

# Organosolv Processes



Nicolas Brosse, Mohd Hazwan Hussin, and Afidah Abdul Rahim

**Abstract** Biofuels and chemicals can be produced from lignocellulosic feedstocks using biotechnological processes. The effective utilization of carbohydrates from biomass for the production of biofuels necessitates the development of pretreatment technologies to enhance their enzymatic digestibility. Among all the various pretreatment methods currently studied and developed, the organosolv processes, in which organic solvents or aqueous organic solvent mixtures are used as the pretreatment medium, appear to be specially promising in the context of the biorefinery because (1) they produce cellulosic pulp with a good enzymatic digestibility for monomeric glucose production and (2) they allow a clean fractionation of the major biomass components (cellulose, lignin, and hemicelluloses) into three process streams. In this chapter we give an updated overview of organosolv methods using conventional solvents and ionic liquids which have recently gained considerable interest as solvents for lignocellulosic biomass and pretreatment.

**Keywords** Ionic liquid, Lignocellulose, Pretreatment

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## 1 Introduction

The most crucial issue faced by the world today is the sustainability of consumption of energy and natural resources. As fossil fuel creates problematic issues (because of global warming, increase in price, and running out), the use of renewable resources to shift the oil-based economy into a bio-based economy is one of the alternative choices. With a goal of reducing net greenhouse gas emissions, this marks an important turning point in the effort to promote the use of renewable energy to fulfill the commitments of the Kyoto Protocol and the COP 21 [1, 2]. Biomass has been considered as one of the potential sources of renewable energy throughout the world. Several agencies worldwide have recently reported an increase in the gross domestic energy and chemical production from renewable energy, especially biomass. It was reported that the European Union (EU) utilized about 66.1% of its renewable energy (including heat generations) from biomass which surpassed the contribution of other energy sources such as hydro, wind, geothermal, and solar power [3]. The development of (bio)technologies and (bio) processes for biomass valorization is focusing not only on the production of energy but also on the production of biofuels and biomaterials.

Dry matter of plants can be referred as lignocellulosic biomass. It has been acknowledged as the most abundant source of renewable energy (approximately  $200 \times 10^9$  tons/year) obtained from crops, wood, and agricultural waste [4, 5]. Lignocellulosic biomass is best suited for energy and chemical applications because of its sufficient availability, and it is inexpensive and environmentally safe. It is composed of cellulose, hemicellulose, and lignin with small amounts of proteins, lipids, and ash that later form the complex structure of the plant cell wall. The composition of these compounds essentially depends on the origin of the plant as listed in Table 1.

The lignocellulosic materials (cellulose, hemicellulose, and lignin) are interconnected with each other through covalent crosslinks. Recent work in this area has mainly focused on the delignification of lignocellulosic biomass separating lignin, cellulose, and hemicelluloses to be used in both physical and (bio)chemical applications. The cellulose and hemicellulose can be hydrolyzed to monomeric sugars and often converted to value added products such as ethanol, additives,

**Table 1** Representation of different fractions of lignocellulosic materials<sup>a</sup>

Lignocellulosic materials	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood stems	40–55	24–40	18–25
Softwood stems	45–50	25–35	25–35
Nut shells	25–30	25–30	30–40
Corn cobs	45	35	15
Grasses	25–40	35–50	10–30
Wheat straw	30	50	15
Cotton seed hairs	80–95	5–20	0
Coastal Bermuda grass	25	35.7	6.4
<i>Typha capensis</i>	34.2	11.6	26.4
<i>Miscanthus x giganteus</i>	38.2	24.3	25
Poplar aspen	42.3	31	16.2
Empty fruit bunch	59.7	22.1	18.1
Switch grass	45	31.4	12
Oil palm fronds	35.7	28.4	24.6

<sup>a</sup>Source: [6–11]

organic acid, and others by chemical and biochemical processes [12]. All of these lead to the utilization of lignocellulosics not only for second generation energy, chemical and material production but also for synthesizing food additives and feed supplements [13].

Organosolv pulping is the process of extracting lignin from lignocellulosic feedstocks with organic solvents or their aqueous solutions. Since the 1980s, organosolv pulping using low boiling point solvent (e.g., ethanol) has been an alternative to Kraft and sulfite pulping, which have some serious shortcomings such as air and water pollution. It was originally developed as Alcell<sup>®</sup> pulping process for hardwood. With the recent emerging need to develop alternative sustainable transportation fuel, the organosolv process for the production of ethanol is among the pretreatment strategies currently being studied and developed on an industrial scale for the conversion of lignocellulosic feedstock to biofuels and biomaterials [14, 15]. Moreover, organosolv pretreatment processes allow a clean fractionation of lignocellulosic feedstocks and the recovery of high-quality lignins, which are of great interest and are currently a focus of attention [16]. The availability of such lignin fractions in large quantities should stimulate development in new lignin utilizations [17]. In the last few years, a new type of solvent, referred to as an ionic liquid (IL), has been extensively described for the pretreatment of biomass and the extraction of lignin and holds great promise. Although the recovery yield is low, the primary advantages of the ILs for pretreatment technologies are the very low emissions of volatile organic compounds and their excellent solvent properties allowing them to dissolve the lignocellulosic matrix [18, 19].

In this chapter we focus on the organosolv process as a method for fractionation of biomass and some discussion on organosolv pulping and pretreatment, together

with the chemistry of organosolv delignification. The current applications of organosolv lignin and the role of ILs in the organosolv process are also discussed.

