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Review

Deep Eutectic Solvent-Driven Refining of Lignin: Selective Fractionation, Depolymerization Mechanisms, and Multidimensional Valorization

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Abstract

Deep eutectic solvents (DESs) with tunable hydrogen-bond network and solvation capacity and acid–base properties are a promising medium for selective fractionation of lignocellulose and valorization of lignin. However, efficient lignin removal and depolymerization, together with the cleavage of lignin–carbohydrate complexes (LCCs), remain critical challenges in DES-mediated lignin-first biorefining. Reactive lignin intermediates may become temporarily stabilized within the solvent environment and subsequently undergo recondensation. Recent developments in DES-assisted selective lignin fractionation, structural regulation, catalytic depolymerization and high-value utilization are critically summarized, and the relationship among molecular structures, the reaction microenvironment, conversion pathways and functional performance are emphasized. The impacts of DES composition, H-bond donors/acceptors, acidity/basicity and solvation parameters on lignin dissolution, LCC bond cleavage, and the stability of major linkages such as β-O-4 are highlighted, along with the intensifying effects of ultrasound and microwave fields. DESs are also regarded as multifunctional reaction platforms with capabilities for selective fractionation, in situ stabilization, and chemical functionalization. Bond cleavage, reactive-intermediate evolution, and radical regulation under thermal, photocatalytic, and electrocatalytic conditions are analyzed, along with strategies to suppress lignin recondensation and enhance aromatic monomer yields. High-value applications in nanomaterials, functional and stimuli-responsive materials, energy materials, and high-energy-density bio-oils are also reviewed. Finally, techno-economic analysis and life-cycle assessment are discussed to identify challenges in DES recovery, stability, mass transfer, energy consumption, and scale-up integration, providing guidance for rational DES design and sustainable lignin-first biorefining.

Keywords: deep eutectic solvent; biomass lignin; selective fractionation; depolymerization mechanisms; multidimensional valorization

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Academic Editors: Celestino Garcia-Gomez, Luis Humberto Alvarez-Valencia and Carlos Abraham Díaz-Quiroz

Received: 19 September 2026
Revised: 6 October 2026
Accepted: 3 November 2026
Published: 6 November 2026

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1. Introduction

Under the combined pressures of fossil resource depletion, greenhouse gas emission reduction, and the valorization of organic wastes, lignocellulosic biomass has been widely regarded as an important non-fossil feedstock for the production of fuels, chemicals, and functional materials because of its abundance, renewability, and role in the carbon cycle [1,2]. However, a considerable proportion of agricultural and forestry residues is still directly burned, disposed of, or used in low-value applications, while fractionation and high-value conversion remain restricted by the intrinsic recalcitrance of lignocellulosic biomass [3]. This recalcitrance arises from the multiscale organization of the crystalline cellulose framework, branched hemicellulose, and the three-dimensional aromatic lignin network, together with covalent linkages, such as ether and ester bonds, within lignin–carbohydrate complexes (LCCs) [4–6]. As illustrated in Figure 1, lignin is composed of p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units linked through β-O-4 and other C–O bonds, as well as various C–C linkages. Such heterogeneity makes it difficult to achieve efficient lignin separation while preserving its native structural features [7,8].

