Ionic Liquids and Organic Solvents for Recovering Lignin from Lignocellulosic Biomass

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Lignin contributes to the recalcitrance of lignocellulosic biomass and affects enzymatic activity during biorefinery operations. Therefore, it must be removed before further processing. Organic solvents (organosolv) and ionic liquids are two important pretreatments for delignifying lignocellulosic biomass. They have proven beneficial for fractionating and recovering cellulose and hemicellulose, as well as lignin with useful physicochemical properties. Volatility and harsh conditions of the acidic systems that result in toxicity, corrosion, and pollution are the main problems of organosolv. Ionic liquids, generally recognized as green solvents, have also been proposed as a possible solution to the challenge of using lignocellulosic biomass. Ionic liquids can either dissolve the lignocellulosic biomass completely or dissolve it into individual fractions. This review considers the advantages and disadvantages of organosolv and ionic liquids, since both are important methods to fractionate lignocellulosic biomass in their main components which can be converted into value added products.

Keywords: Lignocellulosic biomass; Pretreatment; Lignin; Organosolv; Ionic liquids

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INTRODUCTION

Global problems such as climate change and environmental pollution have been associated with the increasing use of fossil fuels (Kumar *et al.* 2008). As a consequence, interest in the use of energy from renewable sources such as sun, wind, water, and lignocellulosic biomass has also increased (de Wild *et al.* 2012). Rice straw (Binod *et al.* 2010), corn stover (Li *et al.* 2011), sugar cane bagasse (Rabelo *et al.* 2011), and wheat straw (Kaparaju *et al.* 2009) are agricultural residues that have been used to obtain second-generation biofuels. Due to its abundance, annual renewability, and limited use in industry, wheat straw has become one of the preferred raw materials for the production of bioethanol, biohydrogen, and biogas in a biorefinery scheme (Kaparaju *et al.* 2009).

Biorefineries allow for the conversion of the major polymeric components of lignocellulosic biomass into energy and chemicals (Kamm and Kamm 2007). Two important biorefinery objectives are as follows: 1) fractionation and use of the components of lignocellulosic biomass, including cellulose, hemicellulose, and lignin;

and 2) use of technology and processes that were both inexpensive and environmentally friendly (Zhang 2008). However, these objectives are not completely met. Only cellulose and hemicellulose are used in a large number of biorefineries for the production of biofuels and paper, whereas lignin is burned to generate low-cost energy. Lignin can be used to make products such as environmentally friendly adhesives, corrosion inhibitors, phenolic resins (Cook and Hess 1991) coatings, composites, and agrochemical and biological products.

An important step in biorefining to obtain cellulosic alcohol biofuels is pretreatment. The pretreatment of lignocellulosic biomass helps modify the highly ordered cell wall structure (Hendriks and Zeeman 2009; Mosier *et al.* 2005), alters the structure of the lignocellulosic matrix, and improves the digestibility of carbohydrates (Chang and Holtzapple 2000; Yoshida *et al.* 2005). Several authors have classified pretreatment technologies based on their mode of action, that is, biological, physical, chemical, and physicochemical (Uju *et al.* 2012; Yang and Wyman 2004). Although there have been several reviews regarding how pretreatment can improve the use of cellulose from lignocellulosic biomass (Huang *et al.* 2011; Kumar *et al.* 2009a; Saritha *et al.* 2012), there is little information on the types of pretreatments that efficiently produce high-quality lignin.

Pretreatment technologies for lignocellulosic biomass, based on organic solvents and ionic liquids were reviewed. Both pretreatments can be used to fractionate lignocellulosic material into their main components; therefore, they are being extensively studied for biorefinery applications. Furthermore, it has been reported that lignin obtained by these processes has better properties than lignin obtained by conventional processes (Cybulska *et al.* 2012; Mora-Pale *et al.* 2011).

The aim of this review is to analyze the pretreatments to obtain lignin with useful physicochemical properties, an overview of both pretreatment is presented, and the advantages and disadvantages of each one are discussed. Furthermore, the properties of the lignin obtained with each pretreatment process are described.

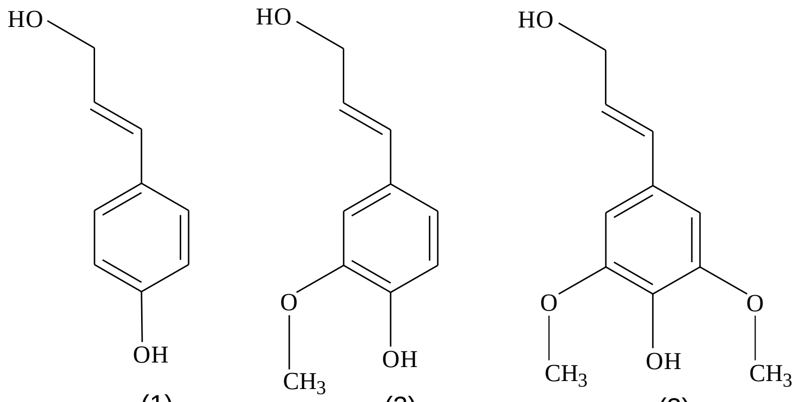
Composition of Lignocellulosic Biomass

Composition of lignocellulosic biomass was thoroughly reviewed by Hendriks and Zeeman (2009). Lignocellulosic biomass contains mainly carbohydrate polymers, cellulose and hemicellulose, and an aromatic polymer, lignin. The percentage of each of these polymers varies from 40 to 50% cellulose, 20 to 35% hemicellulose, and 15 to 20% lignin. Cellulose is the most abundant polymer, with a linear structure that is composed of β-D-glucopyranose units linked by glycosidic β (1-4) bonds. The supramolecular structure consists of cellulose organized into crystalline and amorphous regions. Crystalline regions have well-organized inter-molecular hydrogen bonds, whereas in the amorphous regions, there are fewer and less organized hydrogen bonds (Kondo and Sawatari 1996). The amorphous zone is more reactive because the hydroxyl groups are more accessible (Kondo 1997a,b; Kondo and Sawatari 1996). Hemicelluloses are polysaccharides comprised of diverse hexose and pentose sugars, such as xylose, arabinose, mannose, glucose, and galactose. The structure of hemicellulose is random and amorphous, and it has short side branches of various saccharides that can be easily hydrolyzed (Ademark *et al.* 1998; Mod *et al.* 1981). In woody plants and agricultural crops, the dominant saccharides are xylans (Saha 2000). Hemicellulose forms hydrogen bonds with cellulose and covalent bonds with lignin and these links provide stability to the cell wall (Jarvis 2011). Due to the importance of the lignin, its chemical structure will be described in the next section.

Chemical Structure of Lignin

Lignin is a three-dimensional, irregular, aromatic heteropolymer that is made of phenylpropane units. The lignin molecule is produced by the union of up to three aromatic precursors, *p*-coumaryl, coniferyl, and sinapyl alcohols, which are also known as monolignols (Fig. 1). The respective aromatic constituents of these alcohols within the polymer are p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) moieties (Lewis and Yamamoto 1990). The biosynthetic process of lignin consists of coupling radical monilignol *via* a random polymerization process. This produces a polymer of lignin and a three-dimensional complex structure that is unique for each type of plant (Buranov and Mazza 2008). In herbaceous crops, lignin contains H, G, and S monolignols in different proportions, whereas in woody plants, lignin contains mostly G and S units (Billa et *al.* 1998; Lapierre *et al.* 1995). These different proportions of monolignols influence the physicochemical properties of lignin.

