

Review

The Role of Ionic Liquids in the Lignin Separation from Lignocellulosic Biomass

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Abstract: Lignin is a natural polymer, one that has an abundant and renewable resource in biomass. Due to a tendency towards the use of biochemicals, the efficient utilization of lignin has gained wide attention. The delignification of lignocellulosic biomass makes its fractions (cellulose, hemicellulose, and lignin) susceptible to easier transformation to many different commodities like energy, chemicals, and materials that could be produced using the biorefinery concept. This review gives an overview of the field of lignin separation from lignocellulosic biomass and changes that occur in the biomass during this process, as well as taking a detailed look at the influence of parameters that lead the process of dissolution. According to recent studies, a number of ionic liquids (ILs) have shown a level of potential for industrial scale production in terms of the pretreatment of biomass. ILs are perspective green solvents for pretreatment of lignocellulosic biomass. These properties in ILs enable one to disrupt the complex structure of lignocellulose. In addition, the physicochemical properties of aprotic and protic ionic liquids (PILs) are summarized, with those properties making them suitable solvents for lignocellulose pretreatment which, especially, target lignin. The aim of the paper is to focus on the separation of lignin from lignocellulosic biomass, by keeping all components susceptible for biorefinery processes. The discussion includes interaction mechanisms between lignocellulosic biomass subcomponents and ILs to increase the lignin yield. According to our research, certain PILs have potential for the cost reduction of LC biomass pretreatment on the feasible separation of lignin.

Keywords: lignin; lignocellulose; biochemicals; delignification; ionic liquids

1. Introduction

Lignocellulosic (LC) biomass is the most abundant plant material for the production and sustainable supply of liquid biofuels at a relatively low cost [1]. It mainly consists of sugar polymers (cellulose and hemicellulose) and lignin [2]. These three biopolymers, depicted in Figure 1, are the main constituents of plant cell walls [3]. The lignin and hemicelluloses forms a cross-linked matrix which covers the cellulose fibers and thereby forms a tight and, compact structure [4]. Lignin is one of the three primary components of LC biomass which, protects cellulose and hemicellulose by providing mechanical strength but also hydrophobic and indigestible properties to plant cell walls [5,6].

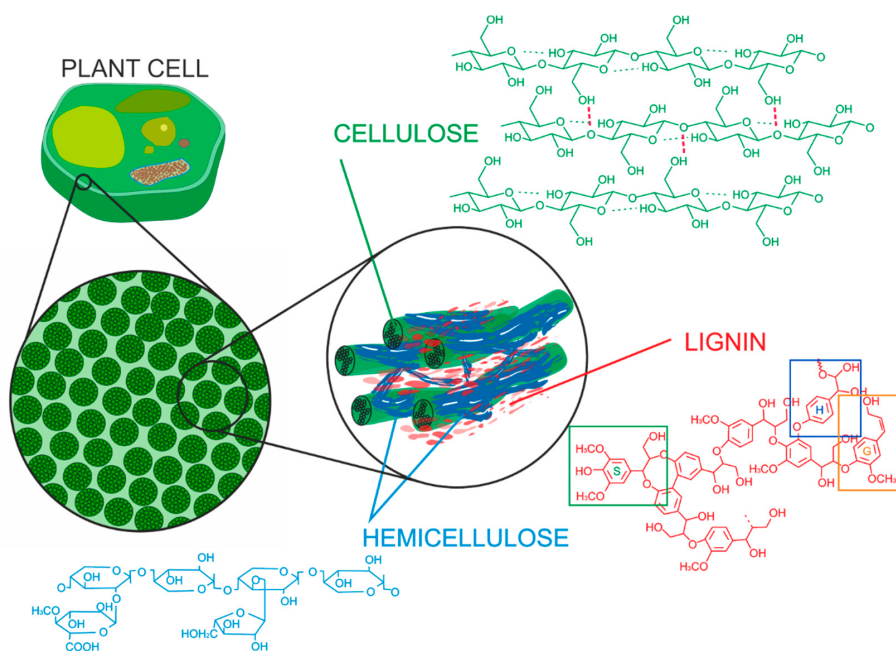


Figure 1. Structure of lignocellulosic biomass (Modified from [7,8]).

However, the large volumes of lignin resources never been cost efficiently used [6]. It is clear that the chemical pulp industries globally produce about 50 million tons of lignin every year [9]. Despite that, the commercially utilized lignin is only about 2% of total, while the rest is used for combustion in order to produce heat and energy [10]. The use of cheap and renewable bioresources, like lignin, has been attractive since the increasing depletion of fossil fuel resources is concerning level [10]. Besides of economic value, the use of renewable bioresources has potential to decrease the negative effects of the production and use of fuels and chemicals on environment and health [10]. Lignin is the only natural biopolymer containing aromatic phenolpropanoid monomers. Therefore, it can be utilized to produce value-added end products, for example fuel components, via a process of depolymerization [11].

An efficient low-cost technique is required to remove and recover the lignin from biomass to gain enable easier access to the biomass polysaccharides in order to produce different products from lignin [12]. Due to the complexed structure of cell wall microfibrils in LC biomass, the immaculate separation of celluloses and lignin resulting minimal degradation of polymers is a great challenge [11]. Among the various reported biomass pretreatment technologies, pretreatment with ionic liquids (ILs) has shown the most feasible results, especially in a sense of lignin separation. [11]. The properties such as no measurable vapor pressure, wide electrochemical window, high thermal stability, nonflammability, excellent solvent power for both organic and inorganic substances, etc.—makes ILs unique and versatile among its kind [13]. More importantly, the ILs properties where they relate to hydrophobicity, polarity, and solvent power can be modified by combining or modifying the cations and anions [14].

The aim of this paper is to review the current condition of the processes within the field of the LC deconstruction with ILs, and the separation of lignin from the biomass for further efficient lignin valorization. The field of LC biomass deconstruction targeting the separation of lignin for further valorization are reviewed and an update on recent advances is provided.

2. The Chemical Composition of Lignocellulosic (LC) Biomass

LC biomass is gaining immense amounts of attention, owing to its enormous biotechnological potential as an inexpensive, renewable and natural source, so that to produce valuable compounds [15]. LC biomass can be grouped into various categories such as grasses, food industry residues, wood residues, agricultural residues, municipal solid wastes, and domestic wastes (lignocelluloses

residuals and sewage) [16]. Agricultural residues which called field residues as well have a wide variety of potential sources including grain crops and processing residues such as husks, chaff, cobs or bagasse straw, stover, peelings, stalks, nutshells, seeds.

The compositions of some LC biomass types are presented in Table 1. It is made roughly, of 40% cellulose, 25% hemicellulose, 25% lignin, and about 10% other elements and some minor components [17]. These polymers are playing the main role in the building of the plant cell walls which provide mechanical support and protection from different stresses [18], but also do regulate the growth of plants [19]. The structure and composition of LC enables biomass to resist degradation and to tender hydrolytic and structural stability to the cell walls of the plants. This kind of recalcitrance is attributable to the lignin structure, different subunits and crosslinking among the polysaccharides and the lignin through ester and ether linkages [20,21]. In addition, lignin provides a physical barrier to polysaccharides and inhibits enzymes by non-productive binding with enzymes to limit enzymatic hydrolysis [22].

Table 1. The major chemical composition of various LC biomasses.