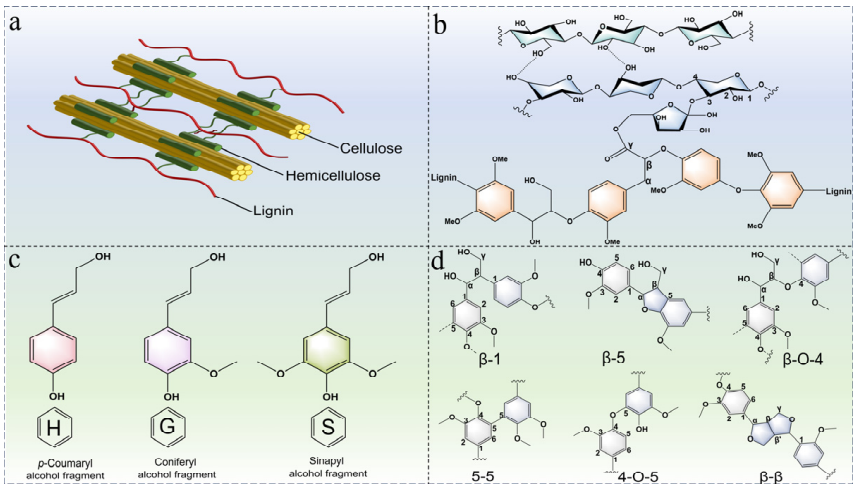

Figure 1. Structural organization and chemical features of lignocellulosic biomass. (**a**) Hierarchical architecture of lignocellulosic matrix showing the interactions among cellulose, hemicellulose and lignin; (**b**) major chemical structures of lignocellulosic components; (**c**) three basic lignin monolignol units (H, G and S); and (**d**) representative lignin interunit linkages, including β-O-4, β-β and 5-5 linkages.

Conventional pulping processes, such as Kraft and sulfite pulping, and conventional solvent-based fractionation methods, including organosolv and acidic or alkaline treatments, can effectively separate lignin, but may involve corrosion, high chemical consumption, or substantial structural modification of lignin [3,9–12]. Ionic liquids constitute a distinct class of designer ionic media and share several physicochemical characteristics with deep eutectic solvents (DESs), including low volatility, tunable solvation behavior, and strong interactions with lignocellulosic components. However, DESs are generally formed through eutectic interactions between two or more components and can often be prepared without the synthetic and purification steps required for many ionic liquids. Their acidity/basicity, nucleophilicity, and in some systems metal-coordination ability can further facilitate the cleavage of lignin–carbohydrate linkages and promote lignin release [13]. Polyol-based and other functional DESs may also stabilize reactive intermediates generated during acid-catalyzed cleavage, thereby reducing irreversible C–C condensation and helping preserve β-O-4 linkages and reactive functional groups [14–16]. However, DES-based processes also face important limitations, including high viscosity and associated mass-transfer resistance,

energy- and cost-intensive solvent recovery, possible toxicity of specific formulations, and chemical or thermal degradation of DES components under prolonged or severe processing conditions. Degradation products and biomass-derived impurities may further accumulate during recycling and progressively alter solvent composition and performance.

Several previous reviews have addressed DES-mediated lignocellulose fractionation and valorization [9,17], process parameters governing lignin extraction [18], and catalytic lignin conversion using ionic liquids and DESs [10]. These studies provide important stage-specific perspectives. The present review instead organizes fractionation, structural evolution, depolymerization, functionalization, solvent recovery, and process-scale considerations within a common-structure reaction-microenvironment product framework. The distinguishing perspective of this review is therefore not simply broader topical coverage. Rather, it examines how DES composition and the resulting reaction microenvironment connect upstream fractionation with lignin structural preservation, subsequent depolymerization, functional performance, and process-scale constraints. Particular emphasis is placed on distinguishing the different technological roles of DESs as fractionation media, direct reaction media or electrolytes, catalyst-synthesis media, and sources of DES-derived lignin/materials because these roles involve different mechanisms and should not be interpreted equivalently.

Accordingly, this review first summarizes the composition and key physicochemical properties of DESs and discusses the molecular mechanisms underlying DES-mediated lignocellulose fractionation, with particular attention to carboxylic acid-based, polyol-based, and emerging DES systems and their effects on lignin removal and structural preservation. The role of physical intensification methods, especially ultrasound and microwave irradiation, in improving mass transfer and biomass deconstruction is then examined. The review further discusses the functions of DESs as solvents, catalytic media, and intermediate-stabilizing environments during thermal, photocatalytic, and electrocatalytic lignin depolymerization. Subsequent sections cover the use of DES-isolated or DES-mediated lignin in nanoparticles, composite materials, and stimuli-responsive functional materials. Finally, the major barriers to scale-up are evaluated from the perspectives of solvent recovery, techno-economic feasibility, and life-cycle performance. By linking DES structure and reaction microenvironment with lignin structural evolution and end-use properties, this review aims to provide a coherent framework for the rational development of DES-assisted lignin-first biorefining toward more efficient, low-carbon, and sustainable biomass utilization.