## 2 Conventional Organosolv Pretreatment

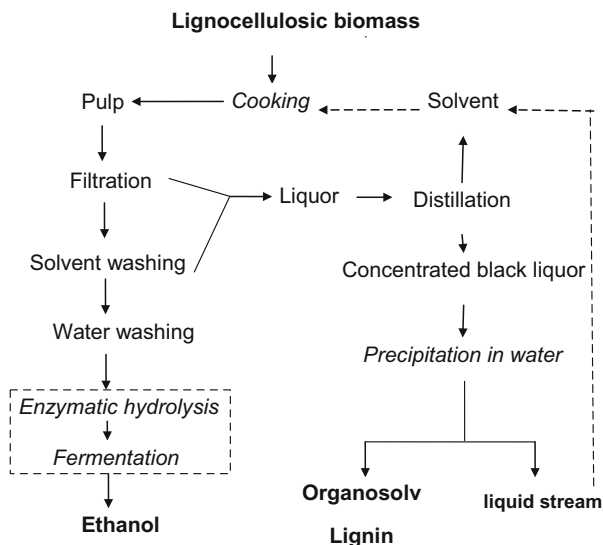
### 2.1 *Organosolv Pulping*

Generally, organosolv pretreatment has been shown to be a very effective process in fractionating lignocellulosic feedstocks into rich cellulose pulp, a water-soluble hemicellulose stream, and a solid organosolv lignin fraction [15, 20]. Since the 1970s it has attracted much interest for addressing the environmental concerns with regards to the conventional Kraft and sulfite processes, which cause serious issues such as water and air pollution [14]. It is important to note that organosolv pretreatment is similar to organosolv pulping except for the degree of delignification which is not as high as that of pulping. Some advantages of organosolv pretreatment are as follows: (1) it allows easy recovery of organic solvents via distillation and (2) it allows isolation of lignin and carbohydrates that show promise as chemical feedstocks [21–23], thus making it more feasible for biorefinery of lignocellulosic feedstocks. The organosolv process utilizes ethanol or methanol as solvent and mineral acids as catalyst. Previous studies have shown that yields of organosolv softwood pulps are higher than those of conventional Kraft and sulfite pulps at equivalent Kappa number [22]. Generally, Kappa number is a measure of the amount of lignin remaining in pulp. The higher the Kappa number value, the greater the amount of bleaching chemicals required to brighten the pulp. At the industrial scale, organosolv pulp mills can be operated on a smaller volume (around 300 tons pulp/day) to that of Kraft pulp mills (1,000 tons pulp/day) [24], which can easily be bleached (chlorine-less) and are environmentally safe.

### 2.2 *Overview of Ethanol Organosolv Pretreatment*

It is important to note that different cooking conditions of lignocellulosic feedstocks on organosolv pretreatment/pulping are very crucial to preserve high quality fiber. Recycling the solvent used in the organosolv process is essential to lower the total costs. Organosolv pretreatment uses a large number of organic or aqueous-organic solvent systems with or without catalysts but the ethanol organosolv pretreatment is more described and is the subject of industrial developments (e.g., lignol process). The general ranges are as follows: cooking temperature of 100–250 °C, cooking time of 30–90 min, ethanol concentration of 35–70 wt%, and solid to liquid ratio from 1:4 to 1:10 (w/w) [15, 25]. Lignin can be recovered as a precipitate by flashing the black liquor to atmospheric pressure followed by

**Fig. 1** Process flowchart of low boiling point alcohol pretreatment



dilution with water. The process of ethanol (and more generally of low boiling point solvent) organosolv pretreatment is illustrated in Fig. 1. Neilson et al. [26] have revealed that ethanol organosolv pretreatment was said to be an effective method for enzymatic hydrolysis of cottonwood. It gave about 1.8–2.5 times the sugar when the pulp was enzymatically hydrolyzed with *Trichoderma reesei* cellulase to that of untreated cottonwood. Ethanol organosolv pretreatment can be performed in the presence or absence of catalyst with auto-catalyzed pretreatment performed at higher temperatures (185–210 °C) [14, 15]. In such conditions, the severity of the organosolv pretreatment can be calculated as the combined severity factor, CS, with specific pH, pretreatment time ( $t$  in minutes), and pretreatment temperature ( $T$  in degrees Celsius; note that  $T_{\text{ref}}$  is 100 °C) [27]:

$$\text{CS} = \log \left[ t \exp \left( \frac{T - T_{\text{ref}}}{14.7} \right) \right] - \text{pH}$$

Additionally, co-products such as hemicellulose sugars and furfural can be recovered from the water stream. During ethanol organosolv pretreatments there are four main reactions or processes that occur: (1) hydrolysis of lignin hemicelluloses linkages via cleavage of 4-*O*-methylglucuronic ester bonds to  $\alpha$ -carbons of lignin and cleavage of  $\alpha$ - and  $\beta$ -*O*-aryl ether linkages, respectively; (2) glycosidic bonds cleavage in hemicelluloses; (3) acid-catalyzed degradation of monosaccharides to furfural, hydroxymethylfurfural (HMF), and other degradation products; and (4) lignin condensation reactions [15]. More information on the mechanism during organosolv pretreatment is discussed in the next section.