Although there is a wide variety of links that form the lignin polymer, two main types have been identified: ether and carbon-carbon type bonds. Alkyl-aryl ether bonds, such as β-O-4', are the most abundant. To a lesser extent, there are also aryl-aryl ether type bonds, such as the 4-O-5' bond. The carbon-carbon type links, also known as condensate bonds, are more difficult to break than the ether type bonds (Karhunen *et al.* 1995). Lignin is not available in plant tissues as an independent polymer. Instead, it is covalently bound to cell wall polysaccharides, such as hemicelluloses, and it thus forms complexes with the polysaccharides. Hemicellulose is associated with lignin primarily through glycosidic bonds with arabinose, xylose, and galactose, as well as through benzyl ether or benzyl ester lignin-complexes (Watanabe *et al.* 2003). Hemicellulose presumably provides the interconnections between cellulose and lignin, thus increasing the mechanical strength of the cell walls.



(1) (2) (3)

Fig. 1. Monolignol monomer species. (1) *p*-coumaryl alcohol (4-hydroxyl phenyl, H), (2) coniferyl alcohol (guaiacyl, G), (3) sinapyl alcohol (syringyl, S) (adapted from Doherty *et al.* 2011)

Types of Lignin

There are several types of lignin, and they can be classified in two categories. The first category includes sulfur-containing lignins; these are obtained either by the sulfite pulping process, which uses a metal sulfite and sulfur dioxide, or the kraft process, which uses sodium sulfide under strongly alkaline conditions to break the bonds of the wood and obtain high quality pulp (Lora and Glasser 2002). Kraft lignin, lignosulphonates, and soda lignin are produced in large amounts, and they are commercially available. The second category comprises sulfur-free lignin, which is obtained from lignocellulosic biomass conversion processes such as organosolv, auto-hydrolysis, and ionic liquids (Ruiz *et al.* 2011). A difference with the first category is that they are produced in small amounts but may evolve into industrial-scale products (Gosselink *et al.* 2004). Both sulfonated and sulfur-free lignins are known as technical lignins.

The worldwide production of kraft lignin and lignosulfonates is above of 100,000 tons/year and 1 million tons/year, respectively (Gargulak and Lebo 2000; Gosselink *et al.* 2004). Kraft lignins are dark and insoluble in water and other solvents. Its low solubility is due to the high concentration of phenolic groups. In addition to the insolubility of kraft lignins, the high sulfur content (1 to 2%) and the characteristic odor restricts their use. Lignosulfonates are highly cross-linked polymers with approximately 5 wt% sulfur content and contain two types of ionizable groups, sulfonates ($pKa \leq 2$) and hydroxy groups (pKa ~10). Lignosulfonates are water-soluble polyelectrolytes in which the charged groups consist of sulfonic, phenol hydroxyl, and carboxylic acid groups. Lignosulfonates are obtained as the byproduct of sulfite cooking, in which delignification of wood is performed by means of the HSO_3^- and SO_3^{2-} ions (Cheng *et al.* 2012). Most of the large amount of kraft lignin and lignosulfonates produced by the paper industry are used as inexpensive fuels in chemical recovery boilers to provide power (Zhang *et al.* 2011). Lignosulfonates are the only lignin-based products that are industrially important, and there is only a small market for this product.

On the other hand, sulfur-free lignins are produced from three sources: 1) conversion processes for biomass that are mainly oriented toward the production of biofuels; 2) pulping using solvents, such as mixtures of acid-alcohol-water and ionic liquids; and 3) particular raw materials, such as agricultural residues (Lora and Glasser 2002). Sulfur-free lignin has different properties than kraft lignins and lignosulfonates (*e.g.* molecular weight, impurities, thermal behavior, and solubility). It has been reported that the properties of lignin depend of the botanical origin as well as the environmental conditions of growth; however, the method used for extraction also has an influence on the lignin properties (Dong *et al.* 2011). For example, lignosulfonates are macromolecules of high molecular weight, whereas organosolv lignin is a molecule of low molecular weight. Additionally, lignosulfonates contain sulfur groups, but sulfur-free lignin is free of ash and carbohydrates. The advantage of low molecular weight molecules of high purity has the possibility of obtaining high-quality lignin (Lora and Glasser 2002). Unfortunately, during most pretreatment processes, lignin ends up as a residue with non-hydrolyzed sugar polymers, minerals, and process chemicals (de Wild *et al.* 2012).

General Applications of Technical Lignins

Technical lignins such as soda-anthraquinone, organosolv, ionic liquid lignin, and ethanol process lignin are obtained in processes related to the treatment of lignocellulosic materials for the production of pulp and biofuels (El Mansouri and Salvadó 2006). Even though large amounts of kraft lignins and lignosulfonates are available from the conversion of wood into wood pulp, problems associated with their sulfur content, smell, and the lack of homogeneity result in the fact that only 2% of kraft lignins and lignosulphonates have been used in low value-added applications. Yet, lignosufonates have been used as surfactants and their properties have been reported by Trufanova *et al.* (2010).

Properties such as high purity, narrow molecular weight, and homogeneity of soda-anthraquinone, organosolv, ionic liquid lignin, and ethanol process lignins make them suitable for applications at the industrial level (Vishtal and Kraslawski 2011). Particularly, soda lignin may have better physicochemical properties than kraft lignin or lignosulfonates; however, compared to organosolv lignin, soda lignin contains moderate-high sugar and ash impurities (Mousavioun and Doherty 2010).

Stewart (2008) reviewed the major industrial uses of lignin, and several specific uses were highlighted, including phenolic resins, adhesives, polyphenols, and other products. Furthermore, Brosse *et al.* (2011) divided their uses into three main categories: the manufacture of corrosion inhibitors, environmentally friendly adhesives for wood, and polymer mixtures. Khitrin *et al.* (2012) reported on the available options for lignin utilization, and the most important were those based on the exploitation of its sorption properties, incorporation into coatings, composites, polymers, introduction into agrochemical and biological products, applications in the building industry, use as a fuel, use as a reducing agent, and as an agent for various synthesis.

Lignin contains both hydrophilic and hydrophobic groups, and this particular feature can be exploited in the biomaterials field. There is increasing interest in the use of lignin in blends with synthetic and natural polymers. Coatings, films, food packaging, and drug delivery systems have been obtained from mixtures of lignin with other polymers. Baumberger *et al.* (1998) reported a mixture of lignin and wheat starch for films that were prepared by extrusion followed by thermoforming. The films that contained 30% lignin showed increased elongation and breaking strength. Doherty *et al.* (2011) reviewed the combinations of lignin-protein, polyolefin-lignin, and lignin-starch; the lignin aromatic structures helped increase the tensile strength, Young's modulus, thermal stability, and elongation at break of protein-based materials. Lignin incorporation stabilized polyolefin oxidation under UV light or elevated temperatures and enhanced the biodegradability of the material (Cazacu *et al.* 2004; Gosselink *et al.* 2004). Çalgeris *et al.* (2012) investigated the effect of lignin on the mechanical and thermal properties of glycerol-plasticized starch/lignin biofilms. The biofilms were used for drug release studies on ciprofloxacin. Both the mechanical and thermal properties of the films improved when the amount of lignin in the formulation was increased.