This article is designed as a critical narrative review rather than a systematic review or meta-analysis. Literature was selected according to its relevance to four interconnected themes: (i) DES-mediated lignocellulosic fractionation and lignin recovery; (ii) effects of DES composition and processing conditions on lignin structure and reactive intermediates; (iii) DES-related lignin depolymerization, functionalization, and material applications; and (iv) solvent recovery, recycling, techno-economic performance, and life-cycle considerations. Priority was given to peer-reviewed primary studies and recent critical reviews that provided mechanistic, quantitative, or process-level information. Studies involving DESs only indirectly were retained only where they provided a clearly identified transferable mechanistic or engineering comparison, and such cases are explicitly distinguished from direct DES-mediated lignin-processing studies. Because the objective was critical integration rather than exhaustive evidence capture, the review does not claim systematic completeness.

The environmental performance of a DES cannot be inferred solely from low volatility, natural origin, or the biodegradability of individual components. Toxicity, biodegradation of the complete formulation, precursor origin, solvent and water consumption, recovery energy, degradation products, and end-of-life behavior must be assessed for each formulation and

process. Accordingly, the terms "green" and "sustainable" are used in this review only where they are supported by formulation- or process-specific environmental evidence.

2. DES-Mediated Fractionation of Lignocellulosic Biomass

Efficient valorization of lignocellulosic biomass requires the disruption of its highly cross-linked structure through an appropriate solvent system. Owing to their tunable hydrogen-bonding networks and solvation properties, DESs can promote lignin separation under relatively mild conditions. This section focuses on the physicochemical and recyclable characteristics of DESs and discusses the main factors governing their selective extraction of lignin during biomass fractionation.

In this review, lignin removal/delignification refers to the decrease in lignin content of the solid biomass during fractionation; lignin extraction or recovery refers to isolation of lignin from the liquid or solvent phase; and lignin depolymerization refers specifically to cleavage of lignin interunit linkages to generate lower-molecular-weight oligomers or monomeric products. These terms are therefore not used interchangeably.

2.1. Physicochemical Properties of DESs

2.1.1. General Characteristics and Structural Classification

DESs are eutectic systems typically formed by mixing two or more components at appropriate molar ratios, often involving a hydrogen-bond acceptor (HBA) and a hydrogen-bond donor (HBD) [19]. Strong intermolecular interactions, particularly hydrogen bonding, promote charge delocalization and result in a melting point substantially lower than those of the individual components [20]. This feature provides considerable flexibility in tuning the physicochemical properties of DESs through rational selection of their components and compositions [21,22] (Figure 2a).

DESs are commonly grouped into five compositional classes based on their precursor composition (Figure 2b). Type I systems combine an organic salt, typically a quaternary ammonium or phosphonium salt, with an anhydrous metal chloride; Type II systems contain an organic salt and a hydrated metal chloride; Type III systems combine an organic salt with a molecular HBD such as a carboxylic acid, amide, or polyol; Type IV systems contain a metal chloride and a molecular HBD; and Type V systems consist of nonionic molecular components, typically including a neutral molecular HBA and HBD. Most ChCl–carboxylic acid, ChCl–polyol, and ChCl–amide systems discussed in lignocellulose fractionation therefore belong to Type III. Importantly, not every low-melting binary mixture should automatically be regarded as a genuine DES: evidence of substantial melting-point depression and nonideal solid–liquid behavior is required to distinguish a DES from a simple eutectic or DES-like mixture [20,23,24].

Among these, systems composed of a quaternary ammonium salt and a molecular HBD have been the most studied for lignocellulose fractionation due to their structure diversity and favorable physicochemical properties. Some Type V DESs, including hydrophobic systems based on thymol or menthol, have more recently been used for selective recovery of lignin-derived monomers and phenolic oligomers from aqueous phases [25–27].

