

Review

# Biomass and Cellulose Dissolution—The Important Issue in Renewable Materials Treatment

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**Abstract:** Sustainable development strategies, as well as the shift toward a circular bioeconomy, has led to high interest in the development and implementation of technologies that efficiently utilize biomass as a raw material. Switching from fossil-based to bio-based resources requires the consideration of many new challenges and problems. One of the crucial issues is the solubility of lignocellulose or at least its ingredients. According to the trends and legislation, the selected chemicals and methods of dissolution/treatment should also be environmentally friendly. The pretreatment processes prepare biomass for further transformations (e.g., chemical, thermal including pyrolysis, or biological) to valuable products such as biofuels, bio-oils, Fine Chemicals, solvents, plastics, and many others. This review discusses the latest findings on the dissolution of biomass and its ingredients. The application of novel, green solvents such as ionic liquids or deep eutectic solvents is discussed in detail. The impact of the composition and structure of these solvents on the biomass/cellulose dissolution process, as well as the mechanism of cellulose–ionic liquid interaction, is presented. Some novel achievements in the usage of inorganic salts and specific metal complexes are also overviewed.

**Keywords:** lignocellulose; dissolution; inorganic salts; ionic liquids; deep eutectic solvents; delignification



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## 1. Introduction

The depletion of fossil resources, as well as extreme environmental pollution, resulted in several strategies and regulations on the use of renewable raw materials and the development of greener, environmentally friendly technologies.

The trends are also reflected in world politics. For example, starting in 2020, the development of the energy sector in the European Union is focused on renewable energy sources (RES), such as solar energy (photovoltaics), wind energy (wind farms), hydropower (hydropower plants), or biomass [1].

The problem with limited fossil resources and the negative environmental impact of fuels based on crude oil derivatives is very serious, so the strategy of many countries is to replace vehicles running on diesel or gasoline with electric ones. However, sustainable development does not only apply to energy. It is also necessary to increase the use of renewable raw materials in the chemical industry, ensuring biodiversity and environmental protection. Lignocellulosic biomass plays a crucial role in renewable materials and can be used in the production of so-called biochemicals. According to the report “Biomass production, supply, uses and flows in the European Union”, prepared for the European Commission, annual biomass production in Europe is estimated at 1466 Mt of dry matter (agriculture 956 Mt and forestry 510 Mt) [2].

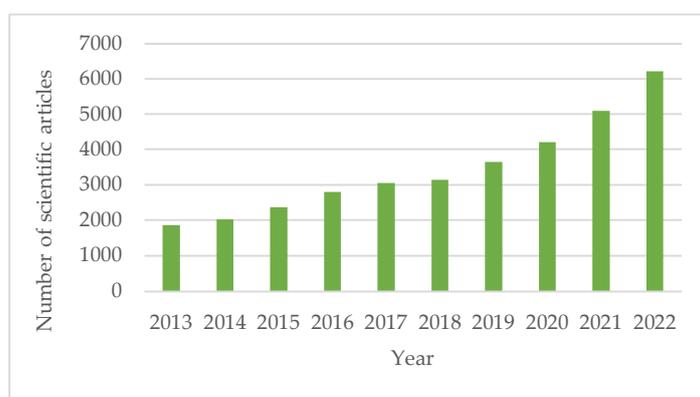
It is estimated that almost 50% of the world’s biomass is lignocellulosic biomass, which is not used as food and has a higher energy value than the world’s demand. For this reason, lignocellulosic biomass is the subject of many studies, aimed at developing efficient methods of its processing. The first goal of biorefineries is to selectively separate the major constituents of biomass (cellulose, hemicellulose, and lignin) and transform them

into valuable bioproducts. This includes the production of *Fine Chemicals* and solvents (e.g., lactic acid, furfural, levulinic acid, 5-hydroxymethylfurfural), biofuels (e.g., bioethanol), or energy (Figure 1).



**Figure 1.** Possible methods of biomass processing in chemical industry.

The interest in biomass treatment is growing each year, which is reflected in the number of publications, e.g., in ScienceDirect (Figure 2).



**Figure 2.** Number of publications for “lignocellulosic biomass” term (according to ScienceDirect).

Biomass pretreatment is an important part of its further conversion and can be classified as physical, physicochemical, chemical, and biological. In many cases, the combination of several methods is used. Selection of the appropriate pretreatment method depends on many factors, e.g., the type of biomass, further conversion methods, or desired products. The goal of this step is to obtain more homogeneous raw materials and overcome all handling difficulties. After pretreatment, the biomass is more susceptible to further transformations (chemical, enzymatic, chemoenzymatic, or thermal) into desired products. When the production of biofuels is considered, many thermal methods have been investigated (e.g., torrefaction, gasification, pyrolysis, and hydrothermal methods). One of the most promising methods is the pyrolysis of biomass (biomass degradation under elevated temperature, in the absence of oxygen), where biofuels, bio-oil, biogas, and biochar can be produced [3].

The dissolution of lignocellulose and/or extraction of its constituents is an important issue, prior to any further transformations to value-added chemicals. In this paper, we discuss novel, environmentally friendly methods and solvents for effective biomass and biomass constituent dissolution. Ionic liquids and deep eutectic solvents are discussed in detail.

## 2. General Characteristics of Lignocellulosic Biomass

The three main components of lignocellulosic biomass are cellulose (35–83% of dry mass), hemicelluloses (0–30%), and lignin (0–43%) [4–6]. It also contains small amounts of other molecules such as proteins, pectins, waxes, and minerals. The type and content of these ingredients depend on the type of plant, e.g., grain husks (rice, wheat) and corn cobs

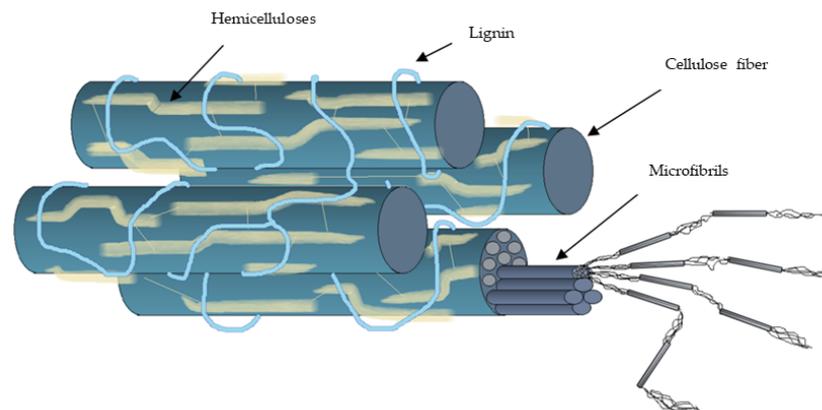
are rich in silicon dioxide, while carbonates and phosphates can be commonly found in wood (e.g., willow) [7–9].