Lignin/starch blends have applications in coatings, food packaging, and drug delivery systems. Lignin can be used to develop antimicrobial paper products for packaging, medical dressings, and clothing. Johnston and Nilsson (2012) used lignin to prepare nanogold and nanosilver composites of cellulose fibers. The gold and silver nanoparticles were formed directly on the fiber surface, where lignin was used as a capping agent. Additionally, the nanosilver composite fibers, and, to a lesser extent, the nanogold composite fibers, exhibited effective antimicrobial activity against *Staphylococcus aureus*.

Lignin also shows potential applications in agriculture and high purity value applications. It has been used as a constituent of agrochemicals, particularly fertilizers (Khitrin *et al.* 2012). Lignosulfonates have been used to formulate aqueous dispersion systems for coating urea granules and soil nutrients, to make them significantly more resistant to rainwater leaching. The use of lignin for the production of vanillin is another example of a high-purity value application. It is a widely used ingredient in food flavors and pharmaceutical products and is a fragrance in perfumes and odor-masking products

(Buranov and Mazza 2008). In regard to other high-purity lignin applications, it has been reported that purified lignin fragments exhibit antimicrobial effects against several microorganisms, such as *Escherichia coli*, *Saccharomyces cerevisiae*, *Bacillus licheniformis*, *Aspergillus niger*, *Candida albicans*, and *Micrococcus luteus* (Baurhoo *et al.* 2008). The bactericidal properties of lignin fragments may help in the control of intestinal pathogens, thereby ensuring the safety of livestock products for humans. Baurhoo *et al.* (2008) reported several nutritional implications of purified lignins on the productivity and health of farm animals. Purified lignins, such as Alcell and kraft lignins, positively affected animal performance, mainly by improving the weight gain of Holstein calves, broiler chickens, and geese (Baurhoo *et al.* 2008). Additionally, the antioxidant effect of lignin acting as a free radical scavenger has been demonstrated (Dong *et al.* 2011; Dizhbite *et al.* 2004; Ugartondo *et al.* 2008). This activity allows for the use of lignin in cosmetic formulations. Vinardell *et al.* (2008) demonstrated that bagasse, lignosulfonates, and steam explosion lignins are not harmful to the eyes or skin when present in cosmetics formulations.

Lignocellulosic Biofuels Alcohols Production, Pretreatment, and the Role of Lignin

As modern society steadily develops, there is an increased demand for energy resources. This high demand has been related to global problems such as pollution and climate change, and has led to the search for renewable energy alternatives to petroleum. In many countries, replacing gasoline with liquid fuels that are produced by renewable sources is a high-priority goal (Geyer *et al.* 2007). Using ethanol-blended fuel or bio-butanol for automobiles can significantly reduce both petroleum use and greenhouse gas emissions (Sun and Cheng 2002). Ethanol is the most important renewable fuel in terms of volume and market, and it has been introduced on a large scale in Brazil, the US, and several European countries (OECD/FAO 2011). Biobutanol has been considered recently as a more efficient alternative to ethanol.

Unlike fossil fuels, alcohol biofuels are renewable energy sources that are produced by the fermentation of sugars and can be obtained using second-generation technologies (de Wild *et al.* 2012). Lignocellulosic biomass, such as agricultural residues (including wheat straw, sugar cane bagasse, and corn stover), forestry wastes (including sawdust and thinning remains, waste paper, and municipal solid wastes), and energy crops (including salix and switchgrass) has been considered a possible raw material for ethanol production because of renewability, low price, production in large quantities, and potential environmental benefits (Chen 2011; Talebnia *et al.* 2010). Lignocellulosic biomass, such as wheat straw and other fibrous by-products from cereals, is excellent raw materials to obtain biofuels and is available in large amounts around the world. Biofuel alcohol production from lignocellulosic materials involves the following steps: pre-treatment, hydrolysis, fermentation, and separation or purification (Galbe and Zacchi 2007; Hendriks and Zeeman 2009; Mosier *et al.* 2005). Pretreatment is necessary to disrupt the highly ordered structure of the lignocellulosic biomass and to improve the rate of monomeric sugar production (Hendriks and Zeeman 2009; Yoshida *et al*. 2008). The hydrolysis step consists of converting cellulose and hemicellulose to fermentable sugars. This step can be performed by either chemical or enzymatic means. During fermentation, yeast and bacteria are responsible for converting the fermentable sugars into alcohol. The purification step is performed using distillation or a combination of distillation and adsorption to remove any unwanted residual components (Hendriks and Zeeman 2009).

Lignin is a primary obstacle when using lignocellulosic biomass as a raw material to obtain second-generation biofuel alcohols, because it acts as a glue that holds the main components of the biomass tightly bound together and hinders their separation. Additionally, lignin has been reported to be an inhibitor of cellulase, xylanase, and glucosidase (Taherzadeh and Karimi 2008). One of the major problems in the manufacture of biofuel alcohols from lignocellulosic biomass is the selection of the most advantageous pretreatment. Successfully breaking the lignin barrier and crystallinity of cellulose, the formation of degradation products that inhibit either the enzymes or microorganisms involved in fermentation, and the recovery of valuable components, such as lignin, are all dependent on the selection of the correct pretreatment. Usually, pretreatments fall into one of three categories: physical (*e.g.* milling, irradiation or microwave), chemical (*e.g.* alkaline hydrolysis, wet oxidation, ozonolysis, dilute and concentrated acid hydrolyses, organosolv processes, and ionic liquids), and biological (*e.g.* brown-, white-, and soft-rot fungi) pretreatments (Galbe and Zacchi 2007; Kumar *et al*. 2009b; Sun and Cheng 2002; Taherzadeh and Karimi 2008). Physical pretreatments are used to increase the accessible surface area and pore size, and also it decreases the cellulose crystallinity. A partial or complete delignification and a total hydrolysis of hemicelluloses are achieved using chemical pretreatments. Meanwhile, biological pretreatments help in the delignification and reduction of the degree of polymerization of cellulose with the advantages that this pretreatment have low energy requirement and the use of chemicals compounds is not required (Taherzadeh and Karimi 2008). Despite the advantages of biological pretreatments, these have not been widely considered for industrial applications. For this reason recent studies often focus on hybrid pretreatments that incorporate advantages from each approach (Ma *et al.* 2010; Yu *et al.* 2009).