Compound	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Reference
Hardwood	40–55	24–40	18–25	[23]
Softwood	45–50	25–35	25–35	[23]
Sugarcane Straw	33–40	21–32	19–32	[23]
Sugarcane Bagasse	36–45	25–35	19–32	[24]
Wheat Straw	33–40	20–25	15–20	[25]
Rice Straw	28–36	23–28	12–14	[26]
Waste Paper	60–65	4–13	1–2	[27]

Cellulose is a polydisperse linear homopolymer. It consists of regio- and enantioselectively beta-1,4-glycosidic linked D-glucopyranose units (otherwise known as an hydroglucose units [AGU]) [28]. Cellulose has been recognized as being highly useful polymer, since it can be depolymerized into mono-saccharide or glucose, which can be used to produce alcohols or other chemicals using different chemical or biochemical methods [29].

Hemicellulose is a polymer consisting in short linear and branched saccharide polymers. These polymers are composed of various hexoses (D-galactose, D-glucose, D-mannose), pentoses (D-arabinose, D-xylose), and sugar acids [30]. In hardwood (such as dicot angiosperms), hemicelluloses are mainly composed of xylans, whereas in softwood (such as gymnosperms) the major constituents are glucomannans [31]. In comparison with cellulose, hemicellulose can be easily hydrolyzed into smaller units due to its amorphous and branched structure.

Lignin is considered to be another main component of the plant cell wall. Lignin is an aromatic polymer that plays important role between cellulose and hemicellulose through strong hydrogen bonding and ester linkages [32]. It contributes significantly to biomass resistance against degradation [33]. Lignin provides strength to the LC biomass and hinders the action of hydrolytic enzymes by providing a physical barrier and inhibiting the enzyme action by having non-productive enzyme binding [33]. It is considered as being the most recalcitrant constituent of LC material owing to its structural complexity and formation of lignin-carbohydrate complexes. Therefore, it has generally been regarded as a by-product during the utilization of biomass. Lignin has the potential substrate for the production of valuable chemicals to use in different applications. However, deeper understanding of lignin as a substrate, its fractionation and subsequent valorization is still an inevitable challenge when it comes to establishing efficient and cost-competitive biorefineries [34].

3. Lignin

As a biopolymer, lignin is unusual due to its heterogeneous structure and the lack of a defined primary structure. This polymer is naturally cross-linked with aromatic subunits and has more than

10,000 Daltons (Da) molecular weight [35]. Therefore, lignin has a complex cross-linked structure and within the molecule, it contains various functional groups, such as aliphatic hydroxyl, phenolic hydroxyl, and methoxyl groups. Reactivity and chemical properties of lignin is affected by this structure. The hydroxyl groups and aromatic structures are especially important since they are precursors on determination of the characteristics and properties of the polymers [36].

Synthesis of lignin occurs in plant cells as a connecting moiety of hetero-polymers, such as phenylpropanoid units (sinapyl (S), coniferyl (G), and *p*-coumaryl (H), alcohols), and it can contain methoxyl groups at 3 and 5 aromatic carbons (Figure 2) [37]. The polysaccharide in the plant cell walls are highly hydrophilic and therefore they are permeable to water, contrary that the lignin which is more hydrophobic [38].

The lignin is classified to G-type (softwood lignin–gymnosperm), GS-type (hardwood lignin–angiosperm), HGS-type (grass lignin), or HG-type (compression wood lignin) based on the content of the three units—coniferyl alcohol units, sinapyl alcohol units, and *p*-coumaryl alcohol units. [39]. The softwood lignin mainly contains of coniferyl alcohol units (95%), whilst hardwood may have between 25–50% of coniferyl alcohol units and 46–75% of synapyl alcohol units. In the case of grasses, lignin is constituted between 5–33%, 33–80%, and 20–54% of *p*-coumaryl, coniferyl, and sinapyl alcohols, respectively (Figure 2) [40]. The lignin in hardwoods and softwoods can be differentiated based on the number of methoxy groups on the aryl rings of the polymer. The softwoods were formed through the polymerization of coniferyl alcohol, which itself was formed from guaiacol and, therefore, contains only one methoxy group per aromatic ring. Therefore, softwood biomasses have a more homogenous lignin composition. On the contrary, hardwood lignin is formed through polymerization of coniferyl and sinapyl alcohols, containing either one or two methoxy groups per aromatic ring.

The functionalization of lignin has demonstrated in various classes of organic solvents the acetylation of aliphatic and phenolic alcohols and the transformation into more hydrocarbons and increased levels of availability for their solubilization [40]. Which means, the common lignin interunit linkages include β -aryl ether (β -O-4'), phenylcoumaran (β -5'), resinol (β - β'), dibenzodioxocin, 4-O-5', β -1, and α -O-4'. The connection among the structural units of lignin is primarily formed of ether bonds, which account for nearly 60–75% of total bonding, and the β -O-4 type ether bond a usual form of bond, accounting for between 45–62% of all connection modes. Following main lignin unit is carbon–carbon bonds, which account nearly 20–35% of total, and which usually include β - β' , β -5', and 5-5' types [41].

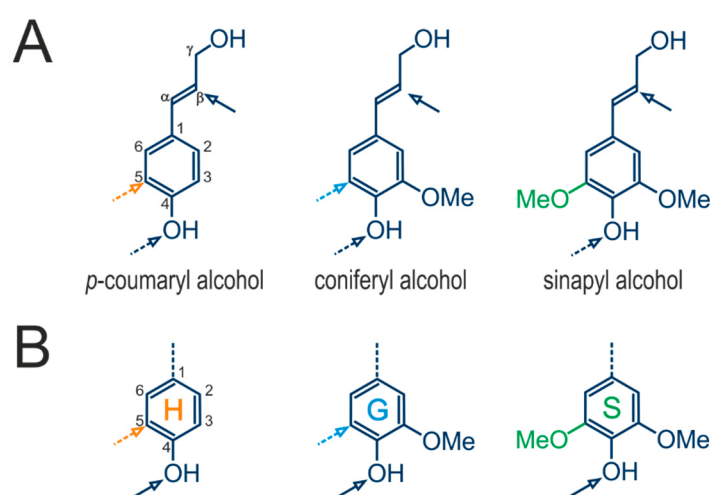


Figure 2. Main lignin building moieties. (A) Monolignols *p*-coumaryl, coniferyl, and sinapyl alcohols and (B) corresponding *p*-hydroxyphenyl, guaiacyl, and syringyl units in lignins. Unit-specific structures are identified with color. The arrows indicate sites for radical coupling during lignification. Dashed arrows indicate less prevalent coupling sites between monolignols (modified from [42,43]).

4. LC Pretreatment for Lignin Isolation

Lignin separation from the LC biomass is carried out by applying various pretreatment processes [44,45]. As a result of complicated structure and molecular interactions with other components like hemicellulose, dissolution of the natural lignin in wood is very complicated and money consuming procedure. The required methods to separate lignin from the plant cell walls and cellulose, are quite harsh and this partially changes its native conformation [46].

Technical lignins are lignins which are separated from various biomasses during one of a number of available technical processes [47]. Among these are kraft lignin, soda lignin, organosolv lignin, ionic liquid lignin, and hydrolysis lignin. On the other hand, native lignin is lignin in its original form present in LC biomasses, which are, wood lignin (MWL), cellulolytic enzymatic lignin (CEL), and enzymatic mild acidolysis lignin (EMAL).