If the pretreatment is performed at high temperature, acid addition is not necessary as it is believed that organic acids released from the feedstock act as

catalyst for the degradation of the lignin–carbohydrate complex [20]. Nevertheless, if the acid catalysts are added, this increases the delignification rate that results in higher yield of xylose. The use of mineral acids (such as hydrochloric acid, sulfuric acid, and phosphoric acid) and organic acids (oxalic, formic, salicylic, and acetylsalicylic acid) as catalysts could be useful to accelerate delignification and degradation of xylan [28]. Sulfuric acid is the most frequently used mineral acid catalyst for ethanol organosolv pretreatment, which has been applied to various types of lignocellulosic feedstocks such as pine, hybrid poplar, miscanthus, switchgrass, and oil palm residues [11, 29–32]. The usual concentration of sulfuric acid based on dry weight of biomass is usually in the range of 0.5–1.75%. Higher concentrations of acid lead to greater delignification and greater hemicellulose degradation.

The cellulose-rich pulp produced during acid catalyzed ethanol organosolv pretreatment is suspected to exhibit high glucose yields after enzymatic hydrolysis than base catalyzed pretreatment. In a previous study, Del Rio et al. [33] have shown that NaOH-catalyzed pretreatment of lodgepole pine gave high lignin removal but low cellulose to glucose conversion. Compiled results of enzymatic digestibility of cellulose after ethanol organosolv pretreatment from different biomass are summarized in Table 2. Some characteristics of ethanol organosolv pretreated pulp are (1) low hemicellulose and lignin content with decreased cellulose chain length and (2) low molecular weight and high pore volume that could improve their digestibility [31, 33]. The resulting pulp can be subjected to any fermentation process for the production of ethanol. There are two most suitable fermentation processes for the production of ethanol: simultaneous saccharification and fermentation (SSF) and separate hydrolysis and fermentation (SHF). For the industrial scale, SSF is more preferable as it leads to lower overall process time, less enzymatic inhibition by hydrolysis products, and thus lower capital and operational costs [34].

### ***2.3 Other Solvents for Organosolv Pretreatment***

The use of solvent for organosolv pretreatment is not only limited to methanol or ethanol. High boiling point alcohols (e.g., ethylene glycol, glycerol, and tetrahydrofurfuryl alcohol) and other organic compounds (e.g., dimethylsulfoxide, ethers, ketones, and phenols) could also be used as solvents for organosolv pretreatment. Table 3 shows some advantages and disadvantages of these solvents.

### ***2.4 Combinative Pretreatment Process***

Recently, combinative pretreatment process of lignocellulosic biomass has become an important process because it promises higher efficiency, higher delignification

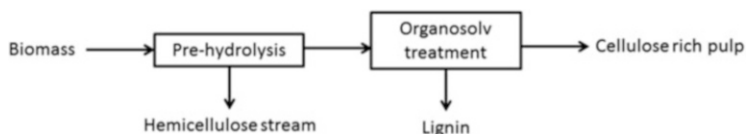
**Table 2** Fractionation of biomass by ethanol organosolv pretreatment as percentage dry weight of untreated feedstocks [15]

Biomass	Cellulose			Hemicellulose			Lignin			
	Untreated	Liquid fraction	Solid fraction	Untreated	Liquid fraction	Solid fraction	Untreated	EOL <sup>a</sup>	Liquid fraction	Solid fraction
Loblolly pine <sup>b</sup>	42.0	3.0	33.3 (55)	21.6	0.5	15.3	29.9	5.4	12.4	11.6
Lodgepole pine <sup>c</sup>	50.5	4.2	37.6 (100)	23.9	1.2	11.1	25.1	19.6	4.8	4.2
Hybrid poplar <sup>d</sup>	48.9	0.6	43.2 (98)	22.4	4.9	11.2	23.3	15.5	5.2	6.2
Miscanthus <sup>e</sup>	37.7	1.7	35.5 (98)	37.3	3.3	25.1	26.3	18.1	0.2	7.8
<i>B. davidii</i> <sup>f</sup>	38.9	1.4	32.3 (98)	26.1	5.7	11.0	30.2	8.9	3.4	19.0

<sup>a</sup>EOL = ethanol organosolv lignin<sup>b</sup>65% aqueous EtOH, 1.1% H<sub>2</sub>SO<sub>4</sub>, 170 °C, 60 min [35]<sup>c</sup>65% aqueous EtOH, 1.1% H<sub>2</sub>SO<sub>4</sub>, 170 °C, 60 min [36]<sup>d</sup>60% aqueous EtOH, 1.3% H<sub>2</sub>SO<sub>4</sub>, 180 °C, 60 min [29]<sup>e</sup>80% aqueous EtOH, 0.5% H<sub>2</sub>SO<sub>4</sub>, 170 °C, 60 min [31]<sup>f</sup>50% aqueous EtOH, 1.8% H<sub>2</sub>SO<sub>4</sub>, 180 °C, 40 min [32]