The content of cellulose, hemicelluloses, and lignin depends on the type of plant, as well as its part, age, and cultivating conditions. Generally, wooden species tend to have a higher amount of lignin compared to green and softer plants such as grass. In Table 1, the content of cellulose, hemicelluloses, and lignin in several examples of different plants is presented.

**Table 1.** Content of cellulose, hemicelluloses, and lignin in different types of lignocellulosic biomass.

Type of Biomass	Content [%]			References
	Cellulose	Hemicelluloses	Lignin	
Grass	28.8–38.0	18.4–30.0	4.0–17.5	[10,11]
Sawmill wood chips	35.0–50.0	15.0–39.0	20.0–34.0	[6,12]
Walnut shells	25.6	22.7	29.9–52.3	[6,13]
Hazelnut shells	25.9	29.9	42.5	[14]
Walnut tree wood	40.8–49.8	33.4	21.8–29.1	[15]
Olive tree wood	31.5–31.9	11.3–15.5	32.5	[16]
Softwood	35.0–45.2	25.0–31.3	21.7–30.0	[14,17]
Hardwood	45.0–50.0	20.0–25.0	20.0–28.0	[14,17]
Poplar	42.7	21.7	26.9	[18]
Willow	44.3	22.6	25.1	[18]
Pine sawmill chips	44.0	26.0	26.0	[19]
Pine bark	19.0–21.9	18.3–25.0	38.0–40.7	[18,20]
Spruce bark	29.7	13.9	45.1	[18]
Olive tree leaves	5.7–8.5	3.8–5.4	39.6	[16]
Wheat straw	28.8–40.0	20.0–39.1	15.0–20.5	[14,17,18]
Switchgrass millet	30.0–50.0	10.0–40.0	5.0–20.0	[17]

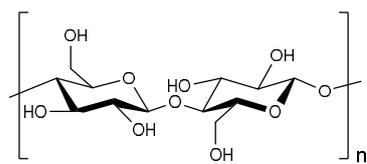
Cellulose is a structural component of cell walls and occurs as microfibrils. A higher number of tightly packed cellulose chains increases the mechanical strength, as can be observed in hard biomass (e.g., wood) [21–23]. Physical resistance is also improved by hemicelluloses, which are responsible for binding cellulose fibers to lignin [24,25]. The major chemical, enzymatic, and mechanical resistance of plant cells is provided by lignin, which is present in the external part of lignocellulose [26,27]. The general structure of lignocellulosic biomass is presented in Figure 3.



**Figure 3.** General structure of lignocellulose.

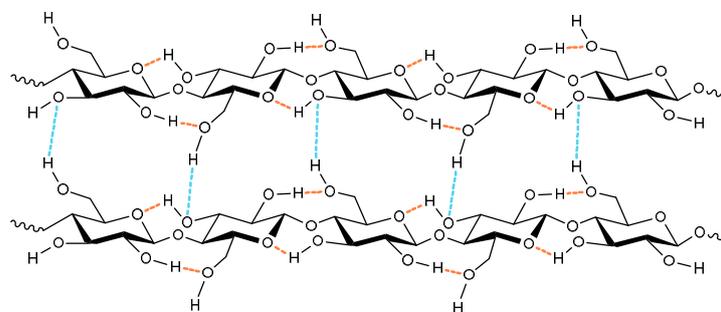
### 2.1. Cellulose

Cellulose is a homopolymer consisting of D-glucose monomers, linked by  $\beta$ -1,4-glycosidic bonds (Figure 4).



**Figure 4.** General chemical structure of cellulose.

A high number of hydroxyl groups on the surface of cellulose enables the formation of hydrogen-bond networks and van der Waals linkages. They stabilize the cellulose molecule and significantly improve its dissolution resistance (Figure 5) [28]. The amphiphilic character of cellulose, derived from the axial hydroxyl groups and ring surface CH groups, dictates the selection of the appropriate solvent [29,30]. The study has shown that the use of organic co-solvents (e.g., ethanol, acetone,  $\gamma$ -valerolactone, and tetrahydrofuran) in water can significantly reduce the number of hydrogen bonds formed between the cellulose chains and solvent [31].

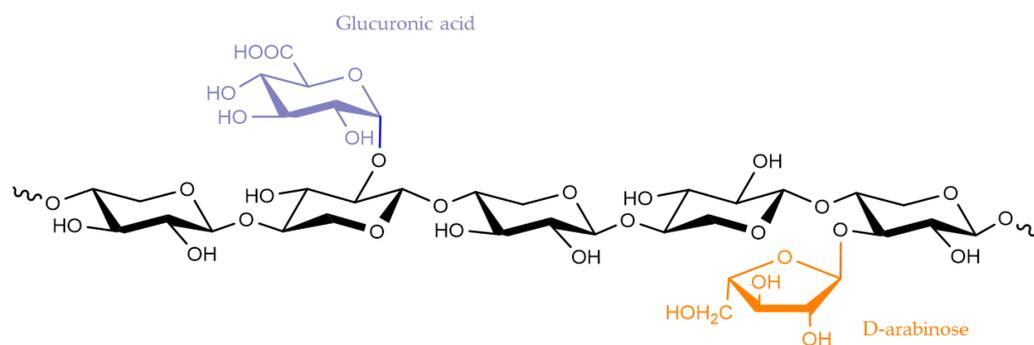


**Figure 5.** Hydrogen bonds present in cellulose structure.

Cellulose consists of crystalline and amorphous domains. The content of highly ordered, tightly packed crystalline regions in cellulose depends primarily on the type of plant, e.g., wood biomass has many regions with high crystallinity (up to 65% crystalline regions), which makes it insoluble in water and much more chemically and mechanically resistant [22,32]. Loosely arranged molecular chains are called amorphous regions [33]. In order to increase the reactivity, solubility, and susceptibility to the transformation of natural cellulose, the crystalline structure has to be destroyed to obtain an amorphous, or at least amorphized, biopolymer [34].

## 2.2. Hemicelluloses

Hemicelluloses are heteropolymers, consisting primarily of six-carbon sugars such as mannose, glucose, fucose, and galactose and five-carbon sugars such as arabinose and xylose. Therefore, several types of hemicelluloses are distinguished due to the dominant saccharide in the polymer structure, such as xylans, mannans, galactans, glucans, glucomannans, and arabinogalactans [35,36]. The sample chemical structure of xylan hemicellulose is presented in Figure 6.