MWL is mostly used as standard lignin because of its closeness to the native lignin structure. Chang et al. reported the CEL treatment procedure, to further reduction for the isolation-induced modifications [48]. Contrary to MWL, the CEL was obtained in higher yields, in the same milling duration, therefore, it was less degraded. Due to that, CEL is considered more similar to the total lignin fraction in wood. Enzymatic mild acidolysis lignin (EMAL) extraction was studied by Guerra et al. which is more complex procedure that combines milling, enzymatic treatment, and an additional acidolysis step [49]. The aim of the study was the further maximize the yield of the isolated lignin. Moreover, to the researches focused on simplifying the methods for lignin isolation in order to make them more environmentally clean, as well as to obtain lignin closer to its native structure [50].

Usually, Kraft lignin, alkaline, or organosolv lignin are used to test the dissolution rate of lignin. The choices are made considering their commercial availability, that they are products of the chemical pulping process [51]. Kraft lignin refers to the use of the alkaline degradation of LC, while sulfonated lignin arises from the use of a sulfite pulping process. In addition, the pulp and paper industries, extract Kraft lignin from black liquor.

Hydrolysis lignin (HL) is a by-product of enzymatic hydrolysis and fermentation processes in cellulosic ethanol plants. It is primarily consist of lignin (up to 60%) balanced with unreacted cellulose and mono- and oligosaccharides. Further modifications are required for the utilization of HL which are too expensive at the moment otherwise the HL-derived materials do not function well. As a result of this, the majority of HL is disposed without any valorization [52].

The structure of isolated lignin, cellulose, and hemicellulose depends upon the pretreatment method being used. For the separation of lignin from the LC biomass the used methods should focus on; increasing of the accessibility surface area, and cellulose decrystallization, partial depolymerization of cellulose and hemicellulose, maximizing the enzymatic digestibility of the pretreated material, minimizing the sugar-losses, and minimizing capital plus operating costs [53].

The used lignin extraction methods affect the dissolution behavior of lignin. For example, lignosulphonate, Kraft, and soda lignin are soluble in aqueous solvent, while alkali and organosolv lignins are soluble in a wide range of organic solvents [54].

For obtaining the separation of lignin from LC biomasses, there are four broad categories of pretreatment processes, which are; physical pretreatment, chemical pretreatment, physiochemical pretreatment, and native lignin separation (Figure 3).

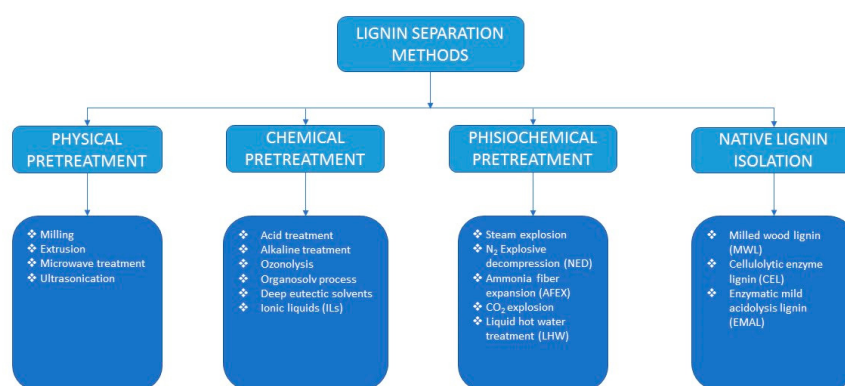


Figure 3. Classification of different lignin separation methods.

4.1. Physical Pretreatment Methods

In the physical pretreatment process, LC biomass particle size is reduced mainly by use of mechanical comminution. The other widely used physical pretreatment methods are milling, extrusion, and microwave treatment, as well as ultrasonication [55].

During the physical pretreatment the increase in surface area of biomass was noticed, which enables one to gain higher efficiencies in further process steps due to better access to the biomass components [56]. Physical pretreatments are often used as a preliminary treatment before the main pretreatment where the goal is the lignin isolation in high yield. There are several advantages of using these methods, which include: environmentally friendly attitude, and less chance of production of any toxic materials in the process [57]. On the other hand, these pretreatment methods are regarded by their high energy consumption, the high costs associated with extensive application, and the ecology and safety hazards [58].

Milling is the most extensively used comminution method. There are various milling methods available, including two-roll milling, rod milling, ball milling, hammer milling, vibro-energy milling, and colloid milling. The selected milling method, the type of biomass being used, and the processing time define the particle size and the crystallinity of biomass [59]. Milling does not result in the production of any toxic or inhibitory compounds and, because of this, it is a suitable first treatment method for a broad range of LC biomass types.

The extrusion process occurs with the help of single or twin screw extruders that spin into a tight barrel, which itself is equipped with forms of temperature control [55]. Extrusion method is easily controllable which is adaptive to modifications and during process the degradation of products does not occur. These points are considered the main advantages of the extrusion process.

Microwave irradiation has commonly been used to pretreat the plant biomass. During the process, dielectric polarization causes the disruption of the LC structure. As a result of this, molecular collisions and thermal energy generations occur [60]. This method has several advantages including the following: easy operability, good energy efficiency levels, high heating capacity, and minimum inhibitor formations [61].

The cavitation principle is the basis of ultrasonication pretreatment which occurs with the engagement of ultrasonic radiation with LC biomass [55]. The cavitation causes shear forces that break down the LC structure and this procedure extracts the desired compounds, including cellulose, hemicellulose, and/or lignin [62]. However, collision and aggregation could be caused between the particles as a result of prolonged use of ultrasonication. [63]. The hydrolysis time of biomass can be decreased up to 80% by the use of ultrasound, which in return adds benefit to bio-fuel production [41]. However, the process requires high energy consumption which means, detailed investigations are important for the optimization of the process parameters for industrial-scale implementations.

4.2. Chemical Pretreatment Methods

Chemical pretreatment methods involve the treatment of the biomass with alkali, Ozonolysis, ionic liquids (ILs), deep eutectic solvents (DES), natural deep eutectic solvents, and organosolv chemicals.

Lignin contents are greatly affected with alkaline treatment. By adding an alkaline solution, the lignin binding with hemicellulose can be disrupted, and the digestibility of hemicellulose can be enhanced as well as increasing the enzyme access to cellulose [64]. Various alkaline pretreatment methods are available which are based on various reagents such as sodium hydroxide, ammonia, and calcium hydroxide [65]. In general, the alkali pretreatment is considered as an effective technique for lignin removal, but it also exposes the carbohydrates for the use in downstream processes.

Ozonolysis is a promising LC biomass oxidative pretreatment method when it comes to lignin degradation with minimal effects on the hemicellulose and cellulose polysaccharides. Different solvents are used to depolymerize lignin in order to produce compounds that are suitable for blending with petrochemical fuels. There are no toxic residues left behind, as any residual ozone in the system will quickly decompose back to O₂ due to its short half-life.

In the Organosolv process, the LC biomass is pretreated with organic solvents, including methanol, acetone, ethanol, and ethylene glycol. The process causes a break in the internal bonds between the lignin and hemicellulose. Organosolv pretreatment is commonly implemented in the presence of a salt catalyst, acid, or a base [66].

Deep Eutectic Solvents (DES) are certain type of a new generation ILs consisting in two or three components, usually connected with hydrogen bonds to form a eutectic mixture which has a lower melting point than each individual component. DESs are mostly produced by mixing a quaternary ammonium salt with a metal salt or hydrogen bond donor (HBD) which forms a complex substance with the halide ion of the quaternary ammonium salt [67].