**Table 3** Advantages and disadvantages of other solvents for organosolv pretreatment

Solvent	Advantages/disadvantages	Reference
Butanol	<ul style="list-style-type: none"> <li>– Excellent delignification agent because of its hydrophobicity</li> <li>– Limited miscibility of aqueous butanol leads to higher pretreatment severity, which leads to the formation of pulp with lower hemicellulose content, lower degree of polymerization (<math>DP_w</math>) and increased in pore size</li> </ul>	[33]
Ethylene glycol and glycerol	<ul style="list-style-type: none"> <li>– Pretreatment can be conducted at atmospheric pressure, which reduces energy costs</li> <li>– Effective for the delignification of wood chips</li> <li>– High costs of solvent recovery</li> </ul>	[9, 37]
Organic acids and peracids	<ul style="list-style-type: none"> <li>– Good lignin solvents</li> <li>– Limited because of their corrosive properties</li> <li>– Xylose did not undergo significant conversion to furfural</li> </ul>	[38, 39]
Acetone and ketones	<ul style="list-style-type: none"> <li>– Excellent solvent of lignin for both auto-catalyzed and catalyzed acetone organosolv pretreatments</li> <li>– Almost all hemicellulose solubilized and about 47% lignin can be recovered as organosolv lignin</li> <li>– 50% of acetone-water mixture gives highest lignin recovery (~60%)</li> </ul>	[40, 41]
Phosphoric acid	<ul style="list-style-type: none"> <li>– Pretreatment can be conducted at atmospheric pressure at relatively low temperature (around 50 °C)</li> <li>– High cellulose enzymatic hydrolyzability</li> <li>– Problem of corrosion</li> </ul>	[42]

**Fig. 2** Schematic of a combinative organosolv pretreatment

rate, less severity of cellulose pulp, and less concentration of fermentation inhibitors [43–45]. The pre-extraction of hemicelluloses could also improve the process economics; the hemicelluloses extracted could be used in high-value-added products such as barrier films, coatings, hydrogels, or paper additives [46]. In this approach, a presoaking or prehydrolysis (as the first step) of biomass is involved to hydrolyze the hemicelluloses and is followed by the organosolv delignification process (as the second step) where the solid residue from the first step is retreated (Fig. 2).

The main objective of the two-step processes is to reduce the degradation of carbohydrate fragments into furfural and hydroxymethylfurfural [31, 45]. It was believed that the lignin deconstruction during the prehydrolysis treatment increases the extractability of organosolv lignin through the breaking of lignin–carbohydrate bonds, resulting in smaller lignin fragments. Nevertheless, the deconstruction of lignin is often associated with repolymerization reactions through the formation of



new C–C bondings ( $\beta$ - $\beta$ ,  $\beta$ -1, and  $\beta$ -5) which sometimes still affect the delignification rate and lignin structure. Some common pretreatment/prehydrolysis for combinative pretreatment processes are listed below.

#### 2.4.1 Acid Pretreatment

Acid pretreatment is the most common method that utilizes mineral acids such as hydrochloric acid (HCl) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) for the treatment of biomass. According to Sun and Cheng [28], acidic treatment of lignocellulosic biomass improves the enzymatic hydrolysis of pulp and at the same time gives higher recovery of fermentable sugars. However, the pretreatment with concentrated acids is not suitable in economic and environment perspectives because it is toxic, hazardous, and corrosive to the reactor. Thus researchers have mainly focused on the utilization of dilute acids for the biomass pretreatment. To date, various kinds of dilute mineral acids such as sulfuric, hydrochloric, nitric, phosphoric, and peracetic acids have been experimented with for this pretreatment [47]. Among these acids, sulfuric acid is of interest because of its low cost and efficiency [48]. It was also reported that the dilute sulfuric acid can be used as an alternative for the production of furfural from biomass hemicellulose [49].

#### 2.4.2 Autohydrolysis

Autohydrolysis is a biomass pretreatment with water at very severe conditions (elevated temperatures and pressures). In this process, the lignocellulosic biomass is heated at high temperature and pressure which results in the solubilization of acid components, de-esterification of ester groups, and formation of organic acids in the hemicellulose structure. The resulting organic acid (such as acetic acid) causes a hydrolytic breakdown of hemicellulose which is spontaneously repeated [50]. Because of the mechanistic action of hydronium ions on lignocellulosic biomass, it was believed that the autohydrolysis process selectively dissolves most of the hemicellulose portion which can be recovered in the residual solution [51]. The hemicellulose-rich liquid portion can be used potentially for the synthesis of furfural derivatives or other green chemicals [48].

The removal of hemicellulose from the lignocellulosic biomass would enhance the hydrolyzability of cellulose, leaving the solid pulp rich in cellulose and insoluble lignin residue [52]. Optimization of the operating conditions during autohydrolysis is considered important to ensure the effectiveness of the delignification ability of treated biomass. Brosse et al. [53] have reported that the operation conditions of *M. x giganteus* during autohydrolysis have affected the removal of hemicellulose, delignification yield and the efficiency of cellulose conversion to glucose during enzymatic hydrolysis.

### 2.4.3 Addition of Organic Scavengers in Combinative Pretreatment

Previous studies have shown that hydrothermal treatments such as autohydrolysis could lead to the change in lignin structures and overall delignification yield because of the repolymerization of lignin [54–59]. The repolymerization of lignin through the formation of carbonium ion intermediates produces new linkages of  $\beta$ - $\beta$ ,  $\beta$ -1, and  $\beta$ -5 bonds [60], where the carbonium ion is formed from the lignin phenylpropane units during acidic conditions of autohydrolysis. The resulting lignin after repolymerization is highly condensed and insoluble with high molecular weight which impairs the delignification of any pulping process [48].