DES acidity/basicity, polarity, viscosity, water content, and hydrogen-bonding characteristics collectively influence lignin solvation, LCC cleavage, mass transfer, carbohydrate retention, and preservation of lignin interunit linkages [17,20,28,29]. These properties control the LCC cleavage, lignin solvation, and the degree to which native lignin structures remain. Typically, carboxylic acid-based DESs demonstrate high deconstruction power, while polyol-based systems exhibit good ability to prevent condensation of lignin and maintain reactive structural motifs. Hence, the design of DESs should be a compromise between

the mass-transfer property and the chemical reactivity, and high fractionation efficiency should be achieved without sacrificing component selectivity or lignin structural integrity.

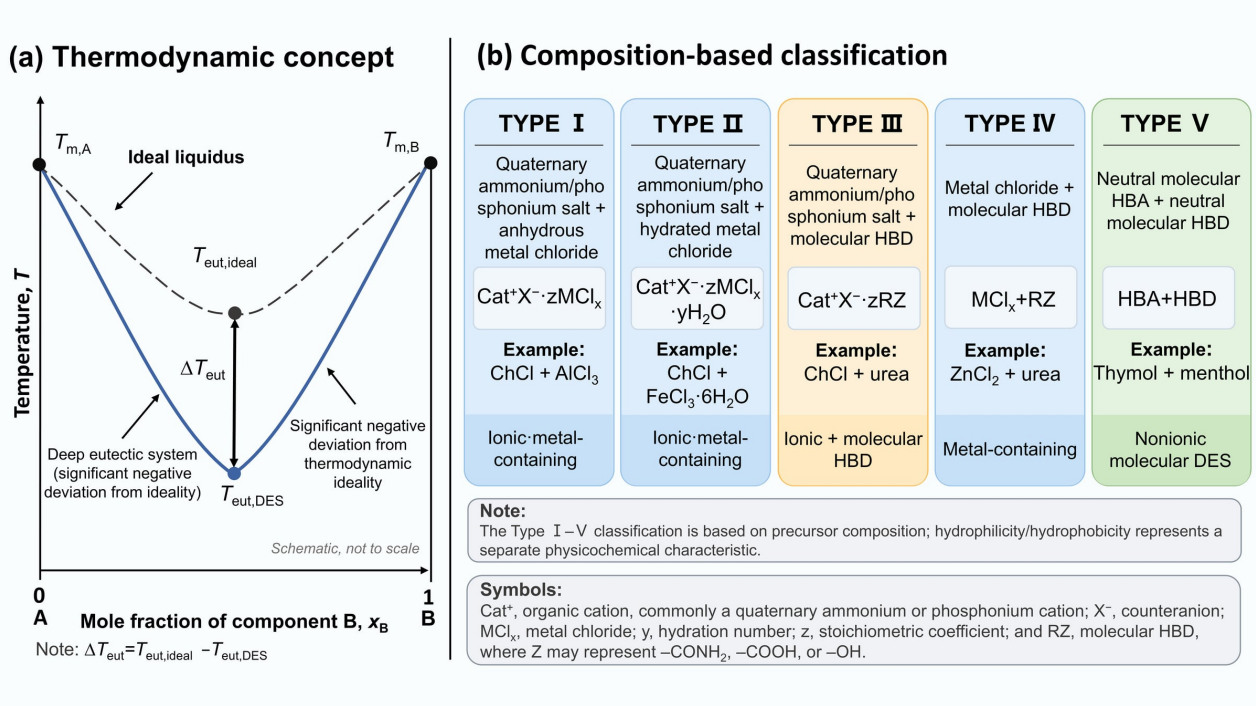

Figure 2. Thermodynamic distinction and conventional composition-based classification of DESs. (**a**) Schematic solid–liquid equilibrium representation illustrating ideal eutectic behavior and a deep eutectic system exhibiting a pronounced negative deviation from thermodynamic ideality. The diagram is conceptual and not to scale. $T_{m,A}$ and $T_{m,B}$ denote the melting temperatures of pure components A and B, respectively; $T_{eut,ideal}$ and $T_{eut,DES}$ denote the ideal and deep eutectic temperatures, respectively; and $\Delta T_{eut} = T_{eut,ideal} - T_{eut,DES}$. (**b**) Conventional classification of DESs according to precursor composition. Type I consists of a quaternary ammonium or phosphonium salt and an anhydrous metal chloride; Type II contains a quaternary ammonium or phosphonium salt and a hydrated metal chloride; Type III comprises a quaternary ammonium or phosphonium salt and a molecular HBD; Type IV consists of a metal chloride and a molecular HBD; and Type V comprises a neutral molecular HBA and a neutral molecular HBD. Cat^+ denotes an organic cation, typically a quaternary ammonium or phosphonium cation; X^-, the counteranion; MCl_x, a metal chloride; y, the hydration number; z, the stoichiometric coefficient; and RZ, a molecular HBD containing functional groups such as –$CONH_2$, –COOH, or –OH. The Type I–V classification is based on precursor composition, whereas hydrophilic/hydrophobic character represents a separate physicochemical classification [24].

2.1.2. Key Physicochemical Properties and Their Relationship with Fractionation Performance