Ionic liquids (ILs) are effective both at decrystallizing cellulose but also in separating lignin and polysaccharide components into different fractions. Furthermore, depending on the process conditions, the lignin output functionality could be altered to form high-value products with its controlled functionality. Many challenges are still viable in the use of ILs as pretreatment method. These challenges include, the high cost of ILs and the recovery and recycling of the ILs following pretreatment. Moreover, the lack of process technologies that permits the efficient use of ILs also needs to be solved. Due to this, the utilization of IL technology within a biorefinery difficult.

Using a chemical pretreatment after the mechanical pretreatment can results in a higher yield of lignin. The extraction and purification of lignin tends to affect its dissolution behavior. For example, pretreatment with ILs following the milling process reveals high dissolution yields [68].

4.2.1. Kraft Lignin Process

The Kraft pulping process is the largest feedstock source for lignin. This is the most used method for removing lignin in the cellulose extraction and purification process [69]. The Kraft pulping process occurs by means of the transformation of wood chips into pulp, from which a very broad spectrum of finished or semi-finished paper products can be manufactured [70].

The process is based on a chemical delignification step in which a mixture of sodium sulfide (Na₂S) and sodium hydroxide (NaOH) is used to dissolve lignin from the LC materials at high temperatures [71,72]. Within the pulping process, the cellulose is separated using filtration, which leaves lignin and hemicellulose in the liquid phase which is referred to as Black Liquor. Within the Kraft process sulfur and sodium are both completely recycled using the recovery process. The theoretical byproducts are only water and carbon dioxide gas. The kraft black liquor however contains totally reduced sulfur (TRS) compounds which include hydrogen sulfide, dimethyl sulfide, methyl mercaptan, and dimethyl disulfides. This mixture produces an unpleasant odor and has some level of hydrophobic attitude. The isolated lignin should be free from any malodorous hazards for utilization in non-fuel applications [73].

4.2.2. Physicochemical Pretreatment

Physiochemical pretreatment is a combination of physical and chemical methods, where LC biomass is simultaneously chemically modified and the cell wall structure is physically altered [74]. Well known physicochemical pretreatment methods are steam explosion, CO₂ explosion pretreatment, ammonia fiber expansion (AFEX), and liquid hot water (LHW) pretreatment. The methods are usually applied to remove some components of biomass and break the biomass structure before further process steps [75].

Steam explosion is the most used physiochemical pretreatment method. It is applied to many types of materials [76]. This procedure can be used to pretreat milled LC biomass without employing any chemicals. As a result of steam explosion hemicellulose is partially degraded and formation of toxic components are inevitable, which are considered the main drawbacks of this method [77]. However, by the implementation of detoxification procedures, it is possible to obtain the reduction of the inhibitory effects to improve the downstream processes. The adequate improvement of this aim can be achieved by the use of catalysts such as H₂SO₄, H₃PO₄, SO₂, or CO₂.

In the AFEX process, concentrated ammonia (0.3–2 kg ammonia/kg of dry weight) is used as a catalyst. This process leads to partial solubilization of hemicelluloses and increased accessibility of the cell wall polysaccharides including lignin. However, AFEX pretreatment shows better results when using agricultural wastes and herbaceous plants like switch grass, rice straw, corn stover etc. which have a low lignin-content. The big disadvantage of AFEX pretreatment is the utilization of ammonia, which results in severe corrosions and comes with negative environmental effects [78].

During the CO₂ explosion process, supercritical CO₂ will diffuse through biomass-gas interspaces acting like gas and however while dissolving biomass acting like liquid. On dissolution of CO₂ the carbonic acid is formed which increases dissolution of hemicellulose, and therefore better access to lignin and cellulose is gained. In addition, small carbon dioxide molecules are able to more easily penetrate into small pores of LC biomass [55].

Liquid Hot Water (LHW) pretreatment is a hydrothermal pretreatment method like steam explosion. As a result of LHW pretreatment, hemicellulose hydrolysis and removal of lignin occurs [75]. In case of LHW, the liquid state of the water is maintained by use of high temperature (between 160–230 °C) and pressure (up to 5 MPa) in place of steam. This method is very effective on different biomass types like sugarcane bagasse, wheat straw, corncobs, and corn stover [66]. LHW pretreatment has several advantages such as it does not require any catalyst or chemicals, while the process forms almost none of any toxic materials. In addition, this method has a low-cost for the solvent when used in large scale applications. However, LHW requires high levels of energy consumption for the downstream process due to large amounts of water used in process [79].

4.3. Lignin Separation with ILs

Several studies have presented that different solvents like ethylene glycol, DMSO [80], ILs [81], *g*-valerolactone [34] and Tween-80/H₂O are able to dissolve up to 70 wt% lignin [82]. Among these solvents, ILs have acquired especial levels of interest due to their particular chemo-physical properties when compared to traditional molecular solvents.

ILs are molten salts which are also named as being room temperature salts because they are in a liquid state at, or close to liquid state, ambient conditions [83]. The IL-s dissolve a wide range of materials including hydrophobic, hydrophilic, and polymeric compounds [84]. The ability of ILs to be an effective form of disruption targeting the non-covalent interactions between these polymers [85].

In essence, the ILs are formed by a combination of organic cations with organic or inorganic anions, and the desired properties of IL were precursor on the choice of ions [86]. Ion pairs are the parts of all ILs, and the possible combinations of cations and anions are endless. Generally, lignin solubility is high for five groups of ILs containing imidazolium, pyridinium, pyrrolidinium, ammonium, and phosphonium cations. The anions of IL usually include BF₄[−], FAP[−], Tf₂N[−], OTF[−], Cl[−], PF₆[−], CH₃COO[−], and N(CN)₂[−]. Large non-coordinating anions, such as [BF₄][−] and [PF₆][−], showed low lignin dissolution ability [68].

ILs attract attentions due to their appealing properties. These properties include a wide electrochemical range, low vapor pressure, high thermal stability, and outstanding ionic conductivity even under anhydrous conditions. The dissolution properties of ILs are unique and can be tuned by choosing suitable cations and/or anions. One of the most desirable advantages of ILs in comparison with traditional molecular solvents is its extremely low vapor pressure [87].

Recent studies report that certain ILs have turned up to be very effective in terms of LC biomass delignification. Due to this, they have been considered as fractionation solvents for LC materials. ILs intensify the access to lignin by dissolving LC biomass, which in response leads to the possible further valorization of lignin. Different strategies can be applied during or after IL-aided fractionation in order to produce fuels, chemicals, and materials. These include the extraction of lignin from lignocelluloses, catalytic delignification to acquire separated lignin components from biomass, and the saccharification of polysaccharides that are attached to lignin fragments [34]. Delignification causes disruption of lignin structure, resulting in biomass swelling, which is not feasible in a sense of native lignin.

Hydrogen bond acceptability in IL anions is necessary for efficient biomass dissolution because it contributes to the formation of the hydrogen bonds with biomass components. Considering that, cations should contain strong acidic protons and short side chains to attain the reduction of the inhibition between the IL and biomass during dissolution [88]. As an exception, Muhammad et al. presented their findings which stated that the [Ch][PrOO] IL has a poor dissolution ability, despite of a high hydrogen basicity [85]. This behavior was explained by the internal interaction between the hydroxyl end group of IL cation and its anion.

The dissolution of lignin has been investigated in several aprotic and protic ILs (PILs) (see Table 2). The ILs with moderate hydrogen-bonding anions represents better ability to dissolve lignin [89].

Table 2. The dissolution of lignin with ionic liquids (ILs) and protic ionic liquids (PILs).