During the last two decades, the approach for fractionating lignocellulosic materials to obtain ethanol has changed. Now, it is not only cellulose and hemicellulose that play an important role in the use of this type of material, but also non-cellulosic components such as lignin have gained importance in the manufacture of high-value products. Many products, including food, materials, pharmaceuticals, and fuel are potentially obtainable from lignin; therefore, considerable effort has been exerted to develop processes that specifically disrupt the linkages in lignin to produce valuable target chemicals (Amendola *et al.* 2012; Zakzeski *et al.* 2010). Some improved pretreatments have been implemented as methods for delignification.

The separation of lignin is a complex process known as delignification (Ruiz *et al.* 2011). This process involves degradation or dissolution of the lignin macromolecules into smaller fragments (Sun *et al.* 2000). Almost all pretreatments can be used to fractionate lignocellulosic biomass; however, in the present context, the term delignification is commonly associated with treatments that use solvents.

In recent years the use of bio-butanol from lignocellulosic biomass as an attractive biofuel has been explored. It is produced from the fermentation of carbohydrates in a process called ABE, after the main products acetone, butanol, and ethanol. The advantages, limitations, and the main findings have been reviewed by several investigators (Bankar *et al.* 2013; Demirbas 2009; Kumar and Gayen 2011). The future outlook on this subject seems to be very promising. Generally, biobutanol has an advantage compared to cellulosic ethanol with respect to the environmental and economic issues. Dürre (2007) have reported the advantages of biobutanol with respect to ethanol; among them, bio-butanol can be used in pure form or blended with gasoline, the use of biobutanol as a fuel does not require modification of existing car engines, it has a lower vapor pressure and is thus safer to handle, it is not hygroscopic, and it is less corrosive. Despite this, much research in this issue is still necessary. Further research must focus on the development and improvement of all the process steps, mainly in obtaining more efficient microorganisms to produce bio-butanol from cellulosic materials, utilization of valuable compounds from effluents, and development of new products (García *et al.* 2011), and solving the problems related to detoxification of inhibitory compounds.

In the following sections, organosolv and ionic liquid pretreatments are analyzed as methods for delignifying lignocellulosic biomass. These processes have proven beneficial for fractionating and recovering cellulose and hemicellulose, as well as releasing lignin with useful physicochemical properties. Each pretreatment is described, and the advantages and disadvantages of each one are discussed. The properties of the lignin obtained from each pretreatment process are also described.

Overview of Organosolv Pretreatment

Organosolv pulping was invented and patented by Theodore Kleinert in 1971 as an environmentally friendly replacement for the kraft process. Recently, due to the popularity of second-generation biofuels, the organosolv process has been considered an important pretreatment for biofuel alcohol production (Huang *et al.* 2011). Organosolv pretreatment is similar to organosolv pulping, but the degree of delignification in pretreatment is not as high as it is in pulping (Zhao *et al.* 2009). Organosolv pretreatment involves the treatment of lignocellulosic biomass with organic solvents and small amounts of water in either the presence or absence of a catalyst, such as sulfuric (H_2SO_4) or hydrochloric acid (HCl), at temperatures ranging from 180 to 210 °C. Regarding the raw material hardwood, softwood and grasses can be fractionated using the organosolv process.

Organosolv pretreatment uses a wide variety of organic solvents, such as methanol, ethanol, acetone, formic acid, acetic acid, ethylene glycol, triethylene glycol, and tetrahydrofurfuryl alcohol (Chum *et al.* 1988; Deng *et al.* 2008; Thring *et al.* 1990). Because ethanol is relatively inexpensive, has low toxicity, and easy to recover, it is the preferred solvent for the organosolv pretreatment process. Two advantages for using ethanol have been reported: it easily penetrates into the structure of the biomass, resulting in uniform delignification, and it reduces the surface tension of the pulping liquor (Sun *et al*. 2010). Zhao *et al.* (2009) also reviewed the progress of lignocellulosic biomass organosolv pretreatment, particularly with regard to alcohol, organic acid, organic peracid, and acetone usage. They concluded that alcohols, such as methanol and ethanol, are preferred for this process because they are relatively easy to recover and are less expensive than solvents like acetone. Furthermore, organic acids, such as formic and acetic acid, can cause serious corrosion problems and cellulose acetylation during pretreatment. Organic peracid can selectively remove lignin in mild conditions, but the high cost limits its use in large-scale applications.

The purpose of the organosolv pretreatment process is to remove lignin and to enhance the digestibility of cellulose. During organosolv pretreatment, the lignin structure is broken into smaller parts, dissolved from the lignocellulosic biomass, and separated in the form of a liquor rich in phenolic compounds (process effluent) (Ruiz *et al.* 2011). Xu *et al*. (2006) suggested that during the organosolv pretreatment, organic acids impregnate the tissues of crop residues; then, the cleavage of the acid-labile bonds occurs. In addition, the acidic media help to stabilize the produced lignin fragments.

Organosolv delignification of the lignocellulosic biomass can be acidic, neutral, or alkaline (Aziz and Sarkanen 1989). In non-catalyzed pulping, the cooking liquor becomes acidified due to acetyl groups liberated during the hydrolysis of hemicellulose. Lignin is dissolved by acid-catalyzed cleavage of bonds, such as α-aryl ether and arylglycerol-β-aryl ether bonds in the lignin macromolecule (Sarkanen 1990). Goyal *et al.* (1992) reported that in acidic conditions, α-ether cleavage occurs to a great extent, while the cleavage of β-aryl ether bonds occurs to a lesser extent and this last increase in strongly acidic systems.

Ruiz *et al.* (2011) reported several advantages of the organosolv process. The most notable is the ability of the organosolv pretreatment to produce relatively high-quality lignins. Organosolv solvents are easily recovered by distillation and recycled, so that all the components of the lignocellulosic biomass can be used. Organosolv pretreatment yields three separate fractions: dry lignin, an aqueous hemicellulose stream, and a relatively pure cellulose fraction (Duff and Murray 1996).

Process variables such as reaction time, temperature, solvent concentration, and type of raw material, affect the yield of extraction and the physicochemical properties of lignin. Due to its importance, the effect of the process parameters on the recovery rate and physicochemical properties of the recovered lignin has been extensively investigated (Shunkry *et al.* 2008; Toledano *et al.* 2011; Xu *et al.* 2006; Zhang *et al.* 2010). In a study performed by Xu *et al.* (2006), the influence of the solvents concentration (organic acids and alcohols) on physicochemical properties of lignins from wheat straw were analyzed. The results showed that aqueous organic acid was more effective for delignification of wheat straw than aqueous organic alcohol. No significant differences in the molecular-average weights were reported. However, FT-IR spectra of lignins dissolved with organic acid had fewer conjugated carbonyl groups and more unconjugated groups than the lignins isolated with organic alcohol. Furthermore, the treatment with organic acid, particularly acetic acid, resulted in noticeable amounts of acetyl groups in the lignin preparations. Toledano *et al.* (2011) have reported the optimization of the variables to extract lignin from olive tree pruning by organosolv treatment. Results showed that high temperatures and low concentration of ethanol render the highest yields. In addition, thermogravimetric analysis of lignin showed the presence of other components from the raw material such as hemicelluloses and degradation products (acetic acid, furfural, hydroxymethylfurfural, and ferulic acid). Furthermore, properties such as the solubility of lignin and the ratio of phenolic OH and aliphatic OH can be affected by the concentration of solvent and time pulping conditions (Shunkry *et al.* 2008). Different residence times and reaction temperatures in the yield of lignin extracted using formic acid as a solvent were analyzed by Zhang *et al.* (2010). They reported that higher yields of lignin resulted when longer times and high temperature were applied. In addition, more cleavage of α-aryl and β–aryl ether of linkages in macromolecular lignin and in wheat straw was achieved under the aforementioned conditions.