The magnitude of these properties varies substantially among DES formulations. Polyol-rich systems such as ChCl–glycerol (ChCl–Gly) are generally relatively viscous, which can restrict diffusion and biomass penetration, whereas some high-temperature guanidinium-based systems exhibit much lower viscosities; for example, a guanidine hydrochloride–lactic acid system (guanidine hydrochloride–LA) was reported to have a viscosity of 8.73 cP at 120 °C [30]. Polarity also spans a wide range. Hydrophilic ChCl–carboxylic-acid systems such as ChCl–LA and ChCl–oxalic acid (ChCl–OA) provide strongly polar environments that favor interactions with hydroxyl-containing biomass components, whereas thymol- or menthol-containing hydrophobic Type V systems provide substantially less polar environments and are more appropriate for partitioning relatively hydrophobic solutes [25–27]. Similarly, strongly acidic OA- or LA-containing DESs generally promote

LCC cleavage more aggressively, whereas less acidic polyol-rich systems such as ChCl–Gly or ChCl–EG often provide milder chemical environments. Therefore, viscosity, polarity, and acidity should be considered together rather than independently when selecting a DES for lignocellulose fractionation.

In addition to these properties, hydrogen-bond donating/accepting ability, water content, and thermal stability also play important roles in determining DES fractionation performance. These properties are related to the penetration and transport of DESs in the plant cell wall, the solvation of lignin, and the retention of carbohydrates [17].

The strong interactions between HBAs and HBDs can cause relatively high viscosity, which can lead to slow molecular diffusion and consequently poor penetration into the lignocellulosic matrix. Fluidity can be improved by increasing the temperature, changing the proportion of the components, by a small quantity of a low-viscosity third component, or even by controlled addition of water. However, these may also alter the hydrogen-bonding network and/or the local solvent environment [28].

The bonds in the molecules are activated in the fractionation process, depending on the acidity/basicity and the hydrogen-bonding ability. The acidic DESs can increase the protonation and the cleavage of the ether and ester bonds of LCCs [20,31]. However, this may lead to degradation of carbohydrates, high cleavage of the β-O-4 linkages and recondensation of lignin at high acidities. The milder reaction conditions that polyol- or some amide-based DESs provide, on the other hand, are more conducive to retaining lignin ether linkages and reactive functional groups [32].

There are close relationships between the polarity, solvation capacity, and selective dissolution of lignin. Appropriate polarity of the hydroxyl groups, side chains and aromatic structures of lignin and the different parts of DES can strengthen the forces of hydrogen-bonding, dipolar, and dispersion interaction. This will help to break down and stabilize the pieces of the lignin and prevent its redeposition [17]. However, high polarity can also cause a greater impact of interactions with the polysaccharide, leading to a reduction in fractionation selectivity.