It was also demonstrated that the presence of carbonium ion scavengers could substantially improve lignin extractability. These aromatic organic compounds compete with the aromatic rings of lignin during the incorporation of the carbonium ion. Therefore, it scavenges the carbonium ion intermediate from the self-condensation process during autohydrolysis. In a previous study, Wayman and Lora [50] have tested on 40 different types of aromatic compounds in combination with the autohydrolysis pretreatment. They have revealed that 2-naphthol gave lower lignin content in the residual pulp. The utilization of 2-naphthol as lignin–lignin recondensation inhibitor in different feedstocks has been further studied by other researchers [55, 57, 59]. More recently, some authors have studied the effect of adding different carbonium ion scavengers (*o*-cresol, *p*-cresol, hydroquinone, and dihydroxyanthraquinone) [58] on the delignification of *M. x giganteus* and oil palm fronds and it was reported that all organic scavengers used gave different organosolv lignin yields and properties.

### 2.4.4 Enzymatic Pre-hydrolysis

Enzymatic pre-hydrolysis using the industrial enzymatic cocktail Cellulyve<sup>®</sup> (Sigma Aldrich) was assessed as a first step in a pretreatment process of *Miscanteus* biomass involving an aqueous-ethanol organosolv treatment. It was demonstrated that, despite a very low impact on the fiber structure and composition (in terms of sugars and polyphenolics content), the enzymatic pretreatment disrupted the ligno-cellulosic matrix to a considerable extent. This weakening enhanced the removal of lignin during the organosolv pulping and the hydrolyzability of the residual cellulosic pulp for the production of monomeric glucose [44].

## 2.5 Organosolv Lignin and Delignification

Lignin is a natural aromatic amorphous macromolecule, a binder that holds together the lignocellulosic fibers to ensure rigidity of all vascular plants. The polyphenolic structure of lignin is known for its role to provide resistance of both chemical and

biological degradations in woody biomass. Perhaps this is because of the hydrophobic and insolubility nature of lignin in aqueous system that prevents the full access of chemicals and organisms. Generally, it is built up of three major C6–C3 (phenylpropanoid) units: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which form a randomized structure in a 3D network inside the cell wall [61–63].

### 2.5.1 Mechanisms of Organosolv Delignification

It has been acknowledged that the cleavage of aryl ether bonds is responsible for lignin breakdown during organosolv pretreatment. The  $\alpha$ -*O*-aryl ether bonds are more easily cleaved (also known as the rate-controlling step in organosolv delignification) than  $\beta$ -*O*-aryl ether bonds, which are normally broken under more severe conditions, especially at elevated acid concentrations [64, 65]. In the organosolv delignification process, several mechanistic pathways have been proposed: (1) solvolytic splitting of  $\alpha$ -*O*-aryl ether linkages through quinone methide intermediate, (2) solvolytic cleavage via nucleophilic substitution benzylic position by S<sub>N</sub>2 mechanism, and (3) formation of a benzyl carbocation under acidic conditions (Fig. 3). The  $\beta$ -*O*-aryl ether bonds (Fig. 4) can be homolytically cleaved with the loss of  $\gamma$ -methylol groups (as formaldehyde), which later give rise to the formation of stilbenes [32]. Additionally, the cleavage of  $\beta$ -*O*-aryl ether bonds can also form Hibbert's ketone functional groups [66].

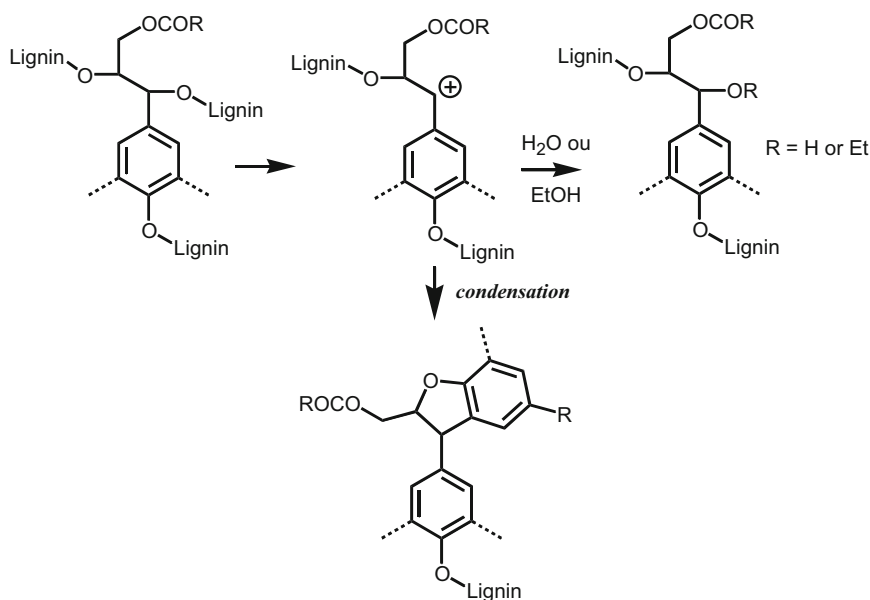
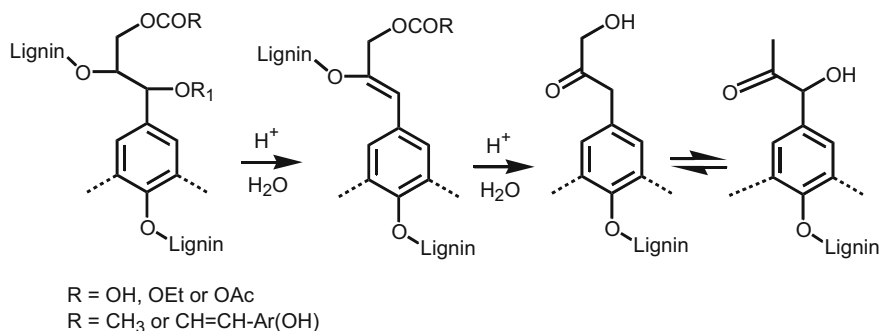