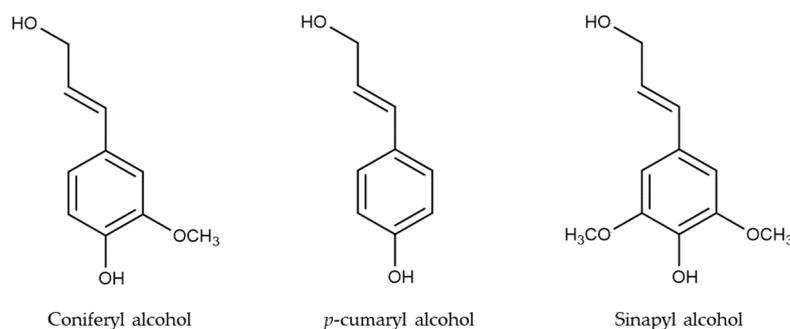


**Figure 6.** Chemical structure of xylan hemicellulose.

The chemical composition mainly depends on the type and part of the plant. Generally, hardwood contains a higher amount of xylan than softwood [37]. For example, in sapwood of broad-leaved trees, the main component in hemicellulose is xylose (approximately 80%), but in the leaves from the same species, the content of galactose and arabinose is higher (15% and 25%) [38].

### 2.3. Lignin

Lignin is an amorphous heteropolymer with both aliphatic and aromatic fragments. The main precursors are monolignols: *p*-coumaryl, coniferyl, and sinapyl alcohols (Figure 7) [39]. Depending on the source, different contents of particular precursors can be found in the lignin structure, e.g., softwood lignin contains mainly coniferyl alcohol, while in hardwood, coniferyl alcohol and sinapyl alcohol predominate. Grass lignin also contains *p*-coumaryl alcohol. The monomers are linked by ether bonds C-O-C and C-C bonds. In biomass, lignin forms a matrix with polysaccharides, which increases the physical strength of tissue and makes it more resistant to chemical and enzymatic transformations [26,32,40,41].



**Figure 7.** The main precursors of lignin.

Natural lignin is insoluble in water and organic solvents. A major part of it is also insoluble in acid solutions (Klason's lignin) and shows better solubility in alkaline solutions [42]. The lignin solubility can be changed via processing or chemical modification, e.g., in the Kraft process, the majority of hydroxyl groups are sulfonated, which makes it more susceptible to solubilization, even in organic solvents such as DMSO [43,44]. Because of this, delignification is one of the main methods of lignocellulose pretreatment. This process allows one to loosen the rigid structure of biomass and make the cellulose and hemicelluloses more accessible for chemicals and enzymes [45,46].

## 3. Dissolution of Biomass and Its Components

Biomass pretreatment and/or fractionation is a key step of the lignocellulose transformation into valuable products. Thanks to the diverse properties of cellulose, lignin, and hemicellulose, it is possible to fractionate the lignocellulose. There are several classic

methods, applying strong acids (e.g.,  $H_2SO_4$ ) or bases (e.g., NaOH), but such media are harmful, corrosive, and have a high negative impact on the environment. Additionally, after the treatment of biomass with alkaline or strong acid solutions, extra water washing steps are required to neutralize the mixture and remove the impurities before further transformations. It results in the need for the disposal of a large amount of wastewater. Because of that, new methods are constantly being developed, with the application of green solvents such as ionic liquids or deep eutectic solvents. The choice of the most suitable solvent depends on the type of biomass/biomass fraction, as well as on further conversion methods and the desired final product. Moreover, the characteristics of a solvent should be taken into consideration, such as toxicity, corrosivity, and thermal stability. In this chapter, all the major groups of solvents used in the dissolution of biomass and its components, especially cellulose and lignin, are discussed. Since classic alkaline and acidic solutions have been discussed in many papers, they will only be mentioned, and major attention will be paid to other, novel systems.

### 3.1. Alkaline Solutions

Cellulose is prone to swelling in alkaline solutions, such as sodium hydroxide or lithium hydroxide, but because of its amphiphilic character, it is not suitable to dissolve it completely [47]. Additionally, in the presence of NaOH, cellulose tends to form aggregates. In order to avoid this, the addition of chemicals preventing aggregation, e.g., urea, thiourea, and polyethylene glycol (PEG), is employed [48]. However, even in the presence of these agents, alkaline solutions are not very efficient at dissolving cellulose, e.g., in a NaOH/PEG mixture (a concentration of NaOH of 9%), only 13% of the biopolymer was dissolved [30,49,50].

Although cellulose dissolution in alkaline solutions is not effective, these solvents are capable of dissolving lignin. For instance, in an 18% NaOH solution, 66.6% (wt.%) of lignin from eucalyptus chips could be dissolved [51]. Hydroxyl groups, present in an alkaline solvent, can interact with lignin phenolic monomers, which results in polymer fragmentation to smaller molecules. Moreover, in alkaline conditions, linkages between lignin and polysaccharides can break [51,52]. However, because of the major disadvantages of alkaline solutions, which make them less attractive from an ecological point of view, they are not considered future solvents for biomass processing.

### 3.2. Acid Solutions

Acid solutions are commonly known for their ability to dissolve cellulose. Diluted acids can be applied for cellulose swelling, but in order to dissolve cellulose completely, more concentrated acids are needed. The treatment of lignocellulosic biomass with diluted acid solutions (lower than 5%) under a moderate temperature and pressure causes the degradation of hemicellulose to monomers. It is a possible way to separate hemicellulose from other components [53]. Sulfuric and hydrochloric acids are the most frequently used agents for cellulose dissolution. Concentrated sulfuric acid (approximately 70%) can break hydrogen bonds in cellulose. Additionally, it has to be taken into account that the esterification of hydroxyl groups in cellulose can occur, which results in replacing hydroxyl groups with sulfate. These processes lead to cellulose depolymerization [54]. Since Klason's lignin is insoluble in sulfuric acid, this method can be used in its separation from plant biomass [55]. Acidic biomass treatment also causes the further transformation of sugars into furfural and 5-hydroxymethylfurfural. Additionally, in the presence of strong acids, polymeric, insoluble polymers called humins are produced, which can significantly decrease the yield of valuable products produced in biomass transformations (e.g., glucose, fructose, levulinic acid, etc.) [56,57].

Organic acids, e.g., trifluoroacetic acid, dichloroacetic acid, and formic acid, can also be applied in biomass processing. This leads to the dissolution of cellulose via derivatization of hydroxyl groups to acyl groups [58].