Another parameter that is important to consider is water content as it influences the mass transfer and the micro-organization of DESs. The inclusion of a moderate amount of water will reduce the viscosity, enhance wetting and encourage penetration into biomass. As the water content increases, there is greater competition for the hydrogen-bonding capacity of the HBA and HBD by the water molecules. The original DES network may then shift toward hydrated individual components, weakening the characteristic solvation behavior of the DES [29].

Thermal stability defines the practical temperature range of a DES during biomass treatment. In rapidly heated systems such as microwave-assisted fractionation, dielectric properties and ionic conductivity also become important because uneven energy absorption may cause local overheating and solvent degradation [33]. Overall, effective DES design requires a coordinated balance among mass transfer, chemical reactivity, fractionation selectivity, and lignin structural preservation so that improved delignification does not come at the expense of lignin quality.

2.2. Mechanisms of DES-Mediated Lignocellulose Fractionation and Selective Lignin Extraction

The efficient and selective extraction of lignin by DES originates from both specific chemical interactions with biomass components and the tunability of DES composition. The process generally begins with the reorganization of hydrogen-bonding networks. HBD and HBA compete with the native interactions in lignocellulose by forming new hydrogen bonds with hydroxyl groups on cellulose, hemicellulose, and lignin surfaces, thereby disrupting the original intermolecular hydrogen-bond network [34]. This results in the non-covalent

swelling of the cell wall, opening up diffusion pathways, and components of the DES enter LCC [35].

Lignin release is largely controlled at the molecular level by the action of both acid-catalyzed bond breaking reactions and nucleophilic reactions [18]. In LCCs, protonation of the acidic sites of DESs may increase the susceptibility of the bonds of ether and ester to be cleaved. Halide anions such as Cl^- can be very effective at solvating the hydroxyl groups of lignin, and along with the HBD can modify the solvation environment around the lignin. These interactions help to dissociate and stabilize the lignin fragments during extraction [17].

Another important parameter for DES-mediated fractionation is avoiding irreversible condensation of lignin. In acid conditions, the side chains of the lignin can undergo cleavage to generate reactive benzylic carbocation intermediates, but when not well stabilized, these intermediates are prone to electrophilic attack on the adjoining aromatic ring to form the condensed C–C linkages that may be difficult to break in the subsequent process. Some of the HBDs like polyols and organic acids can then be employed as solvents and stabilizers. Model-compound experiments and mechanistic interpretations suggest that some polyols and organic acids can react with or stabilize reactive benzylic intermediates through etherification, esterification, or related nucleophilic pathways, thereby decreasing the probability of secondary C–C condensation. The extent to which these pathways dominate under practical biomass-fractionation conditions is formulation- and condition-dependent [36].

All the above effects are not mutually exclusive. Their relative contributions collectively control the degree of lignin removal, lignin purity, molecular-weight distribution, and β-O-4 content. Accordingly, the balance among hydrogen-bond disruption, acid-catalyzed bond cleavage, nucleophilic stabilization, and solvation varies significantly with DES formulation and governs the resulting fractionation behavior.

For example, acidic DESs, especially carboxylic acid-based DESs, have high efficiency in delignification and show strong bond-cleavage capacity, while high acidity can also result in degradation and condensation of the lignin structure [37]. In comparison with strongly acidic DESs, many polyol-rich or less acidic DES formulations can provide milder reaction environments and may reduce the extent of acid-catalyzed lignin degradation and condensation under appropriate operating conditions. However, condensation or structural degradation cannot be excluded because these reactions remain dependent on DES composition, acidity, temperature, residence time, water content, and lignin feedstock structure [38]. Therefore, the selection and combination of the HBA and HBD remain important for controlling fractionation performance. Ternary DESs offer a third component that has the ability to affect the charge distribution, acidity, and local interactions, enhancing the balance of lignin extraction and preservation of reactive structural motifs [39,40].

