic acids.	Clark and Mackie, 1987 ^[11] ; Kaar <i>et al.</i> , 1998 ^[34] ; Ruiz <i>et al.</i> , 2006 ^[56] ; Pielhop <i>et al.</i> , 2016 ^[52]
Ammonia fiber expansion	Lignin and hemicellulose removal	Cellulose crystallinity may be reduced, lignin is delocalized from the structure, high digestibility for herbaceous residues	Requirement of ammonia recycle system, lower digestibility in hardwoods	Holtzapfel <i>et al.</i> , 1991 ^[28] ; Jin <i>et al.</i> , 2010 ^[30] ; Krishnan <i>et al.</i> , 2010 ^[5] ; Lau <i>et al.</i> , 2010 ^[41] .
Acid	Hemicellulose and lignin fractionation	Residence times are short, lignin and hemicellulose are removed.	Reaction vessel corrosion, formation of inhibitory sugar, degradation of products	Foust <i>et al.</i> , 2009 ^[19] ; Shuai <i>et al.</i> , 2010 ^[59] ; Menon <i>et al.</i> , 2012 ^[47] ; Jonsson and Martin, 2016
Alkaline	Lignin and hemicellulose removal	Cellulose crystallinity is reduced, lignin is removed, decreased in the polymerization degree of carbohydrates,	Digestibility enhancement is low in softwoods, releasing of inhibitor	Hassan <i>et al.</i> 2018 ^[24]
Organo-solution	Removal of lignin and fractionation of hemicelluloses	Organic solvent can be recovered by distillation process, removal of lignin	Unremoved solvent may inhibit process, solvent recovery requires high energy, require efficient management because of danger of fire and explosive hazardous.	Zhu <i>et al.</i> , 2009 ^[76] ; Zhao <i>et al.</i> , 2009 ^[74] ; Nitsos and Rova 2017 ^[50]
Oxidation	Lignin and hemicelluloses removal	fewer release of by product	Cellulose is partially degraded, Expensive	Chandel and da Silva 2013 ^[6] ; Hassan <i>et al.</i> , 2018 ^[24]
Liquid hot water	Extraction of Lignin and Hemicelluloses	The remaining lignin can show the negative effect on the succeeding enzymatic reactions	Required more energy and water	Zhuang <i>et al.</i> , 2016 ^[70] ; Hassan <i>et al.</i> , 2018 ^[24]
Ammonia fiber explosion	removal of lignin	High potential and specificity for reaction	less useful for the softwoods, ammonia cost and environmental issues	Bajpai 2016 ^[3] ; Hassan <i>et al.</i> , 2018 ^[24]
Ionic liquid	Reduction in Cellulose complexity and partially hemicelluloses and lignin degradation	Require lower temperature and pressure, functional under the mild reaction condition	Cost	Yoo <i>et al.</i> , 2017

Commercialization of combine pretreatment of lignocellulosic materials using ionic liquid and aqueous ammonia

Pretreatment of lignocellulosic biomasses using ionic liquid (1-n-ethyl-3-methyl imidazolium acetate, EmimOAc) and aqueous ammonia as cellulose and hemicelluloses solvents confers a number of attractive features in comparison to conventional methods. In combine method of pretreatment, aqueous ammonia can efficiently remove lignin by breaking the carbohydrate-lignin linkage and ionic liquid can efficiently solubilize lignocellulosic biomasses by decreasing the residual crystallinity of cellulose thus increase accessibility and efficiency of cellulase enzyme on cellulose, consequently enhanced biodigestibility of biomasses subsequently production of fermentable sugars like glucose and xylose. Generally, imidazolium based ionic liquids have been found to be less toxic, low viscosity and lower melting temperature, leading to safe and easy handling. At room temperature ionic liquid (EmimOAc) are organic salt, liquid and stable up to 300 °C (Lee *et al.*, 2009)^[42]. This procedure does not require high temperature (below 100 °C), high pressure and hazardous condition or substances. Additionally, ionic liquid can be recycled and reused after treatment for

several times, reutilization of ionic liquid is economically significant.

Conclusion

Lignocellulosic biomass is the most abundant material on the planet that can be used for production of alternative energy however crystallinity of cellulose and available surface is defended by lignin and cellulose covering by hemicelluloses, these all contribute to lignocellulosic materials resistance to enzymatic hydrolysis. Therefore, pretreatment of lignocellulosic biomass is necessary for enhanced digestibility of biomasses before enzymatic hydrolysis. There are several pretreatment approaches which are mentioned above, combine pretreatment with ionic liquid and ammonia are the best way to find reactive cellulose intermediates for production of fermentable glucose and xylose monomers.

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