Organosolv Lignin (OSL)

OSL is the common name for lignin that is soluble in the kinds of organic solvents that are generally used during the solvent-based manufacture of pulp for paper manufacture. OSL has been used as a filler in the formulation of inks, varnishes and paints (Belgacem *et al.* 2003). Biocomposites with improved properties have been produced by mixing OSL and other organic polymers (Doherty 2011; Johnston and Nilsson 2012; Stewart 2008). Also, the replacement of chemical phenol for OSL in the manufactured phenol-formaldehyde resin used in particleboard production was reported by Çetin and Özmen (2002). Recently, rigid polyurethane foams were manufactured by replacing polyol with OSL (Pan and Saddler 2013). Unlike other lignins, OSL has a high purity, a low molecular weight, is sulfur-free, has a narrow molecular weight distribution, has a low glass transition temperature, is water insoluble, and has high phenolic and aliphatic hydroxyl content (Lora *et al.* 1989). Other important features of OSL are its homogeneity and the absence of smell (Vallejos *et al*. 2011).

Overview of Ionic Liquid (IL) Pretreatment

In recent years, ionic liquids have been presented as a possible solution for fractionating lignocellulose biomass for biofuel production, and some processes have been patented (Argyropolous 2008; D'Andola *et al*. 2008). Ionic liquids are organic salts, formed by cations (organic) and anions (inorganic), which separate polymeric components (Anugwom *et al.* 2012). Ionic liquids can either dissolve the lignocellulosic biomass (Ang *et al.* 2011) or its subcomponents (Zhu *et al.* 2013). Ionic liquids have unique physicochemical properties. For example, they have a melting point below 100 °C, are not flammable or volatile, have high thermal stability, and are easy to recover (van Rantwijk and Sheldon 2007). Because of these key characteristics, ionic liquids have been proposed as good substitutes for more the traditional, flammable, and volatile solvents (Cull *et al.* 2000).

The main applications of ionic liquids for different types of lignocellulosic biomass have been to remove lignin, disrupt the crystalline structure of cellulose, and increase the accessibility of cellulose (Liu *et al.* 2012). These applications are very important to enhance biofuel production. The ionic liquid that is most commonly used for this purpose is 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc) (Ahn *et al.* 2012; Fu *et al.* 2010; Fu and Mazza 2011; Li *et al.* 2010a; Qiu *et al.* 2012; Sun *et al.* 2013), which has been used alone or in combination with the organic solvents 1-allyl-methylimidazolium chloride ([AMIM]Cl) (Yang *et al.* 2013) and 1-butyl-3-metylimidazolium chloride ([BMIM]Cl) (Tan and Lee 2012). The success of [BMIM]Cl has been attributed to the chloride ions (Cl^-) disrupting the hydrogen bonds that are present in the cellulose. Imidazolium cations with various side groups that are combined with anions such as Cl^-, acetate, and formate appear to be the most efficient for breaking the cellulose structure (Maki-Arvela *et al.* 2010).

There are several studies that support the importance and efficacy of ionic liquids for dissolving lignocellulosic materials. All of these studies are focused on the use of ionic liquids as a more efficient pretreatment than traditional pretreatment methods (Li *et al.* 2009a; Qiu *et al.* 2012; van Spronsen *et al.* 2011). The use of ionic liquids as an additional pretreatment for lignocellulosic materials is also currently being investigated. Many of these investigations have evaluated the effectiveness of ionic liquids at reducing the crystallinity of cellulose (Liu *et al.* 2012) or the effectiveness of different types of ionic liquids to fractionate the lignocellulosic materials (Fu *et al.* 2010; Fu and Mazza 2011a,b; Uju *et al.* 2012). Several investigations focused on explaining the changes in the components of the lignocellulosic biomass. Other studies have analyzed the potential and limitations of lignocellulosic ethanol production using ionic liquids (Mora-Pale *et al.* 2011; Zhu *et al*. 2013). However, it must be also considered that not only is the cellulose important, but that polymers such as hemicelluloses and lignins are also very important. Because of the tunable solvation properties of ionic liquids, they can be designed for specific purposes. For example, the selective extraction of hemicellulose from spruce

(*Picea abies*) can be performed using an ionic liquid produced from alcohols (either hexanol or butanol), CO_2, and an amidine, 1,8-diazabicyclo-[5.4.0]-undec-7-ene (Anugwom *et al.* 2012). Wood flour treated with this ionic liquid contained 38% less hemicellulose compared to the native spruce; however, this treatment had no effect in removing lignin. The main force involved in the dissolution process is hydrogen bonding. Electrostatic and van der Waals forces are of minor importance (Casas *et al.* 2012). Using COSMO-RS analysis, Casas *et al.* (2012) verified that the most promising anions are acetate, formate, and chloride with different cations.

One of the key points for efficiently using ionic liquids as a pretreatment for lignocellulosic biomass is the proper selection of the compounds that selectively extract lignin, reduce the cellulose crystallinity, and do not negatively affect enzymatic hydrolysis and the fermentative capacity to obtain ethanol. For example, 1-ethyl-3-methyl imidazolium diethyl phosphate ([EMIM]Dep), an ionic liquid of low viscosity, accelerated enzymatic hydrolysis, and the treatment did not affect the ability to produce ethanol from wheat straw (Li *et al.* 2009b). In another study, it was shown that neither crude glycerol nor the ionic liquid 1-butyl-3-methylimidazolium acetate ([BMIM]Ac) negatively affected treated wheat straw.

An ionic liquid was found to be the best in terms of hydrolysis and reducing sugars production (Guragain *et al.* 2011). The conditions for pretreatment of wheat straw with [BMIM]Ac were optimized (158 °C, ionic liquid concentration of 49.5%, and duration of 3.6 h), establishing a compromise between fermentable sugar recovery and cellulose and xylan digestibility (Fu and Mazza 2011a).

A significant change in the dissolution rate of the lignocellulosic biomass has been related to the viscosity of the ionic liquids. For this purpose, ionic liquids can be mixed with water to reduce their viscosity (Brandt *et al.* 2011; Li *et al.* 2008). However, while it favors the ionic liquid application due to less cost and the recovery of ionic liquid, it was found that it reduces the solubility of cellulose (Mazza *et al.* 2009).

Acids have been added to ionic liquids. Sulfuric, nitric, and maleic acids have been mixed with ionic liquids (Li *et al.* 2008). Acid compounds can function as catalysts, increasing the rate of hydrolysis and the rate of dissolution. Van Spronsen *et al.* (2011) hydrolyzed pine flour and wheat straw with three ionic liquids, [EMIM]Cl, [EMIM]OAc, and [BMIM]Cl, with the addition of acetic acid in [EMIM]Cl as a catalyst. This acid was chosen because it was found in the lignocellulose biomass as acetyl groups on the hemicellulose. The results showed an increased lignin extraction yield when the amount of acetic acid was increased. Acetic acid not only worked as a catalyst for hydrolysis, but it also improved the solubility of the lignin.