Sample	Solvent	Temp (°C)	Time (h)	Lignin (%)	Cellulose (%)	References
Kraft lignin	Py	90	24	>50	0.10 ± 0.00	[90]
Kraft lignin	Mim	90	24	>50	0.24 ± 0.02	[90]
Kraft lignin	Pyrr	90	24	7.98 ± 0.10	0.63 ± 0.00	[90]
Kraft lignin	HAc	90	24	0.72 ± 0.04	0.07 ± 0.01	[90]
Kraft lignin	[Py] [For]	75	1	70	<1	[91]
Kraft lignin	[Py] [Pro]	75	1	55		[32]
Kraft lignin	[Py] [Ac]	75	1	64		[92]
Kraft lignin	[Mmim] [MeSO ₄]	80	24	50		[92]
Kraft lignin	[Bmim] [CF ₃ SO ₃]	80	24	50		[90]
Kraft lignin	[Py] [Ac]	90	24	>50	0.12 ± 0.03	[90]
Kraft lignin	[Mim] [Ac]	90	24	>50	0.20 ± 0.05	[90]
Kraft lignin	[Pyrr] [Ac]	90	24	>50	0.79 ± 0.04	[93]
Kraft lignin	GVL/[Bmim]Ac	30		20.9		[93]
Kraft lignin	GVL/[Bmim]Ac	60		28.0		[93]
Kraft lignin	GVL/[Amim]Cl	30		13.4		[93]
Kraft lignin	GVL/[Amim]Cl	60		43		[94]
Kraft lignin	[Emim]Ac/water	60		38		[50]
Pinus radiata	[C ₂ mim] Ace	100	2	58		[50]
Pinus radiata	[C ₄ mim] Ace	100	2	63		[50]
Pinus radiata	[C ₄ mim]Ace/DMSO	100	2	51		[95]
Maple	[Emim]Ac	110	1.5	9		[95]
Maple	[Emim]Ac	130	24	6		[95]
Maple	[Mmim] [MeSO ₄]	80	24	43.4a		[95]
Maple	[Bmim] [CF ₃ SO ₃]	80	24	5.8b		[32]
Birch	[Emim] [OAc]	110	16	97c		[96]
Polar wood	[Emim] [OAc]	110	16	85.3c		[97]
Bagasse	[Emim] [ABS]	190	1–1.5	60.0c		[98]
Bamboo	[Emim] [Gly]	120	8	13.7a		[34]
Corn stover	[Emim] [OAc]/NMP	140	1	10.51a		[34]
Cotton stalk	[Amim] [Cl]/DMSO	130	4	74.4c		[34]
Bagasse	[Bmim] [Cl] + NaOH	110	12	12.73b		[34]

Table 2. Cont.

Sample	Solvent	Temp (°C)	Time (h)	Lignin (%)	Cellulose (%)	References
Polar wood	[Emim] [OAc] + NaOH	110	12	8.72b		
Bamboo	[Amim] [Cl] + NaOH	100	5	4.04b		
Corn cob	[Emim] [OAc]/H ₂ O + NaOH	110		9.78b		
Corn cob	[Emim] [OAc]/DMF + NaOH			7.24b		
Corn cob	[Emim] [OAc]/DMSO + NaOH			19.5a		[99]
Corn cob	[Emim] [OAc]/DMAc + NaOH			32a		
Eucalyptus	[Bmim] [Ace] + NaOH	120	3	37.3a		
Eucalyptus	[Bmim] [Ace]/DMAc + NaOH			25.8a		
Eucalyptus	[Bmim] [Ace]/Dioxane + NaOH			29.9a		
Eucalyptus	[Bmim] [Ace]/Ethylacetate + NaOH			70		[34]
Eucalyptus	[Bmim] [Ace]/Toluene + NaOH			74		[34]
Eucalyptus	[Ch] [Lys]			21		[34]
Switchgrass	[Ch] [Lys]	140	1			
Pine	[Ch] [Lys]					

a Based on dry biomass; b based on Klason lignin; c based on the original lignin content in raw biomass.

4.3.1. PILs Targeting

Several research groups have been working with PILs since they are cost effective and easily synthesized [100]. PILs are salts that are formed from acid/base reactions at a mild temperature (<100 °C) [101]. In compare with AILs, PILs contain exchangeable proton. Synthesis of PILs occurs by proton transfer between a Brønsted–Lowry acid (acetic acid or hexanoic acid) to the Brønsted–Lowry base (2-Hydroxyethylamine or Bis (2-hydroxyethyl) amine). The precious nature of PILs is their ability to dissolve lignin while almost not dissolving the cellulose. This property makes possible the selective dissolution of lignin from LC biomass (Table 2). Gschwend et al. reported that PILs which had been synthesized with a suitable combination of aqueous acid and amine base selectively extracts the lignin from LC biomass [90,100].

Increase in alkyl chain lengths taken as a precursor when specific three PILs synthesized by Rashid et al. These PILs are pyridinium formate ([Py] [For]), pyridinium acetate ([Py] [Ac]) and pyridinium propionate ([Py] [Pro]). Pyridine cation easily attaches to different anions, while also has a high mobile proton with a tendency both towards being an electron pair donor and a proton acceptor [102]. The initial performance of these PILs was investigated through their dissolving ability of Kraft lignin [32]. They found, therefore, that three PILs could dissolve large amounts of lignin in a wide temperature range such as between 20 and 140 °C. Their lignin dissolution efficiency levels follow the order [Py] [For] > [Py] [Ac] > [Py] [Pro] and was improved at higher temperatures (Figure 4). By comparison with imidazolium ILs, the pyridinium PILs were obtained by means of proton transference from a carboxylic acid to pyridine. [Py] [For] dissolved 696 g/kg of Kraft lignin after only 1 h of stirring at 75 °C [68]. Based on these outcomes, lignin solubility decreased with the increase in alkyl chain length of the precursors for pyridinium-based compounds, whereas the lignin solubility yield in pyridine was 47% (w/w) [32].

Lignin and carbohydrates solubilization ability of PILs depends on the fact that these compounds act on the complex bonds that are formed by the destruction of the LC complex [101]. The anionic part of the solvent breaks down the intramolecular hydrogen bonding network in LC, thereby making possible the dissolution of the lignin [32]. According to Varanasi et al. the order of efficiency in terms of reducing the lignin molecular weight of specific anions is as follows: sulphates > lactates > acetates > chlorides > phosphates [34].

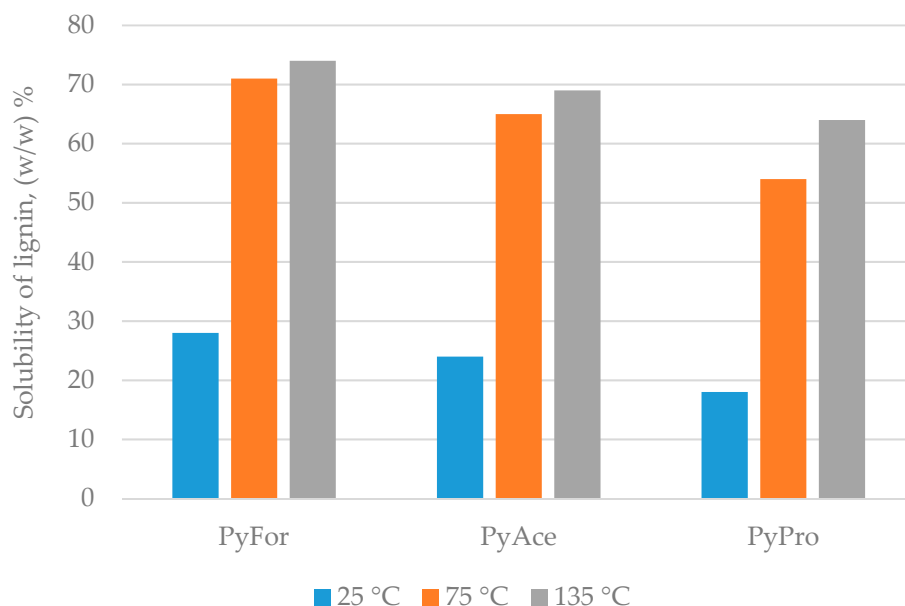


Figure 4. Solubilities of kraft lignin in pyridinium formate [PyFor], pyridinium acetate [PyAce] and pyridinium propionate [PyPro] at different temperatures. (Modified from [32]).