Fig. 3 Solvolytic cleavage of  $\alpha$ -*O*-aryl ether bonds in lignin [66]



**Fig. 4** Solvolytic cleavage of  $\beta$ - and  $\gamma$ -*O*-aryl ether bonds in lignin [66]

Lignin condensation can occur under severe conditions (normally under acidic condition), which are counter-productive to organosolv delignification [15]. In such a situation the lignin condensation occurs when the benzylic carbocation intermediate interacts with the electron-rich carbon atom of a neighboring lignin unit (Fig. 3). Condensation of lignin leads to the formation of high molecular weight (HMW) lignin fractions that are not soluble in organosolv pretreatment solvent, thus making the lignin recovery difficult. It has been reported that lignin condensation reactions can be prevented by blocking the reactive benzyl position (via electrophilic aromatic substitution) with phenolic solvents [15, 64]. In addition, the use of organic scavengers during combinative pretreatments can impede lignin condensation reactions (as mentioned in the previous section).

### 2.5.2 Current Applications of Organosolv Lignin

Much research work is ongoing toward the use of lignin for new green approaches [16]. This includes the use of lignin as dispersant in cement [67, 68], emulsifier [69], chelating agent for heavy metals removal from industrial waste effluents [70], absorbent [71], and phenol formaldehyde adhesives [72, 73] and tannins-based adhesives [74]. Organosolv lignin contains diverse functional groups of phenolic and aliphatic  $-\text{OH}$ , carbonyls, and carboxyls, which can also act as neutralizer or inhibitor in oxidation processes, via stabilizing reactions induced by oxygen radicals and their respective species. Thus, recent studies have been done on the applicability of lignins from different sources as potential antioxidants [57, 58, 75–77]. Hussin et al. [76] have revealed that organosolv lignin has a good antioxidant tendency with an inhibitive value of 60%. The antioxidant properties exhibited by lignin can lead to broader applications as anti-microbial, anti-aging agents and corrosion inhibitors. Recent findings have agreed that organosolv lignin and its derivatives possess inhibitive properties toward the corrosion of metals in corrosive media [76, 77]. Potential high-value products could also be produced from isolated lignin; these include low cost carbon fiber, engineering plastics and

thermoplastic elastomers, polymeric foams and membranes, and a variety of fuels and chemicals all currently sourced from petroleum [17]. However, the complexity and the multifunctional nature of lignin have yielded multiple extraction product streams, which require extensive separation and purification procedures. Proper modification/alteration of the organosolv lignin structures is still required to increase its applicability.

### 3 IL Pretreatments

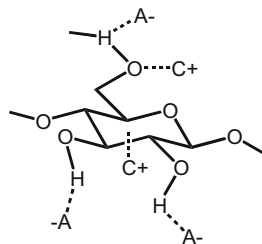
Lignocellulose pretreatment for the production of bioethanol using ILs as solvent is an organosolv technology receiving growing interest from the biofuels community. ILs have been developed as a potentially ‘greener’ alternative to organic solvents. ILs are salts that are in liquid state at ambient temperatures. ILs present a high thermal stability (~200–250 °C) and a low vapor pressure. ILs have often been called green solvents mainly because of their negligible vapor pressure, which mitigates any emissions of volatile organic compounds (VOCs). The possible number of combinations cations/anions is huge although only around 100 ILs are described in the literature to this day. It is thus possible to modulate their physico-chemical properties (melting point, viscosity, density), except for vapor pressure which always remains extremely low [78].

The capacity of certain ILs to solubilize the (ligno) cellulose and to increase its enzymatic digestibility [79] has also been highlighted. The advantages are that ILs do not inhibit cellulose hydrolysis enzymes or accelerate enzymatic hydrolysis. The ILs can be supplemented with an antisolvent such as water, ethanol, or acetone for better cellulose regeneration, and can be recovered and recycled [80].

#### 3.1 *IL in Biomass Dissolution*

Biomass dissolution is dependent on variables such as type and size of biomass, IL/biomass ratio, temperature and time of dissolution, and water content in the solution mixture. The dissolution of cellulose and lignocellulosic biomass has been extensively reviewed in recent years [19, 81–85]. ILs have been found to influence the biomass dissolution via several mechanisms. The lignocellulose dissolution is induced by the formation of electron donor–electron acceptor interactions (1) between cellulose oxygens and the cations of ILs and (2) between cellulose hydrogens and the anions of ILs [83]. It was shown that the dissolution is promoted by the presence of a high chloride concentration and activity of [BMIM][Cl] which is responsible for breaking the hydrogen bonding network of cellulose [79]. The imidazolium cation has also been proposed to have hydrophobic interactions with the hydrophobic side of the cellulose [86, 87] (Fig. 5).