### 3.3. Inorganic Molten Salt Hydrates

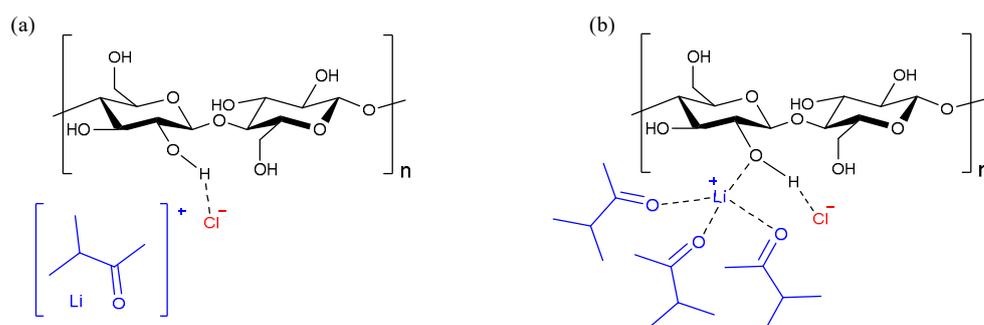
Inorganic molten salt hydrates such as  $\text{Ca}(\text{SCN})_2 \cdot 3\text{H}_2\text{O}$  can dissolve cellulose at 120–140 °C within 40 min, without any additional pretreatment. Other salts or their mixtures can act differently: From dissolving this polysaccharide (e.g.,  $\text{ZnCl}_2 \cdot 3\text{-}4\text{H}_2\text{O}$ ,  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ ; or  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) or swelling it (e.g.,  $\text{LiCl} \cdot 2\text{-}5\text{H}_2\text{O}$ ,  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Mg}(\text{ClO}_4)_2/\text{H}_2\text{O}$ ; or  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{NaClO}_4/\text{H}_2\text{O}$ ), and even decomposing it ( $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZnCl}_2/\text{MgCl}_2/\text{H}_2\text{O}$ ; or  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) [48,59]. The ability to dissolve this polymer depends on the level of hydration, e.g., by increasing water content in lithium perchlorate to  $\text{LiClO}_4 \cdot 4\text{H}_2\text{O}$ , cellulose solubility decreases [60]. Iron salts can also be effectively applied in biomass pretreatment, especially upon dissolving hemicelluloses.  $\text{FeCl}_3$  and  $\text{FeSO}_4$  can dissolve this fraction at a level above 90%. In this process, cellulose is intact, so it could be used as a method for the separation of these fractions [61,62]. Biomass pretreatment with inorganic salts can also prepare the material for enhanced enzymatic transformations, without delignification. Zhang et al. used  $\text{AlCl}_3$  with intense mechanical milling of sugarcane bagasse. It resulted in a significant reduction of biomass crystallinity and more efficient further biological hydrolysis of cellulose [63]. Nevertheless, applying inorganic salts has many disadvantages—they are expensive, unstable, toxic, and difficult to regenerate after processing [64].

### 3.4. Metal Complexes

Metal complexes containing a transition metal and an amine or ammonium component are good solvents of cellulose. One of the important examples is Schweizer's reagent ( $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{OH})_2$ ), which was originally used in the production of artificial silk. Today, many alternatives exhibiting good solution properties are known, e.g.,  $[\text{Cu}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_2](\text{OH})_2$  (Cuoxen),  $[\text{Ni}(\text{NH}_2\text{CH}_2\text{CH}_2)_3\text{N}](\text{OH})_2$  (Nitren),  $[\text{Pd}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)](\text{OH})_2$  (Pden), and  $[\text{Cd}(\text{NH}_2(\text{CH}_2)_2\text{NH}_2)_3](\text{OH})_2$  (Cadoxen). The last one was very efficient in dissolving cellulose with high DP. The mechanism involves deprotonation and coordinative binding of hydroxyl groups in the C2 and C3 positions of the anhydroglucose units [59,65,66].

### 3.5. Inorganic Salts in Organic Solvents

Cellulose can be effectively dissolved in an *N,N*-dimethylacetamide solution of lithium chloride ( $\text{LiCl}/\text{DMAc}$ ) [67–69]. It is possible to dissolve up to 16% of the polymer present in various biomass sources, e.g., wheat straw, wood waste, and sugar cane bagasse, at 85 °C [70]. There are two proposed mechanisms of this process, both based on hydrogen bonding occurring between glucose monomers and chlorine anions, which results in the formation of the  $\text{Li}^+(\text{DMAc})_x$  cation complex. The first mechanism (Morgenstern) suggests direct linkages between lithium cation and hydroxy group oxygen atoms. The second one (McCormick) states that this type of hydrogen bond does not occur. Instead, the cellulose structure is charged negatively because of interactions with the chlorine ion. It results in cellulose fibers spreading apart and polymer solvation. Figure 8 presents both of these simplified mechanisms [67,70,71].



**Figure 8.** Proposed mechanisms of cellulose dissolving in  $\text{LiCl}/\text{DMAc}$  solution: (a) McCormick mechanism, (b) Morgenstern mechanism.

The combination of LiCl with DMAc is unique because only this certain mixture is able to dissolve cellulose effectively. By changing lithium to another metal or replacing DMAc (e.g., with DMF), the efficiency of the solvation effect decreases. Despite many advantages of LiCl/DMAc (the limitation of side effects, no need for applying additional chemicals), it was not introduced into the industrial scale due to the long processing time, high price, toxicity, corrosivity, and vapor pressure of solvent [70].

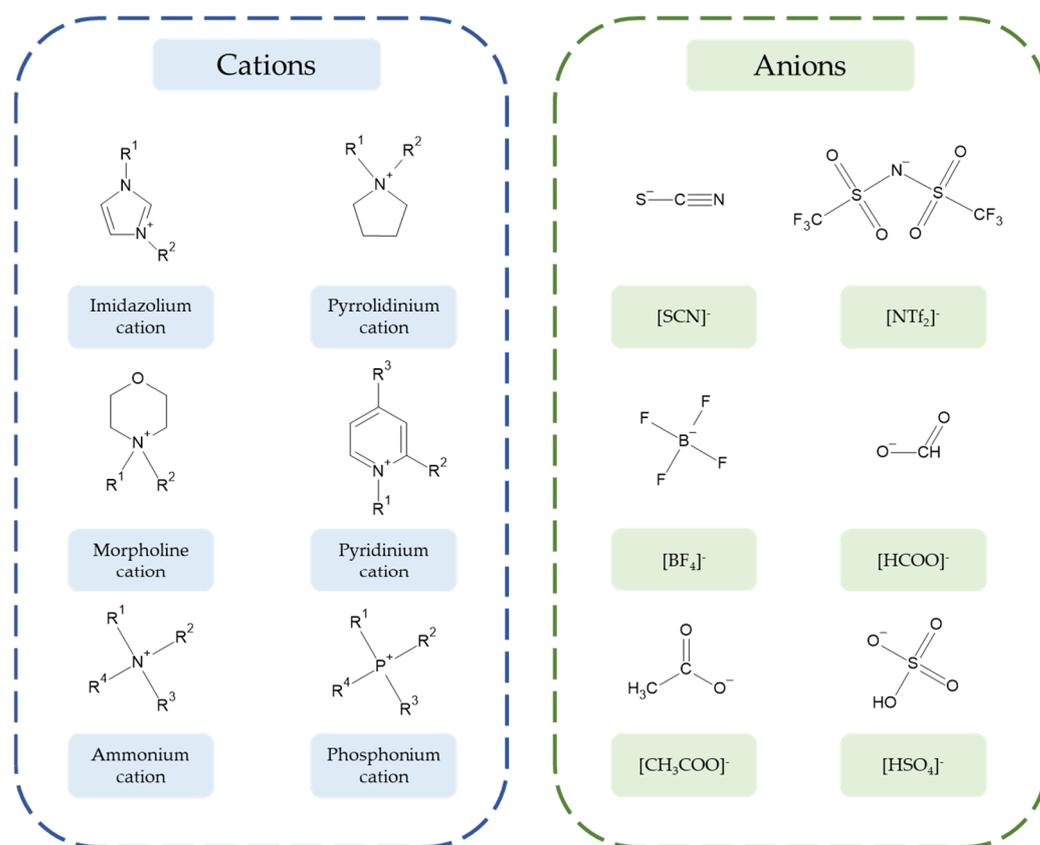
Another mixture that could be applied to dissolve cellulose is DMSO with tetrabutylammonium fluoride (TBAF). Similar to the previous example, changing fluoride to other anions causes a decrease in the effectiveness of such a mixture [72]. Fluoride is a very strong hydrogen bond acceptor. It has the ability to efficiently reduce the interaction between cellulose chains by competing with the hydroxyl and acetal oxygen atoms of cellulose. The other anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) are not strong enough [73,74]. Additionally,  $\text{TBA}^+$  cations prevent cellulose aggregation, which additionally enhances the process [75]. The main problem with TBAF application is its high hygroscopicity. The presence of a small amount of water causes an increase in viscosity and gelation [73]. Additionally, water is able to remove the fluoride anions from the cellulose chains, which results in the reformation of hydrogen bonds between cellulose chains. Anhydrous TBAF is unstable and expensive. The commercially available trihydrate  $\text{TBAF}\cdot 3\text{H}_2\text{O}$  is an alternative to be used in cellulose treatment [48,76].