Pyridinium and pyrrolidinium cations are relatively cheaper than conventional ILs. Due to this it is possible to reduce the large volume IL production costs by the use of PILs, as has been used in the BASF BASIL process and in all recent large-scale IL industrial processes [103].

Glas et al. investigated the dissolution rate of Kraft lignin in ammonium, phosphonium, and pyrrolidinium-based ILs [104]. In the case of these ILs the same disadvantages have not been noticed as the imidazolium-based systems. Furthermore, higher thermal stability noticed during the use of phosphonium-based ILs in compare imidazolium-based systems. Phosphonium-based ILs, such as tributylmethylphosphonium methylsulphate ([P₄₄₄₁] [MeSO₄]), tributyl(hexadecyl)phosphonium chloride ([P₄₄₄₁₆] [Cl]), and trihexyl(tetradecyl)phosphonium dicyanamide [P₆₆₆₁₄] [N(CN)₂] can dissolve reasonably high amounts of lignin ranging from 270 to 460 g/kg at 90 °C. Similar to the imidazolium-based ILs, PIL showed highest lignin dissolution rate by the use of [MeSO₄][−] as anion [95].

Achinivu et al. demonstrated the three PILs with different cations ([Py] [Ac], [Mim] [Ac], [Pyr] [Ac]) (Table 2). These showed how ion structure influences lignin extraction. The solubility of lignin is high in the three ILs, while cellulose is almost insoluble in them. As a result of corn stock treatment at 90 °C for a period of 24 h, more than 70% of the lignin extraction obtained with leaving a polysaccharide-rich stream behind. Lignin extraction ratio increased in the order [Py] [Ac] < [Mim] [Ac] < [Pyr] [Ac] [90].

Additionally, with assistance of microwave irradiation at 60, 80, 100, and 120 °C, combined with DMSO and LiCl, the lignin extraction has shown that it increases lignin yield by 2.4%, 8.8%, 13.5%, and 24.6% (% Klason lignin), respectively. Despite that, these lignin fractions demonstrated relatively low content of neutral sugars compared to the results of milled wood lignin (MWL) which had been obtained by means of the classic method [105].

Martínez-Palou et al. demonstrated the effect microwave irradiation had on lignin solubility in eighteen novel PILs [82]. They showed that the protic multi-aromatic ILs could dissolve 42% lignin at 90 °C within 5 min when under microwave irradiation. Furthermore, according to the theoretical calculations, the lignin-ILs mixture has negative Gibbs free energy that causes the formation of spontaneous adducts. The results of the experimental studies show that lignin solubility is maximum at lower temperatures. Additionally, the lignin structure was connected with hydroxyl groups and had strong molecular interaction with the oxygen atoms of the anionic groups of ILs [82].

Sun et al. used polyoxometalate catalysts to cleave lignin-carbohydrate bonds selectively and by these the enhancement of the dissolution of lignin, which caused the decrease in the lignin ratio in the recovered pulp [106].

Recent reports on ILs shows that ILs derived from sustainable sources have shown efficiency on pretreatment and lower levels of toxicity. A renewable IL, Cholinium lysinate ([Ch][Lys]), is reported to be effective in excellent biomass pretreatment and it has been successfully employed in a one-pot IL-based configuration with improved economics. Additionally, ILs which contained cholinium cations and amino acid anions ([Ch][AA]), have shown high levels of efficiency, especially in selectively removing lignin from rice straw. These ILs are prepared from natural and renewable sources and are, therefore, expected to be more biocompatible with enzymes and microbes than the acetate-based ILs, and also less costly compared to imidazolium-based ILs [107].

For quantifying the compositions of different biomass components Tanmoy Dutta et al. studied output streams from the lignin removal processes with cholinium lysinate [Ch][Lys]-pretreated switchgrass, eucalyptus, and pine. This study demonstrated that the removed lignin and the extent of lignin depolymerization for switchgrass and eucalyptus were higher than they were in pine which results in the following order: switchgrass > eucalyptus > pine. The aim of this work was to gain deep understanding of the physiochemical properties of the pretreatment process with [Ch][Lys], which in response offering better lignin valorization strategies [108].

According to Ana Casas et al. the anion plays the main role in the lignin dissolution process and the most promising anions are acetate, formate, and chloride [109].

4.3.2. Post Reaction Lignin Properties

Lignin derived from the process of IL recovery should be able to be used as a valuable chemical source [110]. To determine the value of recovered lignin, some analysis should be done. Elemental and FT-IR analyses are used to characterize the extracts of PIL-lignin, parallel to the evaluation of the molecular weight distribution (MWD). FT-IR analysis is feasible for characterization of the absorption levels in order to demonstrate functional groups in the lignin extracts. The molecular weight (MW) and dispersity of lignin are the main properties that influence the valorization of lignin [100].

Basic phenylpropane units are usually considered identification factor of lignins from various plant sources. These units are: guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl (H) [111]. The source of the lignin and the intensity of the lignin extraction process are the determination signs of the characteristics of the obtained lignin [112]. PILs for lignin dissolution results in a “reduction in polydispersity and the average molecular weight”—which is recently reported according results of researchers [91]. However, according to the observations of Achinivu et al., the lower ionicity PILs ([Py][Ac] and [Mim][Ac]) have both increased dispersities [100]. They conclude that the recovered lignin from PIL-lignin solution keeps its functionality towards the production of thermally stable chemical products.

To yield lower MW lignin with a low dispersity, the ionicity of the PIL should be considered as an important factor. While high MW lignin causes better performance in mechanical properties of material, lower MW lignin is a model feedstock to produce adhesives [113]. Additionally, researchers have found that, due to a higher content of functional groups, such as phenolic hydroxyl groups and methoxyl groups, the lower MW fractions have greater solubility in a sense of polymeric solutions. The low MW fractions were also dispersed more uniformly in polymeric composites, yielding materials with recyclable mechanical properties.

Typically, a simple distillation apparatus is a tool to achieve PIL recycling and following lignin recovery [90]. Minimizing intensive energy consumption optimizes the process for obtaining cost-efficiency, therefore, (2 to 5)% *w/w* of the PIL was unrecovered after the distillation [90]. PILs can also dissolve small amounts of xylan (C5 monomer from hemicellulose) besides lignin, which makes the extraction of small amounts of mono-/oligosaccharides possible. The solution of this problem can be achieved with washing and regenerating of lignin using a suitable solvent which removes any residual PILs, as well as dissolved sugars.