Ionic liquids, particularly acid functionalized or paired ionic liquids, have been used in catalytic reactions as catalysts or as solvents. A significant conversion of cellulose to industrially useful chemicals has been reported by Long *et al.* (2011a) using the $C_4H_8SO_3HMIMHSO_4$/BMIMCl pair. Ionic liquids have been functionalized with acid which acts as catalyst for liquefaction of lignocellulosic materials. In this sense, Long *et al*. (2011b) reported on the use of SO_3H-functionalized ionic liquid. Under the conditions of the experiment, 96.1% of bagasse was liquefied using SO_3H-functionalized with a set of imidazolium ionic liquids, with SO_3H providing more efficient liquefaction of bagasse than COOH-functionalized and HSO_4-paired imidazolium ionic liquids. The results were attributed to $C_4H_8SO_3HMIMHSO_4$ showing the strongest acid strength, as it has acidic centers on both the cation and anion (Long *et al.* 2011b). Sievers *et al.* (2009) dissolved pine wood in [BMIM]Cl ionic liquid. The acid catalyst, trifluoroacetic acid, was added to convert the carbohydrate fraction to water soluble products. However, this method does not extract pure lignin, and it may be susceptible to modifications due to the acidic conditions used.

The catalytic liquefaction of agricultural residual without any chemical pre-treatments has been also investigated using cooperative ionic liquid pairs. Long *et al.* (2012) used [BMIM]Cl as the ionic liquid solvent for the dissolution of the lignocelluloses and acidic imidazolium ionic liquid as the catalyst. The results showed that cellulose and hemicellulose are much more easily transformed than lignin by cooperative ionic liquid pairs. Recently, an efficient method for the separation of lignin from sugarcane bagasse in the presence of acidic ionic liquids catalyst has been reported. Lignin was extracted in the presence of $C_4H_8SO_3HMIMHSO_4$ ionic liquid at 200 °C for 30 min, and the delignification of 100% of sugarcane bagasse using a series of acidic ionic liquids and ethanol/water solvent was achieved. The physicochemical characterization demonstrated that this isolated lignin is pure and similar to that obtained by other techniques (Long *et al.* 2013).

Sun *et al.* (2009) achieved the complete dissolution of lignin with an ionic liquid with added dimetilsulfoxide (DMSO) as co-solvent. They evaluated different variables including particle size, wood species, initial wood concentration, and pretreatment using [EMIM]OAc as solvent in softwood and hardwood. They extracted lignin from the solution using acetone/water anti-solvent (Muhammad *et al.* 2001). However, recycling of the ionic liquid was not investigated and evaluated in the published report. Pinkert *et al.* (2011) reported using a food additive-derived from ionic liquid (imidazolium acesulfamate) for lignin extraction from *Pinus radiate* and *Eucalyptus nitens* wood flour. They also evaluated different variables including extraction temperature and time, water content, wood load, particle size and species, types of ionic liquid cation, effect of ionic liquid recycling, multi-step treatment, and use of co-solvents. The result showed that the extracted lignin has a larger average molar mass as well as uniform molar mass distribution. An increased efficiency of extraction of almost 50% was achieved using DMSO as a co-solvent. The lignin extraction was achieved without disrupting the cellulose crystallinity.

On the other hand, the effect of ionic liquid cation and anion combination on the macromolecular structure of lignins has been reported by George *et al.* (2011). They reported that the degree of lignin structural modification seems to be influenced by the anion. Sulfates > lactate > acetate > chlorides > phosphate, in this order, reduced the lignin molecular weight. It was hypothesized that fragmentation of lignin is produced either via catalytic means or through nucleophilic attack of inter-lignin β-O-bonds. In contrast, Pu *et al.* (2007) examined the solubility of lignin isolated from pine kraft pulp in several ionic liquids as aprotic green solvents for lignin. The results indicated that the solubility of lignin was mainly influenced by the nature of the anions. Ionic liquids containing the large, non-coordinating anions [PF4]- and [PF6]- were unsuitable as solvents for lignin. For the [BMIM]+-containing ionic liquids, the order of lignin solubility for varying anions was: $[MeSO_4] > Cl_2 \sim Br_2\text{-} >>> [PF6]\text{-}$. Ionic liquids $[HMIM][CF_3SO_3]$, $[MMIM][MeSO_4]$, and $[BMIM][MeSO_4]$ were effective solvents for lignin.

Because of the special properties of ionic liquids, they can be synthesized for specific purposes, and specific ionic liquids can have specific interactions with the biomass. Tan and Macfarlane (2009) reported the synthesis of a new ionic liquid to investigate the chemical and physical changes of sugarcane bagasse. The ionic liquid contained 1-ethyl-3-methylimidazolium as the cation and a mixture of alkyl benzenesulfonates and xylenesulfonate as the primary anion. Under the conditions used in the extraction process, the performance of the ionic liquid was greater than 93%, and lignin with a molecular weight of 2220 g/mol was obtained. The lignin could be recovered by precipitation, and the ionic liquid could be recycled. Diop *et al.* (2013) synthesized the ionic liquid 1.8 iazabicyclo[5.4.0]undec-7-ene by quaternization of a nitrogen atom with a hydrogen atom and alkyl chain, to dissolve kraft lignin from black liquor. Decreases in the molecular weight and reduction of solubility demonstrated that the dissolution of kraft lignin in ionic liquids is possible.

Some ionic liquids have been compared to acidic and alkaline methods. Prado *et al.* (2012) reported the extraction of lignin from apple tree (*Malus domestica*) pruning using organosolv, soda process, and [BMIM][$MeSO_4$], [EMIM]Ac, and [BMIM]Cl ionic liquids. At the same time, [BMIM][$MeSO_4$] was used to purify soda and organosolv lignin. Purity of 91.2% was obtained from raw material using the ionic liquids, whereas organosolv lignin purity ranged from 85.7% to 90.9% and soda lignin from 12.9% to 89.6% after treatment with [BMIM][$MeSO_4$]. Results showed that [BMIM][$MeSO_4$] is a suitable solvent to extract lignin and for its subsequent recovery with no further treatment. While [EMIM]OAc was compared with dilute acid for the removal of lignin, Li *et al.* (2010b) reported values of 69.2% recovered lignin in switchgrass samples using [EMIM]OAc against 22.4% total lignin using dilute acid. These results demonstrated that ionic liquid pretreatment produces significant delignification. However, [EMIM]OAc has not been effective in removing the lignin from all types of biomass. Different values of lignin removal using [EMIM]OAc have been reported (Lee *et al.* 2009; Tan and Macfarlane 2009). Reasons for the differences include: the lignin glass transition temperature that must be exceeded to efficiently solubilize lignin; specific interactions of the ionic liquid with the biomass are dependent on the cation, the anion, temperature, and duration of the pretreatment process; and the extent and degree of biomass recalcitrance is influenced by the inherent variations in the biomass such as age, harvest method, extent of drying, and storage conditions (Li *et al.* 2010a). Process conditions and percent lignin removal, using ionic liquids in wood and non-wood materials, are shown in the Table 1.