### 3.6. Ionic Liquids

There are many problems and limitations related to the application of the above-mentioned organic and inorganic solvents in biomass treatment, such as toxicity, corrosivity, high vapor pressure, and negative impact on the environment. It leads to intense activity in academic and industrial investigations to find more ecological alternatives. Ionic liquids are one such alternative, composed of organic cations and organic or inorganic anions. Because of the wide range of components, which can be used in ionic liquids, it is possible to alter their properties to the specific process. Many advantages of ionic liquids, such as a melting point below  $100\text{ }^\circ\text{C}$ , miscibility with many chemicals, low vapor pressure, chemical and thermal stability, non-flammability, and low toxicity, make them an ecological, green alternative to classic solvents [77]. Ionic liquids can be applied to many various chemical processes, and one of them is biomass transformations. In Figure 9, the most frequently applied ionic liquids are presented [78].

#### 3.6.1. Ionic Liquids in Biomass Dissolution

Ionic liquids (ILs) can be applied in biomass pretreatment before further transformations into valuable products, as well as in transformation processes [79]. Plant biomass is a difficult material to dissolve due to its complex structure and differences in material composition and hardness. Soft biomass, e.g., grass, is easier to process than wood biomass [80]. Moreover, the level of biomass fragmentation is crucial—smaller particles have a larger contact surface with the solvent, which increases the efficiency of dissolution [81]. In addition to biomass properties and type, the viscosity of solvent has a major impact on process effectiveness. Lower viscosity facilitates mass transfer, which enhances the dissolution process. Rahim et al. (2021) examined ILs with ether-functionalized methylimidazolium cations (e.g.,  $[\text{MOE-mim}]\text{Cl}$  1-(2-methoxyethyl)-3-methylimidazolium chloride), with significantly lower viscosity, than the widely used  $[\text{bmim}]\text{Cl}$ . In  $[\text{MOE-mim}]\text{Cl}$ , the bamboo dissolution level was 96.45%, and in  $[\text{bmim}]\text{Cl}$ , it was 78.35%. Additionally, due to the extra oxygen atom present in the methoxy group, functionalized IL can create more hydrogen bonds with biomass fractions, which additionally enhances its dissolution [82]. Furthermore, the type of anions in IL matters in biomass processing. Solvents with higher basicity of hydrogen bonds, such as  $[\text{emim}][\text{CH}_3\text{COO}]$ , are more effective for biomass dissolving [83]. Examples of biomass solubility in different ionic liquids are presented in Table 2.



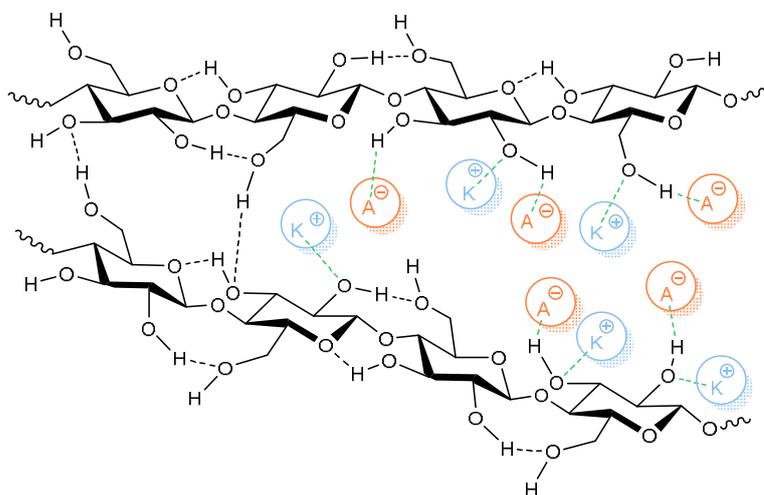
**Figure 9.** Ionic liquids cations and anions, which are the most frequently applied in biomass transformations (R—hydrogen atom or alkyl group).

**Table 2.** Biomass solubility in ionic liquids.

Biomass Type	Ionic Liquid	Temperature [°C]	Solubility [wt.%]	References
Hybrid poplar	[emim][CH <sub>3</sub> COO]	80	5.3	[84]
	[emim][HCOO]		5.3	
	[amim][CH <sub>3</sub> COO]		7.0	
	[amim][HCOO]		7.4	
Miscanthus	[emim][CH <sub>3</sub> COO]	100	1.7	[85]
	[emim][CH <sub>3</sub> SO <sub>3</sub> ]		4.0	
	[emim][HSO <sub>4</sub> ]		9.6	
Peanut shells	[bmim]Cl	120	2.3	[86]
	[emim][CH <sub>3</sub> COO]		5.8	
Chestnut shells	[bmim]Cl	120	4.7	
	[emim][CH <sub>3</sub> COO]		7.0	
Miscanthus	[bmim][CH <sub>3</sub> COO]	130	4.0	[87]
	[bmim]Cl		3.0	
	[emim]Cl		4.0	

The mechanism of biomass dissolution is based on the breakage of hydrogen bonds between lignocellulosic components. At the same time, the solvent's anion creates new hydrogen bonds with hydroxyl groups, especially cellulose. The possible role of the cation in polymer dissolution is connected to its size and hydrophobic character [88,89]. The biomass component, which is primarily dissolving ILs, is cellulose. Because of that, the effectiveness of biomass dissolution is dependent on the level of cellulose dissolution [80]. Uto et al. (2018) proposed a three-step mechanism of cellulose dissolution—first, IL's anion

penetrates through cellulose chains, which promotes hydrogen bond cleavage. At the same time, the cation increases the distance between these chains due to its size. Finally, cellulose chains are scattered [90]. The general idea of the cellulose dissolution mechanism is presented in Figure 10.