4.4. The Recovery and Reuse of ILs

Costs that are related to the use of ILs are not the only consideration here. It is very important to resolve any environmental concerns with the use and recycling of IL, such as the disposal, biodegradation, and toxicity, but it is also important to decrease the processing costs.

Additionally, for the industrial scale implementation of ILs, some problems should reach the solution, which was highlighted by Badgujar and Bhanage: (i) to achieve complete recovery of the regenerated product, (ii) eliminating impurities (side-products), and (iii) maintaining the stability of the IL for subsequent efficient recycling [114].

Several recovery methods have been studied to achieve a green and cost-efficient IL recovery. These methods include: distillation, extraction, adsorption, membrane separation, aqueous two-phase extraction, crystallization, and force field separation [115]. Distillation under pressure is always preferred for the recovery and recycling of ILs, because of its low vapor pressure. However, non-volatile and thermal-sensitive solutes are separated by other methods including, extraction with organic solvents or supercritical carbon dioxide and membrane separation processes [116].

One non-destructive way for recovering ILs from an aqueous solution is adsorption process. [115]. The aqueous two-phase system, where traditional volatile organic solvents are not used in the process. It is usually applied to the recovery of hydrophilic ILs. Crystallization and force field separation, have also been developed as alternative methods in order to obtain high purity ILs, and to increase cost efficiency.

Crystallization can occur as a result of natural or artificial process. During the process the atoms or molecules are organized into a structure called a crystal. Employment of cooling or compression procedures are usual ways of attainment of crystallization. Different crystallization methods have been investigated in order to purify ILs. These methods include, solution crystallization, melt crystallization, and pressure-induced crystallization [117].

During ILs synthesis the generation of impurities occurs, which should be further separated for efficient use of ILs. Solution crystallization is a suitable method for separation of such impurities from ILs [115,118]. During this method cooling and evaporation procedures used to crystallize the pure compound out of the liquid.

Melt crystallization occurs by cooling down the structure in a controlled way so that a fraction of the melting structure is crystallized [119]. Different melt crystallization techniques have been used to remove diverse impurities from ILs, efficiently. These techniques include zone melting and layer melt crystallization.

During the zone melting, a molten zone traverses a long ingot of impure solid with a specific velocity [120]. Melting procedure occurs by the move of molten regions towards the edge gradually, which leaves behind a solidified purer substance, while the impurities concentrate in the melt and are moved to one end of the ingot. With the help of this method Choudhury et al. was the first to determine the features of the crystal structures of five ILs. A small sample of an IL was cooled down to $-150\text{ }^{\circ}\text{C}$ at $6\text{ }^{\circ}\text{C min}^{-1}$ for turning into a solid followed by being heated at steps of $10\text{ }^{\circ}\text{C}$. Eventually, the single crystals of five ILs grew from their melts [121].

It is possible to achieve layer melt crystallization, by implementing freezing procedure the melted part under controlled conditions of a heat exchange. During the process a solid layer of crystals is generated adjacent to a cooled surface [122]. König et al. also succeeded in applying the layer melt crystallization method for the purification of some ILs [123].

In case of pressure-induced crystallization, crystallization of IL occurs by elevating pressure [117]. Su et al. studied the $[\text{C}_4\text{mim}][\text{PF}_6]$ by crystallizing it under the pressure of up to 2 GPa [117]. According to the research there might be a relation between conformational changes in the butyl chain of IL and the structural changes in the crystalline and liquid states under high pressure. This study indicated the purification and recovery possibility of ILs by using high pressure.

Force Field separation methods can be applied, to recover some specific ILs systems. These methods include Gravity separation, Centrifugation, and Magnetic separation methods. Gravity separation

is referred to as the differences in the specific weight of liquids. The process has several noticeable advantages such as no need for additional chemicals, low manufacturing and operating cost, easy to scale-up, etc. Thus, it is a feasible method in industry in a sense of the separation and recycling of ILs [115].

Birdwell et al. used centrifugal contractor to separate the aqueous dispersions of hydrophobic ILs [124]. However, gravity settling was not successful to properly separate some systems but, all of the studied systems were separated, thanks to the application of the centrifugal contactor technology. Even despite the low interfacial tensions, low viscosities, and large density differences, the rapid separations still could be achieved [115].

Another feasible method of recycling ILs, is magnetic separation procedure. During the procedure high-spin transition metal ions connecting into the structure of conventional ILs, which show a strong response to the magnetic field [125]. Thanks to this feature it is possible to use the magnetic field to recover ILs [126].

The techniques that are being used in the recovery of ILs are determined by the interaction among ILs and water. There some factors affecting this process such as the size of ILs, the hydrophobicity and hydrogen bonding ability both of cations and anions. The properties of anions largely determine the behavior of the IL-water mixture [127,128]. Hydrophobic ILs can easily be separated from water using decantation thanks to its water immiscible structure. However, the hydrophilic ILs show better results for biomass pretreatment than the hydrophobic ionic liquids [129]. Therefore, for the extraction of water and remaining monosaccharide hydrolysates from the IL solution, applying additional separation procedures are necessary. Further separation is needed in order to extract water and any remaining monosaccharide hydrolysates from the IL solution [130]. The salt type and its concentration are determents of the recovery feasibility of ILs. Cation and anion type on the IL also plays crucial role on the recovery procedure [131]. A recovery of over 95.0% for [BMIM] [OAc] in K_3PO_4 -containing systems (pH 12–13) was reported [131]. The recovery of hydrophilic ILs, on the other hand, is more difficult in the case compared with hydrophobic ILs. For example, the distillation process consumes a lot of energy; therefore, it is not a feasible method to recover ILs from their diluted aqueous solutions.

There is a misconceived belief that, because of the non-measurable vapor pressure of ILs, they cannot be distilled [132]. This thought in connection to the non-volatility of ILs has led Øye and co-workers towards first generation ILs. The Franklin acidic $[C_2mim]Cl-AlCl_3$ system (in which $[C_2mim]^+$ is 1-ethyl-3-methylimidazolium) does not have a measurable vapor pressure, even at raised temperatures, whereas the analogous $NaCl-AlCl_3$ system demonstrated a significant vapor pressure of Al_2Cl_6 [132]. Actually, this is not a vapor of ions which is created as a result of dissociation of the IL—the vapor consisted of uncharged molecular components [132,133]. Furthermore, most ILs can be distilled at high temperature and low-pressure. Even though the distillation process consumes massive amounts of energy, in most published studies it is usually preferred as a final step to recover and recycle ILs [84].

The PIL recovered by lignin separation from solution and recycling it back to the reactor following cosolvent distillation, results in the high hydrolysis yield converting cellulose into glucose. The maximum observed PIL recovery was at 98% while using [Py] [Ac] PIL [90]. Additionally, in case of these PILs, both ions play roles in lignin dissolution [100].

Recycling of IL-s cannot be carried out indefinitely. The complex set of steps are required in order to remove lignin and other extractives from LC biomass. These steps are usually includes precipitation by antisolvents like deionized water or alcohols [134]. Furthermore, this procedures would be followed by filtration, the adsorption of impurities by activated carbon, organic solvent washing, evaporation, and purification with neutral-activated alumina.