Table 1. Ionic Liquids Used to Remove Lignin from Wood and non-wood Materials

Ionic liquid Abbreviation	Raw material	Conditions	Lignin removed (%)	Reference
[EMIM][OAc]	Maple wood	130 °C, 1.5 h	52	Lee *et al*. 2009
[EMIM][OAc]	Oak	100 °C, 16 h	35	Sun *et al*. (2009)
[EMIM][Na] [ABS]	Sugarcane bagasse	170–190 °C, 30-120 min	93	Tan et al. (2009)
[EMIM][OAc]	Corn stover	125°C, 1 h	44	Miyafuji *et al*. (2009)
[EMIM][OAc]	Switchgrass	160 °C, 3 h	69	Li *et al.* (2010b)
[EMIM][Cl]	Triticale straw	90 °C, 24 h	15	Fu *et al.* (2010a)

[EMIM][OAc]	Switchgrass	120 °C, 3 h	34	Arora *et al*. (2010)
[EMIM][OAc]	Triticale straw	150 °C, 1.5 h	64	Fu and Mazza (2011)
[EMIM][OAC] (50% water)	Triticale straw	150 °C, 1.5 h	29	Fu and Mazza (2011)
[BMIM][$MeSO_4$] (20% water)	Miscanthus	120 °C, 2 h	27	Brandt *et al.* (2011)
[BMIM][HSO_4] (20% water)	Miscanthus	120 °C, 22 h	93	Brandt *et al.* (2011)
[BMIM][HSO_4] (20% water)	Willow	120 °C, 22 h	85	Brandt *et al.* (2011)
[BMIM][HSO_4] (20% water)	Pine	120 °C, 22 h	65	Brandt *et al.* (2011)
[EMIM][OAc]	Bagasse	165 °C, 10 min	34	Li *et al.* (2011)
[EMIM][OAc]	Rice hull	110 °C, 4 h	46	Lynam *et al.* (2012)
[EMIM]Cl	Legume straw	150 °C, 2 h	30	Wei *et al*. (2012)
[BMIM][$MeSO_4$] (7% H_2SO_4)	Sugarcane bagasse	125 °C, 2 h	26	Diedericks *et al*. (2012)
[EMIM][OAc]	Energy cane bagasse	120 °C, 30 min	32	Qiu *et al.* (2012)
[BMIM][SO_3] [HSO_4] (ethanol/water)	Sugarcane bagasse	200 °C, 30 min	100	Long *et al.* (2013)

Ionic liquid names: [EMIM]OAc 1-Ethyl-3-methyl imidazolium acetate, [EMIM][Na] [ABS] 1-Ethyl-3-methylimidazolium sodium alkylbenzenesulfonate, [EMIM][Cl] 1-Ethyl-3-methyl imidazolium chloride, [BMIM][$MeSO_4$] 1-butyl-3-methylimidazolium methyl sulfate, [BMIM][HSO_4] 1-Butyl-3-methylimidazolium hydrogen sulfate, [BMIM][SO_3] [HSO_4] 1-4-sulfobuty-l-3-methyl imidazolium hydrosulfate.

The use of harsh chemicals, high temperatures, and/or long pretreatment times during biomass conversion results in an increased lignin condensation. Depending on the pretreatment method, a decrease in the number of β-O-4 linkages, which are fragmented and recondensed, have been observed (Yelle *et al.* 2013). Sathitsuksanoh *et al.* (2013) have reported that [EMIM]OAC is suitable as a pretreatment to hard wood and two grasses to obtain lignin with non-condensed structures and different molecular sizes. Condensed structures of lignin limit the possibilities to enhance their properties (Huber *et al.* 2006).

There is extensive literature showing the benefits of ionic liquids, with the many advantages to the extraction and purification of the main components of lignocellulosic biomass listed above. However, the information in open literature about the disadvantages of ionic liquids is limited. Ionic liquids are very selective for the dissolution of lignocellulosic biomass, even though there are several disadvantages that limit the extensive use of ionic liquids. In some cases, ionic liquids are expensive, recycling of pure ionic liquids energy-intensive, and some ionic liquids become extremely viscous during pretreatment, making them difficult to handle. If mixing ionic liquids with water were a feasible alternative, these constraints could be substantially mitigated. In this way, a smaller quantity of ionic liquid would be used and operations would be easier because of reduced viscosity. In addition, recycling of the mixture instead of a pure ionic liquid would be facilitated because separation of ionic liquid and water usually by energy-intensive evaporation or reverse osmosis would not be necessary. In addition, there are toxicity concerns regarding imidazole-based compounds. Ionic liquids have been reported that are poorly biodegradable, toxic to micro-organisms, and may form hazardous hydrolysis products (Walker 2008). Two factors that will ultimately decide whether these systems are viable on a larger scale are likely to be the ability to reuse the catalyst without a decrease in activity and whether the products can be separated efficiently without contamination from the ionic liquid or catalyst (Gordon 2001).

Ionic Liquid Lignin (ILL)

There are a few applications in which ionic liquids are used to extract lignin. Pretreatment of lignocellulosic biomass with ionic liquids involves the removal of lignin to improve the accessibility of cellulose. Because of its complex structure and multiple links that form the lignin macromolecule, lignin is more difficult to separate than other polymers. Recent studies have indicated that the ionic liquid [EMIM]OAc is effective for removing lignin (Samayam and Schall 2010). Six ionic liquids were evaluated for removing lignin in flax, triticale, and wheat straw (Fu *et al.* 2010a). The results demonstrated that [EMIM]OAc was more efficient for this purpose than others. Lynam *et al.* (2012) determined the effect of [EMIM]OAc, [AMIM]Cl, and [HMIM]Cl on the fractionation of the main constituents of rice hulls. [EMIM]OAc (110 °C, 4 h) removed 46% of the lignin in the rice hull, whereas adding 4 h more of reaction time removed all of the lignin. The additional time allowed the [EMIM]OAc to penetrate further into the rice hull. This indicates that cellulose and lignin extraction yields improve with long incubation times and high temperatures. Extraction conditions affect lignin removal and yield. Temperatures of 122 °C and long extraction time (22 h) were optimal.

Kim *et al.* (2011) compared the structural features of two different lignins, ionic liquid lignin (ILL) obtained with [EMIM]OAc and milled wood lignin (MWL). Spectroscopic analyses of the structures (FT-IR, ^{1}H, and ^{13}C-NMR) demonstrated that the ILL was quite similar to MWL. However, gel permeation chromatography data revealed that the average molecular weight (M_w) of ILL was lower than that of MWL, indicating that lignin from IL extraction is of rather uniform size. This suggests that some form of depolymerisation had occurred. MWL was more thermodynamically stable than ILL. The thermal stability of lignin increased with an incrementally higher molecular weight (Sun *et al.* 2000). The ionic liquid [EMIM]OAc can be used to obtain lignin with similar properties to the MWL, but in shorter times. It is hypothesized that the usefulness of [EMIM]OAc is because the structure of the ionic liquid contains an imidazolium-based salt and two alkyl groups; because of the cationic nitrogen in the imidazolium, the ionic liquid may be physically and chemically associated with lignin at electron-rich oxygen, such as the β-O-4, α-O-4, and β-β linkages.