**Figure 10.** The mechanism of cellulose dissolution in ionic liquid.

The ability of ionic liquids to dissolve whole biomass results from the fact that some of the solvents can dissolve lignin, rather than only cellulose, e.g., imidazolium and ammonium ionic liquids with  $\text{Cl}^-$ ,  $\text{Tf}_2\text{N}^-$ , and  $\text{CH}_3\text{COO}^-$  anions [24]. In *Eichhornia crassipes* (water hyacinth) dissolution using ionic liquids, the most effective solvent was the mixture of [bmim][ $\text{CH}_3\text{COO}$ ] and water (water content of 40% *v/v*, and the level of biomass dissolution was approximately 85% of dry biomass). During this process, lignin was also dissolved [91]. Another popular ionic liquid [emim][ $\text{CH}_3\text{COO}$ ] was applied in the production of composite fibers from hybrid poplar, where 6.5 wt. % of biomass could be dissolved [92]. The acetate anion has moderate basicity of hydrogen bonds ( $\beta$ ), which enhances binding with lignin [85,91]. The addition of water to IL can increase lignin's dissolution level due to the formation of a higher number of hydrogen bonds [93,94]. The interactions between IL and hemicelluloses are also based on hydrogen bonds. Xylose, as a representative component of the hemicellulose monomer, can create fewer linkages with the solvent compared to glucose, due to the lower number of hydroxyl groups. Because of that, the hemicellulose solubility in IL is not as effective and might be a limiting factor in whole biomass dissolution [84].

### 3.6.2. Cellulose Dissolution in Ionic Liquids

The first patents on cellulose dissolution in melted ammonium and pyridinium salts were published in 1933–1934, but the application of 1-butyl-3-methylimidazolium chloride ([bmim]Cl) in 2002 began the intensive development in the field of ionic liquid applications.

The ability of ionic liquids to dissolve cellulose depends not only on the polymer characteristics, e.g., the degree of polymerization, crystallinity, type of plant, and process conditions (temperature, time, and presence of additional solvents), but also on ionic liquids properties [95–98]. Table 3 presents examples of cellulose solubility in ionic liquids.

**Table 3.** Cellulose solubility in ionic liquids.

Cellulose Type	Ionic liquid	Temperature [°C]	Solubility [wt. %]	References
MCC	[bmim][HCOO]	70	12.5	[99]
	[bmim][CH <sub>3</sub> COO]		15.5	
	[bmim][CH <sub>3</sub> CH <sub>2</sub> COO]		17.5	
	[bmim][CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COO]		14.0	
MCC	[emim][CH <sub>3</sub> COO]	90	27.0	[100]
	[emim]DEP		15.0	
MCC	[DBUH][HCOO]	90	18.9	[101]
	[DBUH][CH <sub>3</sub> COO]		14.8	
	[DBUH][CH <sub>3</sub> CH <sub>2</sub> COO]		12.6	
MCC	[N <sub>2226</sub> ][CH <sub>3</sub> COO]	80	15.0	[102]
		90	22.0	
Commercial Cellulose	[emim][CH <sub>3</sub> COO]	80	35.2	[103]
	[emim][DEP]		23.0	
	[DBUH][CH <sub>3</sub> COO]		22.5	
	[DBUH][Prop]		4.3	
	[DBNH][CH <sub>3</sub> COO]		22.0	
	[DBNH][Hex]		16.1	
MCC	[amim][CH <sub>3</sub> CH <sub>2</sub> COO]	30	19.0	[104]
	[amim][C <sub>6</sub> H <sub>5</sub> COO]		<5.0	
MCC	[DBUH][Lev]	100	15.0	[105]
	[DBNH][Lev]		20.0	
MCC	[emtr <sub>124</sub> ][CH <sub>3</sub> COO]	80	30.0	[106]
	[emtr <sub>123</sub> ]Br		4.0	
	[emim][CH <sub>3</sub> COO]		21.1	
MCC	[amim][MP]	80	22.0	[107]
Commercial cellulose	[hmim][CH <sub>3</sub> CH(OH)COO]	80	5.0	[108]
MCC	[ammorp][CH <sub>3</sub> COO]	80	17.0	[109]

MCC—microcrystalline cellulose, DEP—diethylphosphate anion, DBUH—1,8-diazabicyclo [5.4.0]-undec-7-enium cation, DBNH—1,5-diazabicyclo [4.3.0]-undec-5-enium cation, N<sub>2226</sub>—triethylhexylammonium cation, Prop—propanoate anion, Hex—hexanoate anion, emtr<sub>124</sub>—1-ethyl-3-methyl-1,2,4-triazolium cation, emtr<sub>123</sub>—1-ethyl-3-methyl-1,2,4-triazolium cation, MP—methyl phosphonate anion, hmim—2-methylimidazolium cation, ammorp—N-allyl-N-methylmorpholinium cation.

### 3.6.3. The Impact of Anion in Ionic Liquid on Cellulose Dissolution Effectiveness

The anion in ionic liquid has a major impact on cellulose dissolution. Generally, anions that are strong hydrogen bond acceptors, e.g., chloride, acetate, formate, and sulphate, are considered the most effective [100,110]. In order to estimate the anion effect on cellulose dissolution, Kamlet–Taft parameters describing the three independent polarity parameters (the hydrogen-bond-donating ability ( $\alpha$ ), the hydrogen-bond-accepting ability ( $\beta$ ), and the polarizability/dipolarity ( $\pi^*$ )) of a solvent are used. The most important seems to be the  $\beta$  parameter, related to the hydrogen bond basicity of the anion. The higher the  $\beta$  value of the anion, the better the dissolution properties of ionic liquid [111,112]. For example, 1-allyl-3-methylimidazolium formate [amim][HCOO]<sup>−</sup> is more effective than 1-allyl-3-methylimidazolium chloride ([amim]Cl) because of the higher basicity of hydrogen bonding of the [HCOO]<sup>−</sup> anion [96]. It has been also shown that replacing a hydrogen atom in the [CH<sub>3</sub>COO]<sup>−</sup> anion with an electron-withdrawing group (e.g., [HOCH<sub>2</sub>COO]<sup>−</sup>, [H<sub>2</sub>NCH<sub>2</sub>COO]<sup>−</sup>) decreases the solubility of cellulose [104].