In general, the rational design of DESs should be based on the needs of downstream valorization of lignin. The effective DES system must not aim at the maximum recovery of lignin by delignification, but it should aim at the two following targets: a high lignin purity and a high content of β-O-4 structures. A minimum amount of secondary condensation products should be produced during fractionation. Formulation-dependent effects of different DES systems are discussed in detail in Section 3.1.

3. DES Pretreatment and Synergistic Integration with Other Methods

This section first compares the roles of carboxylic acid-based, polyol-based, and emerging DES systems in lignocellulose fractionation from the perspectives of molecular composition and dominant chemical functionality, with particular emphasis on how HBD structure governs the trade-off between delignification efficiency and lignin structural integrity. It

then discusses the effects of physical fields, including ultrasound and microwave irradiation, on heat and mass transfer, treatment time, and lignin reaction pathways. Synergistic strategies coupling DESs with Lewis acids, single-atom solid acids, and biocatalytic enzymes are further reviewed. Overall, current DES pretreatment research is increasingly shifting toward approaches that simultaneously consider structural preservation and application-oriented functionality.

3.1. Roles of Different DES Systems in Lignocellulose Fractionation

According to their prevailing chemical components and formulation methods, DESs applied in lignocellulose fractionation may be roughly distinguished as carboxylic acid-based DESs, polyol-based DESs and emerging non-conventional/biomass-derived DESs. This section compares the above systems on the bases of fractionation efficiency, preservation of lignin structure and mass-transfer performance.

3.1.1. Carboxylic Acid-Based DESs

Carboxylic acid-based DESs generally exhibit high delignification capacity because of their pronounced Brønsted acidity [41]. Their acidic environment promotes cleavage of ester linkages in LCCs and can also induce acidolysis of susceptible ether bonds, including β-O-4 linkages. Monocarboxylic acid-based systems, particularly those containing LA, have shown broad applicability to both herbaceous and woody biomass, including corn stover [42], passion fruit peel [43], corncob [44], grapevine residues [45], sugarcane biomass [46] and eucalyptus [46], as summarized in Table 1.

Table 1. Representative DES-mediated lignocellulose fractionation and lignin-removal studies.

Category	DES (HBA:HBD)	Biomass	Conditions	Lignin Removal (%)	Highlighted Properties	Reference
Acidic binary DESs	ChCl–LA (1:2)	Corn straw	800 W microwave-assisted treatment, 45 s	79.6	Fast fractionation; cellulose content reached 65–67%.	[42]
	ChCl–LA (1:2)	Oilcane bagasse	140 °C, 2 h	78.8	High hemicellulose removal (80.4%); increased lipid yield.	[47]
	ChCl–LA (1:2)	Passion fruit husk	130 °C, 2 h, 20% H_2O	34.0	High cellulose retention (81.5%); positive roles of ChCl–LA confirmed.	[43]
	ChCl–LA (1:5)	Corncob	123 °C, 6 h	90.08	High glucose conversion (68.77%), good hemicellulose removal.	[44]