**Fig. 5** Proposed dissolution mechanisms for cellulose in ILs



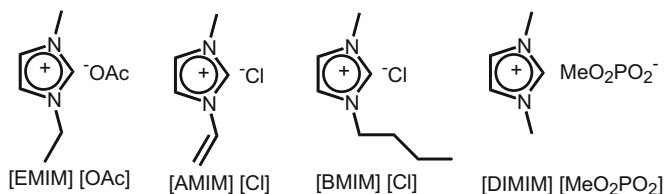
**Table 4** Application of ILs for dissolution of lignocellulosic biomass

IL	Biomass	Loading (w/w)	Particle size (mm)	Conditions	References
[C2MIM][OAc]	Pine	5%	<0.125	175 °C, 30 mn	[93]
	Oak	5%	0.25–0.50	185 °C, 7 mn	[94]
	Spruce	5%	0.1–0.5	115 °C, 72 h	[95]
	Miscanthus	4%	4	130 °C, 8 h	[96]
[BMIM][OAc]	Corn stover	10%	<4	140 °C, 3 h	[97]
	Spruce	5%	0.3–0.8	120 °C, 1 h	[98]
	Rice hulls	10%	1.5	110 °C, 8 h	[99]
[BMIM][Cl]	Pine	5%	0.25–0.5	110 °C, 16 h	[94]
[C2MIM][Cl]	Beech	3%		120 °C, 24 h	[100]

These interactions lead to the disruption of the intra/inter-chain H bond network of cellulose and thus to its dissolution. These mechanisms of dissolution are enhanced by effective stirring and microwave and ultrasound irradiation [88–90]. Dissolution improvements have also been associated with hydrogen bond basicity of the IL anion such as  $[\text{CH}_3\text{COO}^-]$  wherein strong hydrogen basicity are effective in weakening the hydrogen bonding network of the polymer chains [91, 92]. However, increased hydrogen bond basicity could lead to the incorporation of water molecules in the IL structure, thus reducing the dissolution of biomass. Another important parameter to be considered is the viscosity of ILs that has an impact on the mixing and mass transfer of lignocellulose and the IL itself. Low viscosity ILs are able to extract higher amounts of carbohydrates from bran [92]. Table 4 summarizes recent examples of lignocellulosic dissolution in ILs.

### 3.2 ILs in Pretreatment of Biomass

In view of some of the drawbacks of the classical methods of biomass pretreatments (recycling issues, toxicity, hazardousness, etc.), application of ILs is an alternative solution. However, the complexity of the biomass matrix and ILs themselves makes



**Fig. 6** The most used ILs for lignocellulosic pretreatment

the process very challenging. Among the advantages of the pretreatment with ILs are (1) the physicochemical properties of the biomass macromolecular components could be altered, (2) the specific property of the IL enables specific macromolecular components to be extracted, and (3) different fractionation approaches after biomass dissolution in IL could be performed. The success of the pretreatment is dependent on the IL, lignocellulosic biomass (type, moisture, size, and load), temperature, time of pretreatment, and the precipitating solvent. By far, [EMIM][CH<sub>3</sub>COO<sup>-</sup>], [AMIM][Cl<sup>-</sup>], [BMIM][Cl<sup>-</sup>], and dialkylimidazolium diphosphonates have been considered as the most suitable ILs for the pretreatment of lignocellulosic biomass because of their good solvent power (Fig. 6).

The use of [EMIM][CH<sub>3</sub>COO<sup>-</sup>] for various types of biomass utilizing pretreatment processes of various conditions has been reviewed extensively by da Costa Lopes et al. [101]. With the use of ILs in these pretreatments, cellulose, hemicellulose, and lignin fractions were obtained with higher purity than with conventional methods. Following the pretreatment step, different fractionation approaches for selective fraction separation can be applied using the specific properties of ILs. The entire process was found to be more economical than other conventional pretreatments such as alkali and acid pretreatments with respect to the energy consumed.

Recent approach to biomass pretreatment involves the addition of water to the dissolution process. This new approach allows the usage of small amounts of IL, easier processing operations because of reduced viscosity, and recycling of the aqueous IL mixtures is facilitated. In one of the earlier works to pretreat wood flour, a blend of 5% and 10% of water and [EMIM][CH<sub>3</sub>COO<sup>-</sup>] yielded a decrease in glucose and xylose that is attributed to a moderate inter-crystalline swelling effect with the wood fibers still intact and the crystallinity and lignin content being greater than in pure IL [102].

### 3.3 Enzymatic Saccharification of IL Pretreated of Biomass

For biofuel production, the polysaccharide fraction must be depolymerized into monomers before a fermentation step. The saccharification yield (e.g., monomeric glucose yield) is an important measure of the success of any lignocellulose pretreatment and remains as one of the critical bottlenecks. The development of

**Table 5** Example of recent studies using ILs and glucose yields after enzymatic hydrolysis

Biomass	IL	Conditions	Glu%	References
Corn cob	Choline chloride and imidazole	15 h, 150 °C	94	[104]
Corn stover	[EMIM][OAc]	3 h, 110 °C	88	[105]
Softwood	[BMIM][Cl]	15 h, 130 °C	78	[106]
Miscanthus	DMIMMPH	6 h, 100 °C	72	[107]
	[BMIM][Cl]		68	
	[EtOHMIM][Cl]		66	
	[EMIM][SCN]		44	
	[DMIM][MPh]		72	
Spruce	[DMIM][MPh]	40 min, 110 °C	73	[108]
Oak	[DMIM][MPh]		79	
Douglas	[C2MIM][Ac]	3 h, 160 °C	92	[109]
Maple	[BMIM][OAc]	24 h, 90 °C	74	[102]
Willow	[BMIM][HSO <sub>4</sub> ] + 20% H <sub>2</sub> O	22 h, 120 °C	81	[110]
Miscanthus	[BMIM][OAc]	6 h, 110 °C	91	[111]
Typha			82	