### 3.6.4. The Impact of Ionic Liquid Cation on Cellulose Dissolution Effectiveness

The general order of cations in ionic liquids, which are most effective for cellulose dissolution, is imidazolium ILs > pyridinium ILs > ammonium ILs, which makes imidazolium-based solvents the most frequently studied in biomass dissolution processes [113]. In the imida-

zolinium cation structure, alkyl substituents are common, e.g., 1-ethyl-3-methylimidazolium [emim]<sup>+</sup>, 1-butyl-3-methylimidazolium [bmim]<sup>+</sup>, 1-hexyl-3-methylimidazolium [hmim]<sup>+</sup>, 1-octyl-3-methylimidazolium [omim]<sup>+</sup>, and 1-allyl-3-methylimidazolium [amim]<sup>+</sup>. With the increase in the alkyl chain length, the effectiveness of cellulose dissolution decreases. For instance, the solubility of cellulose at 100 °C in ionic liquids [alkylmim]Cl decreased from 14 wt.% for [emim]Cl and 10 wt.% for [bmim]Cl to 5 wt.% for [hmim]Cl and nearly 0% for [omim]Cl [114,115]. It was also revealed that smaller cations in ILs enhance the solubility of cellulose. For example, 14.5 wt.% cellulose can be dissolved in 1-allyl-3-methylimidazolium chloride [amim]Cl at 80 °C [116]. This process is additionally supported by the entropic effect, which is a result of possible hydrogen bonds, due to the presence of a double bond in the cation structure [97]. The double bond is also responsible for the lower viscosity of the solvent, which has a beneficial impact on the process efficiency [117]. It could be concluded that cellulose-dissolving effectiveness increases if the imidazolium cation contains electron-donating substituents.

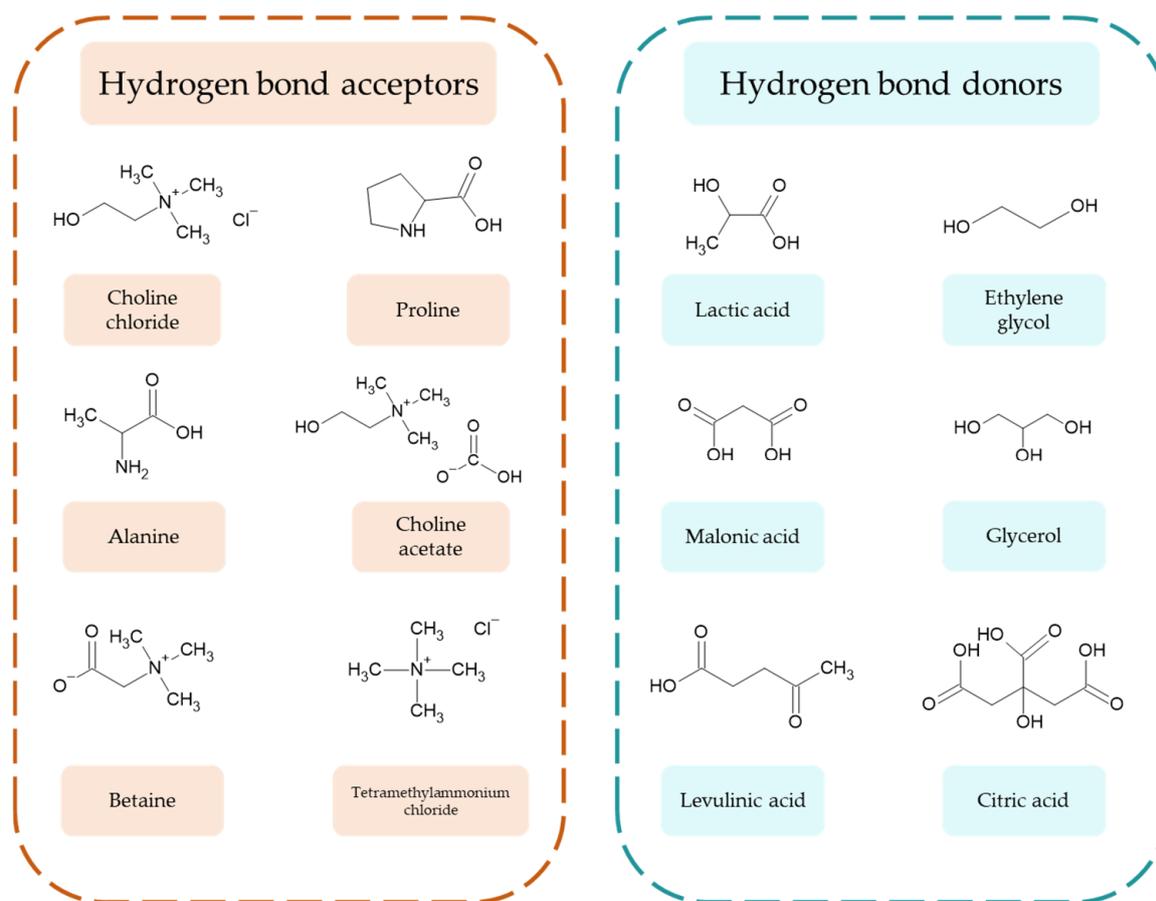
### 3.6.5. The Impact of the Addition of Other Chemicals and Process Conditions on Cellulose Dissolution Effectiveness in Ionic Liquids

Ionic liquids, despite the many advantages mentioned in this paper, have some drawbacks as solvents. Many ILs are viscous liquids, and their production costs are also quite high. In order to solve the viscosity problem, many researchers have added other solvents to the process. Organic polar aprotic solvents, e.g., DMSO or DMF, can significantly reduce the viscosity of ionic liquids, which results in better mass transport and increased polymer dissolution efficiency, without cellulose modifications [95,118,119]. Other solvents, such as acetonitrile or ethylene glycol, have a similar effect—they can reduce the viscosity of IL, e.g., [emim][CH<sub>3</sub>COO] and [bmim][CH<sub>3</sub>COO], by up to 50% [120]. In order to increase the efficiency of cellulose dissolution, inorganic additives can also be used. By adding 1% lithium salts (chloride, bromide, perchlorate, and nitrate) to ionic liquid [bmim][CH<sub>3</sub>COO], the solubility increases from 15.5 wt.% (in IL) to 18–20 wt.% (IL+salt), at 70 °C [121]. It was also shown that the addition of water as a co-solvent decreases cellulose solubility in IL. It leads to the aggregation of cellulose. Water can be applied as an antisolvent in the precipitation and regeneration of dissolved polymers [122–125].