Physicochemical Properties of Organosolv Lignin and Ionic Liquid Lignin

Organosolv and ionic liquid lignins are unique from the rest of lignins due to their low molecular weight, high purity, homogeneity, and the ease of dissolution in certain solvents. In addition, both organosolv and ionic liquid processes have demonstrated several advantages when compared to kraft and other processes. Molecular weight in ILL is typically narrower than OSL, and because of this the polydispersity index in OSL is wider. It can probably be attributed to the fact that the organosolv process is less selective to the removal of lignin than that of the ionic liquid process.

Regarding purity, OSL has more ash and carbohydrate content than ILL. The problem with the impurities (carbohydrate and ash) is that there is a necessary extra step to remove them completely, which implies greater economic cost. In a study performed by Toledano *et al.* (2012), olive tree pruning lignin was dissolved by treating the raw material in a water-ethanol mixture. The black liquor was subjected to ultrafiltration using different membrane cut-offs (300, 150, 50, 15 and 5 kDa). Results showed that a small percentage (0.20%) of ash can pass through the smallest pore membrane (5 kDa). According to Glasser and Jain (1993), glass transition temperature (T_g) values are usually higher in softwood lignin and lower in organosolv lignin. It should be mentioned that there is limited information regarding the physicochemical properties of lignin obtained with ionic liquids. The most abundant information reported is about the molecular weight and polydispersity index. The data shown in Table 2 provides information on the properties of lignin from different raw materials (softwood, hardwood, and no-wood). Factors such as genetic origin of raw material and some variables of the extraction process may affect the final properties of lignin. Vishtal and Kraslasky (2011) mentioned that lignin from non-wood plants typically has lower molecular weight, higher polydispersity, and higher ash content than wood lignin. If minor components such as carbohydrates, ash, and extractives are not separated from lignin, these impurities may cause the formation of undesirable compounds to result in low yields of lignin and release the deterioration of the properties of the final product. Furthermore, some impurities such as sulfur may affect the catalysts used in the chemical conversion process (Vishtal and Kraslawski 2011). The complete physicochemical properties of OSL and ILL are given in Table 2.

Table 2. Chemical Composition of Ionic Liquids and Organosolv Lignins

Impurities and properties	Organosolv lignin	Reference	Ionic liquid lignin	Reference
Ash (%)	1.13-4.9	Wörmeyer *et al.* (2011), Toledano *et al.* (2012), Cybulska *et al.* (2012), Gosselink *et al.* (2004)	0.6-2.0	Tan *et al.* (2012)
Carbohydrates (%)	0.32-9.0	Cybulska *et al.* (2012), Gosselink *et al.* (2004)	0.1	Kim *et al.* (2011
Acid soluble lignin (%)	1.86-3.89	Montiel-Rivera *et al.* (2013)	ND	
Glass transition temperature	90-180	Shukry *et al.* (2008), Alriols *et al.* (2010),	ND	

(°C)		Zhao and Liu (2010), García *et al.* (2012)		
Molecular weight (*Mw*)	500-4000	Manjarrez-Nevárez *et al.* (2011), Vishtal and Kraslaski (2011)	2220-6347	Tan *et al.* (2009), Kim *et al.* (2011)
Polydisperdity	1.3-4.0	Zhang *et al.* (2010), Majcherczyk and Huttermann (1997), Delmas *et al.* (2011)	1.62	Kim *et al.* (2011)

Lignin Recovery

An important factor in the use of OSL is its recovery, which takes time, consumes energy, and may use solvents that are toxic to humans. Various techniques have been developed to recover OSL; however, they have not been very successful. Centrifugation of precipitated lignin has been reported, but this is not a good technique because of the high maintenance costs (Lora *et al.* 1989). In other cases, there were problems filtering the OSL because of the high viscosity of the solvent (Thring *et al.* 1990). Botello *et al.* (1999) reported the recovery of solvent and by-products from organosolv black liquor. The dilution of black liquor with acidified water causes precipitation of lignin which can then be recovered by centrifugation. Botello *et al.* (1999) also determined that the greatest dilution and lowest pH resulted in the best lignin recovery yields. Macfarlane *et al.* (2009) reported a novel method of organosolv lignin recovery that consists of simultaneous precipitation and dissolution by air flotation (DAF). Air flotation is advantageous compared to centrifugation and filtration because of the low energy use and the low maintenance costs. The hydrophobic nature of organosolv lignin also makes flotation an ideal method of separation. Recently, Luong *et al.* (2012) reported a simple, efficient, rapid, and non-toxic method to recover OSL from cooking liquor. The addition of sodium and aluminum bisulfate ($AlK(SO_4)_2{\cdot}12H_2O$), which is a non-toxic compound used for water purification, allows the precipitation of lignin in a rapid, controlled, and safe manner. From an ecological and economic viewpoint, the recovery of lignin should be performed without the use of any additional chemicals. Currently, there is a method to fractionate lignocellulosic biomass and to recover lignin, which is precipitation in water (Fellisa *et al.* 2010). For ionic liquids, lignin precipitation by adding a non-solvent has been reported as a suitable method (Qiu *et al.* 2012; van Spronsen *et al.* 2011). More information regarding methods for the separation and recovery of OSL and ILL are given in Table 3.

Table 3. Methods for Separation and Recovery Organosolv and Ionic Liquid Lignins

Lignin	Separation and recovery method	References
Organosolv	Precipitation (pH change addition of non-solvent or $AlK(SO_4)_2 \cdot 12H_2O$)	Botello *et al.* (1999), Cook *et al.* (1991), Sun *et al.* (1998), Luong *et al.* (2012)
	Filtration and ultrafiltration	Alriols *et al*. (2010), Toledano *et al.* (2012)
	Dissolved Air Flotation	Macfarlane *et al.* (2008)
Ionic Liquid	Precipitation (addition of non-solvent)	van Spronsen *et al.* (2011), Qiu *et al.* (2012)

SUMMARY

Lignocellulosic biomass is an abundant renewable commodity for energy and chemical production. One of the components is lignin, and large amounts of this compound are obtained as by-products in the fabrication of cellulosic fuels, pulp, and paper. However, lignin is mainly used to obtain low-cost energy. Two pretreatments were presented in this review, organosolv and ionic liquids, which release lignin with interesting and useful chemical characteristics and of higher purity than alkali lignins. Pretreatment using ionic liquids can be the best tool to fractionate lignocellulosic biomass and to obtain lignin, since they are non-toxic, non-volatile, and the lignin is easily recovered. This last characteristic is one of the main disadvantages of the alkali and organosolv pretreatment processes. However, the use of ionic liquids for this purpose still needs to be explored, and it is necessary to evaluate their effectiveness and to find the optimal combinations and conditions to extract lignin.

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