new and efficient IL-tolerant lignocellulosic enzymes to attain simultaneous pretreatment and saccharification is attracting vigorous scientific attempts [18, 103]. To date, the saccharification experiments have generally been performed after IL pretreatment (through separation of the cellulosic pulp from the IL liquor) and then adding the enzymes. Recent examples of glucose yields after enzymatic saccharification of IL treated and washed biomass are given in Table 5. Pretreatments with ILs permit the removal of a large part of the lignin and the hemicelluloses, increasing the porosity of the biomass and the accessibility of the cellulose fraction to hydrolytic enzymes.

Combinative pretreatments have also been proposed with ILs: a prehydrolysis step using aqueous ammonia, sodium hydroxide, or dilute sulfuric acid followed by treatment with ILs ([EMIM][OAc] and [BMIM][OAc] were reported to improve cellulose recovery and enzymatic glucose conversion) [111, 112].

### 3.4 IL Recycling

Because ILs are more expensive than conventional pretreatment agents, such as sulfuric acid, reusability of recycled ILs is a crucial factor to be considered economically. Generally, after the regeneration process, a mixture of antisolvent (antisolvent is a solvent in which the compound is less soluble), dissolved IL, and soluble biomass compounds are present. These compounds can be recovered with proper fractionation steps which allow limitation of the deactivation of enzymes because of high concentrations in residual IL in the medium [80, 113]. In fact it was demonstrated that low concentrations of ILs, such as [EMIM][OAc] or [BMIM]



[Cl], provoked an important decrease of the cellulase activity [114, 115]. Audu et al. [111] studied the recyclability of [BMIM][OAc] during the pretreatment of typha grass. The IL was recovered after precipitation of the pulp with an antisolvent (water or ethanol), dried under reduced pressure, and reused for up to 20 cycles. Treatment of the recycled IL at the 10th and 15th cycles (by washing with an acetone/water solution) enabled recovery of about 93% of the IL-soluble lignin released into the liquid stream and improved the effectiveness of the process [111]. To date, three types of IL recovery processes have been developed, the easiest way being evaporation of the antisolvent after the regeneration process with 94–98% recovery for legume straw. The drawback of this method is that some impurities may still be present in the IL [116]. Alternatively, IL recovery can be achieved by their ability to form a biphasic liquid–liquid system with the addition of an aqueous solution of a kosmotropic anion such as phosphate or sulfate whereby the salting-out effect leads to precipitation of a solid-phase rich in cellulose. The main advantage of this process is the decreased amount of water in the IL to be evaporated, thereby reducing energy costs [117]. For the third process, as proposed by Dibble et al. [97] when using [EMIM][CH<sub>3</sub>COO<sup>-</sup>], an antisolvent mixture of ethanol and acetone creates a quaternary solution of IL–water–ketone–alcohol that would be separated accordingly. This process requires minimal addition of reagents and minimal IL degradation and resulted in 89% of the initial IL.

As presented above (Sect. 2.5.2), the organosolv lignin fraction is potentially valuable for new applications. In the case of IL pretreatment, a two-stage process appears promising for lignin recovery. After the precipitation of the cellulosic pulp using a protic solvent, the lignin fraction is precipitated from the solution through acidification, which lowers the lignin solubility [94].

### 3.5 *Techno-Economic Analysis of IL Pretreatment*

IL pretreatments present several advantages over other pretreatment technologies, including low solvent toxicity, high monomeric sugar yields, short saccharification times, and efficient delignification. Nevertheless, there are several issues to overcome before commercialization and this new technology is facing great challenges with respect to its economic viability. These include (1) the high cost of ILs, (2) a lack of knowledge regarding the industrial processes to be developed for a biorefinery based on these solvents, and (3) the ability of the co-products of the pretreatment (lignin and hemicelluloses) to make significant impact as a substitute for fossil resources [118]. To address these challenges, the development of suitable IL regeneration technologies, including the removal of impurities and the understanding of their mechanism of formation, is essential. The development of new low-cost ILs and the reduction of IL loading are also important. Klein-Marcuschamer et al. [119] demonstrated that reducing IL cost could be the most important challenge which could positively impact the competitiveness of the whole process.

## 4 Conclusions and Recommendations

Development of technology for generating biofuels and platform molecules from lignocellulosic biomass is arousing a growing interest. Organosolv pretreatments are especially promising in this context because (1) they are capable of fractionating lignocellulosic biomass into separate streams rich in lignin, hemicellulose, and cellulose, (2) they produce a cellulosic pulp which is very amenable to enzymatic deconstruction and subsequent fermentation, and (3) they produce large amounts of lignin fractions which are relatively pure, unaltered, sulfur-free, and less condensed than other pretreatment lignins. All around the world, pilot plants based on the organosolv biorefinery concept are being progressively established. There are tremendous opportunities for future research and industrial developments in this area, including (1) development of efficient solvent and co-product recovery systems, (2) pre-extraction of hemicelluloses and extractive compounds and their contribution to improving process economics, and (3) development of ILs-based processes. Thus, the future development of organosolv pretreatment should be focused on the integrated utilization of biomass components and decrease of the pretreatment costs.

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