One of the most crucial factors in cellulose dissolution in ILs is temperature. An increase in temperature causes more efficient hydrogen bond breakage in cellulose, which relates to the better dissolution of this polymer. The solubility can additionally be enhanced by using a microwave-assisted process [114]. However, it must be noted that high temperatures cause the intensification of side reactions, such as polymer degradation or the formation of humins [126].

### 3.7. Deep Eutectic Solvents (DESs) in Biomass Processing

According to the latest publications, a new type of ionic liquid, namely, deep eutectic solvents (DESs), is being widely explored. They consist of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD), which are often natural compounds (Figure 11). Some properties of DESs are even better than classic ionic liquids, e.g., lower toxicity, lower production costs, biodegradability, and stability [127,128].



**Figure 11.** Hydrogen bond acceptors and donors most frequently applied in DESs, used in biomass processing [129–131].

### 3.7.1. Delignification of Biomass with DESs

The big advantage of DESs in biomass treatment is their higher activity in lignin dissolution compared to ionic liquids or alkaline solutions [132,133]. The main goal of biomass delignification is to increase the access of catalysts/enzymes to cellulose in further transformations into valuable chemicals. It was shown that efficient delignification can occur at elevated temperatures (above 100 °C). Lower temperatures are not sufficient for the breakage of the ether bonds in lignin. Poor mass transfer at lower temperatures is also a problem [45,134]. However, it must be noted that higher temperatures (above 160 °C) may, in turn, decrease the delignification level, because of phenolic side-product formations and their polymerization [135]. The effective delignification depends mostly on the properties of DESs. Generally, DESs based on acids are more effective (e.g., oxalic acid, lactic acid) than those based on polyols. It can be explained by the mechanism of lignin dissolution—ether bonds tend to break easier under acidic conditions [136,137]. Despite the large number of recent reports on biomass processing in DESs, the selection of the most effective solvent and process parameters still needs to be examined due to biomass variety and differences in its structure and chemical composition. Several examples of biomass processing with DESs are presented in Table 4.

**Table 4.** Delignification of plant biomass with DESs.

Biomass Type	DES (HBA:HBD Molar Ratio)	Temperature [°C]	Dissolution Technique	Time [h]	Delignification Level [%]	References
Rice straw	ChCl:Lac (1:5) Bet:Lac (1:5)	60	Stirring and heating	12	60.0 53.0	[138]
Miscanthus	ChCl:Fa (1:2)	60 130	Microwave	1	4.8 82.0	[135]
Birchwood	ChCl:Ox (1:1)	60 130	Microwave	1	43.0 85.0	
Bamboo stem	ChCl:U (1:2) ChCl:Ox (1:2)	120	Stirring and heating	10	19.4 25.4	[139]
Wheat straw Corn stalk Rapeseed stem	ChCl:Lac (1:5)	100	Stirring and heating	16	8.5 9.5 11.8	[140]
Sorghum straw	ChCl:Lac	150	Stirring and heating	0.5	49.0	[141]
Bamboo residues	ChCl:Lac (1:4) ChCl:Lac (1:8)	110 130 110 130	Stirring and heating	1.5	42.3 83.6 41.2 84.1	[142]
Masson pine	ChCl:Lac (1:10)	110 140	Stirring and heating	6	58.1 87.5	[143]
Bagasse	ChCl:Ox (1:1) ChCl:Et (1:2)	100	Stirring and heating	4	47.9 8.6	[144]

(HBA—hydrogen bond acceptor, HBD—hydrogen bond donor, ChCl—choline chloride, Bet—betaine, Lac—lactic acid, Fa—formic acid, Ox—oxalic acid, U—urea, Et—ethylene glycol).

### 3.7.2. Hemicelluloses Dissolution in DESs

Some deep eutectic solvents can also be useful in the dissolution of hemicelluloses. Because of bonds connecting lignin and hemicelluloses, lignin removal is often followed by hemicelluloses extraction. By applying a solvent with a basic hydrogen bond acceptor and cholinium lysine with urea as the hydrogen bond donor, it was possible to extract approximately 62% of hemicelluloses from poplar wood [145]. Similar results (the removal of 63.3% hemicelluloses) were achieved in the process with DES consisting of choline chloride and monoethanolamine [146].

### 3.7.3. Cellulose Dissolution in DESs

Cellulose is the most difficult biomass fraction to dissolve in DESs. Recent reports show that it is still problematic to dissolve cellulose in DESs [147]. The amount of dissolved polymer depends on the source—microcrystalline cellulose is more soluble in DESs compared with that isolated from plant waste. For instance, the solubility of microcrystalline cellulose in ChCl:Lys 1:2 (*n/n*) (choline chloride:lysine) was approximately 8% of the initial amount, while in the case of cellulose isolated from wheat straw, it was only 6% (24 h, 90 °C). It is worth mentioning that these yields were obtained by applying ultrasound assistance in order to increase the solubility [148,149]. The poor solubility of cellulose and significantly better solubility of lignin in DESs allows one to separate biomass fractions, which is one of the main goals of plant waste pretreatment before further transformation into valuable chemicals.

## 4. Conclusions

The effective dissolution of biomass or its fractions is still a challenge in lignocellulosic waste processing. The wide variety of plant materials and differences in chemical compo-

sition makes the selection of an appropriate solvent even more difficult. The key step in making the process more efficient is to understand the mechanisms of biomass dissolution, which is generally based on the breakage of hydrogen bonds existing in lignocellulose and the creation of new ones between solvent and biomass components. Nowadays, the rules of the sustainable development strategy and green chemistry should be followed in the selection of appropriate solvents. Classic acidic and alkaline solutions, known for their ability to dissolve biomass fractions, should be replaced by more ecological solvents. Ionic liquids and deep eutectic solvents are promising groups of solvents. Ionic liquids are especially effective in cellulose dissolving. This ability mostly depends on the solvent's anion—the higher the hydrogen bond basicity of the anion, the better the biomass dissolution properties. Moreover, in many works, a substituted imidazolium cation is presented as the best one. However, the length of alkyl chains in cation substituents has a significant impact on the effectiveness of the process. Shorter chains are more suitable for dissolving cellulose (e.g., [emim]<sup>+</sup>). If the process is devoted to lignin dissolution, it is recommended to use deep eutectic solvents, especially those with an acidic hydrogen bond donor. They are more effective than alkaline solutions. Because of the different abilities of ILs and DESs to dissolve lignocellulosic components, it is possible to use them in the separation of biomass polymers. Additionally, these solvents are considered green chemicals, which makes them a promising alternative to acidic and alkaline solutions. Except for the tunability of DESs and ILs, the primary advantage is their low toxicity and vapor pressure, high chemical and thermal stability, and miscibility with many chemicals. However, the novel systems also have some disadvantages. One of them is the high viscosity of many DESs, which significantly influences mass transfer. This problem can be overcome by using co-solvents or increasing the temperature (usually over 100 °C). Furthermore, the costs of some ILs and DESs might be considered a drawback.

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