4.5. Lignin Recovery

As in the case of cellulose, it is possible to recover lignin from the solvents using anti-solvents such as excess water or ethanol. Glas et al. used precipitation with an excess of water from [BMPyr] $[N(CN)_2]$

and the recovered lignin structure was not noticeably changed after the dissolution and regeneration process [68,135]. Lateef et al. used ethanol to recover lignin from solutions with [CNmim] [Br], [Pmim] [Br] and [Bmim] [Cl] with yields between 83% and 97% [68]. On the other hand, Rashid et al. used distilled water for recovering the lignin which had been solubilized in [Py] [For], and the recovered lignin had a satisfactory level of similarity with the pure Kraft lignin. Furthermore, a lower polydispersity, higher thermal stability, as well as average molecular weight, have been noticed among the characteristics of recovered lignin. Additionally, the process did not affect the glass transition temperature [32].

Rashid et al. showed that with the addition of water, it is possible to recovery the lignin dissolved in formic acid [32]. According to the authors, it can be concluded that the thermal treatment of lignin with formic acid results in decrease on the absorbance of O-H bands. Conversely, in a case of the increase in phenolic O-H groups of the thermally treated lignin with formic acid boosts its reactivity toward other reactions [68].

ANDRITZ designed a portable pilot plant unit for lignin recovery based on a flexible system. This plant contains one stage without washing, two stages with acid washing, or two stages with acid washing and drying. The aim of ANDRITZ Lignin Recovery process is to remove lignin from black liquor at between 35% and 45% dry solids with a pH of 12–13. Following filtration and washing, the dry solids ratio of lignin is typically between 60% and 62% before the drying stage, and 95% after it [136].

5. Lignin Valorization

Lignin is considered the second most prevalent biopolymer on the planet [68]. Therefore, lignin valorization is crucial in a bio-based economy. Lignin is usually obtained as a by-product in the paper pulping process, as well as in the production of cellulosic ethanol. Lignin has ability to transform directly into aromatic compounds and fine chemicals, thanks to its unique functionality. These compounds can be utilized as a basic building block in the chemical industry. Lignin is a natural and renewable source of aromatic biochemicals, which include materials for automotive brakes, wooden panel products, bio dispersants, polyurethane foams, and epoxy resins for printed circuit boards. Additionally, it has shown a degree of potential in terms of various medical applications, as bio-based support for drugs and food supplements, or as a curing agent for certain diseases [137]. Lignin can be employed as a binding and dispersing agent in various areas of industry [138]. It can also be used in composite materials to improve the properties of other polymers.

At the moment, the lignin valorization is still in its development stage, and there are still some challenges to overcome in order to attain large-scale operations. The valorization of lignin increases annually by a rate of less than 2%, of which amount lignosulphonate is mainly used as a supplement in construction materials, which requires technological advancement to use lignin in wide range of industries. A requirement of critical review on the recent improvements of lignin valorization has increased.

Upstream processing (the bioengineering of the lignin structure) and downstream improving are possible procedures during lignin valorization. The dominant strategies for the valorization of lignin into chemicals and fuels involve the depolymerization of lignin polymers into monomeric aromatic compounds and fragmentation (ring scission). This is done using reduction, supercritical fluids, and ILs in order to obtain the lignin modification, and the fractionation by ultrafiltration and selective precipitation [139,140]. Forms of technology that use lignin in the natural polymeric structure (like chemically modifying the lignin to get synthesized polymeric materials) are appealing since simpler forms of processing can be used [141]. Lignin has also been recent source on the production of innovative products such as oleogels and organic antioxidant/antimicrobial nanoparticles as a result of chemical treatment or modification, as well as biorefinery/environmental catalysts and energy storage materials through pyrolysis.

In case of post ILs treatment, it might be crucial to modify the surface of lignin regarding valorization.

At the moment, two main streams for lignin fractionation and conversion are indicated with biochemical and thermochemical methods. Thermochemical methods such as pyrolysis, gasification, hydrogenolysis, chemical oxidation, and hydrolysis have the advantage of high output thanks to the shorter reaction time of the process. Furthermore, with the latest comprehensive studies, the efficient lignin use through forms of thermochemical technology can produce aromatics (such as 4-n-propanolsyringol, ethyl benzene, and aryl ketones), bio-oil, and carbon materials [141]. However, lignin can be used as a supporting agent in case it is chemically modified or a filler for polymer blends and composite materials. Lignin was oxidized under various oxidation conditions for the production of vanillic acid, aliphatic acids, aromatic acids, aromatic aldehydes, quinones, cyclohexanol, dimethyl sulfoxide, and β -keto adipate [142].

The complete solubilization of lignin is important before the reaction, in order to convert or depolymerize the lignin into value-added products. The insoluble form of lignin mostly results in the production of side products such as chars, gases, and many others [143]. One of the greatest challenges for the lignin-conversion technologies is linked to its irregular polymeric structure. The complex three-dimensional amorphous polymer is relatively recalcitrant, which consist of methoxylated phenylpropanoid units [144].

Lignin Valorisation after ILs Treatment

Lignin extraction maintaining a high yield and minimal structural changes is considered crucial to reach its high-valued utilization [145]. In most cases, the separation of lignin from LC biomass creates difficulties in valorization because of its complicating catalytic upgrading. For instance, when alkali and sulphate used to isolate lignin, changes in lignin structure occurs, which is revealed by the decrease in β -O-4 aryl ether linkages and the formation of new stable C-C bonds, creating non-feasible situation for valorization of lignin [146]. Additionally, the production of large amount of wastewater and odor also make this process less attractive. Therefore, finding efficient lignin separation methods create a possibility to isolate lignin without modification and degradation under mild conditions, maintaining its native form.

Low molecular weight lignin recovered from IL solution keeps its native properties and activity, which is the beauty of pretreatment with ILs. Broad studies show that the lignin dissolution in IL is can be linked with the formation of stronger H-bonds between anions in ion pairs and lignin dimer model compounds, guaiacyl glycerol-b-guaiacyl ether (GG), as well as the more π - π stacking interactions between cations and GG [147]. Due to this information, it is possible to design appropriate ILs for separation of lignin from LC biomass.

6. Conclusions and Future Remarks

This review paper gives an introduction and overview of the characteristics and properties of the lignin and its dissolution and extraction methods. The aim of research on LC biomass delignification is to develop forms of technology that will be necessary for converting LC feedstocks into cost-efficient commodities.

The exploitation of ILs in LC biomass treatment shows the tremendous potential in this research filed, especially within the context of the separation of lignin from LC biomass. The successful dissolution of lignin in ILs has broadened the sight when it comes to utilizing biomass for the production of biofuels, chemicals, and materials in a sense of technical and economic growth. The dependence of the ILs physical properties and their ability to solubilize LC biomass is considered important in the production of biochemicals. Due to its easily synthesizing process, various ILs can be used to design solvents with desired physicochemical properties that focus on the specific subcomponents of LC biomass.

To take into account the possible use in biorefinery scale is necessary for the practical considerations of pretreatment with ILs techniques. The results of experiments that have been carried out in relation to regeneration and the potential for recycling when it comes to pyridinium and pyrrolidinium-based PILs showed that the present dissolution processes that are using them could open the door to the diverse production of high-value products from lignin, including, binders, carbon fibers, phenolic compounds lignin-based polymers, and sorbents.

In all likelihood, lignin is a promising resource when it comes to replacing petroleum products in the chemical industry. Numerous studies have also shown there is undeniable potential for the depolymerization of lignin for the production of chemicals. However, these studies have mostly focused on experiments at a laboratory scale. The product characterization from the upgraded scale of lignin depolymerization can improve utilization of the lignin depolymerization process in the production of chemicals. Such an advance could afford what would be considered the foundation of biomass utilization and a green future.

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