Table 1. *Cont.*

Category	DES (HBA:HBD)	Biomass	Conditions	Lignin Removal (%)	Highlighted Properties	Reference
	ChCl–LA (1:6)	Grapevine	110 °C, 4 h, 20% H_2O	66.05	Combined pretreatment increased glucose yield 3-fold.	[45]
	ChCl–LA (1:10)	Eucalyptus, pine, sugarcane bagasse	140 °C, 6 h	83.46–88.05	Lignin with high purity and uniform structure.	[46]
	ChCl–OA (1:2)	Sunflower straw	160 °C, 12 min	65.8	Rapid process; high xylose removal (73.9%).	[48]
Acidic ternary DESs	ChCl–OA–LA (1:1:4)	Pine needle	160 °C, 3 h	95.8	High-purity LNPs; recyclable and economical.	[49]
	ChCl–CA–LA (0.1:0.3:0.6)	Acacia wood	140 °C, 4 h	99.63 ± 1.24	High lignin removal; high purity; recyclable.	[50]
Polyol-based DESs	ChCl–Gly (1:2)	Rice straw	150 °C, 15 h	74	Simple; biodegradable; non-interfering.	[51]
	EaCl–EG (1:2)	Eucalyptus	140 °C, 3 h	85.0	High-purity LNPs with 97.8% yield.	[39]
DES-based multifunc-tional systems	ChCl–CA (1:2) + EtOH	Bamboo	130 °C, 1 h	78.81	High cellulose retention; lignin with high β-O-4 content.	[52]
	ChCl–OA-1,2-butanediol (5:1:10)	Reed straw	100 °C, 24 h	74.65	ChCl showed high interaction energy with lignin.	[53]
	ChCl–TEG–OA (1:2:1.5)	Wheat straw	130 °C, 60 min	65.2	Mild conditions; high glucose yield.	[54]
Emerging non-ChCl DESs	GH-LA (1:2)	Castor stalk	130 °C, 30 min, 400 W (MW)	92.02	Higher lignin purity than ChCl–LA; recyclable.	[30]
	GH-LA (1:2)	Oil palm EFB	120 °C, 30 min	57.12	Lignin with high phenolic content.	[55]

Table 1. *Cont.*

Category	DES (HBA:HBD)	Biomass	Conditions	Lignin Removal (%)	Highlighted Properties	Reference
	TEBAC-LA (1:9)	Sugarcane bagasse	120 °C, 4 h	88.72 ± 1.63	Improved enzymatic digestibility (5 cycles).	[56]
Bio-derived HBD-containing DESs	ChCl–VAN (1:2)	Corn straw	140 °C, 3 h, 30% H_2O	61.4	High biohydrogen yield post-treatment.	[57]

Note: Lignin-removal values are reported as provided in original studies and should be interpreted with consideration of biomass type, DES composition, loading ratio and treatment conditions. Abbreviations: ChCl, choline chloride; LA, lactic acid; OA, oxalic acid; CA, citric acid; Gly, glycerol; EG, ethylene glycol; EaCl, ethylammonium chloride; GH, glycine hydrochloride; TEG, triethylene glycol; TEBAC, triethylbenzylammonium chloride; VAN, vanillin; CBSA, chlorobenzene sulfonic acid; EtOH, ethanol; MW, microwave; LNPs, lignin nanoparticles; EFB, empty fruit bunch.

For example, treatment of corncob with ChCl–LA at a molar ratio of 1:5 and 123 °C for 6 h achieved a delignification efficiency of 90.08% [44]. In another study, microwave-assisted pretreatment of corn stover using ChCl–LA (1:2) at 800 W reached 79.6% delignification within only 45 s [42]. To enhance the deconstruction of more recalcitrant lignocellulosic structures, polycarboxylic acids such as OA and citric acid (CA) are often incorporated into DES formulations. A ChCl–OA system (1:2) removed more than 65% of lignin from sunflower stalks at 160 °C within 12 min [48]. Likewise, the efficient extraction of lignin from bamboo was achieved in 1 h using ChCl–CA (1:2), which also displayed high co-fractionation efficiency of hemicellulose [52].

However, the efficiency of delignification does not necessarily increase with increasing acidity. It is also strongly affected by the native constitution of the lignin (e.g., relative amount of S units, G units, H units). In order to shed light on this correlation, Pan et al. performed molecular dynamic simulations [58]. When different carboxylic acid-based DESs were evaluated using representative lignin dimers, their binding affinities differed significantly. For example, the stronger interactions of ChCl–OA with guaiacyl–syringyl (G–S) lignin dimers were ascribed to the spatial conformation and charge distribution of OA and their effects on non-covalent interactions between the aromatic units. Conversely, the important hydrogen-bond interactions between ChCl–LA and guaiacyl–guaiacyl (G–G) lignin dimers produced a more stable solvation environment around the G–G lignin dimers, which can facilitate the dissolution of the lignin.

From these observations, it is concluded that the use of carboxylic acid-based DESs should be optimized for the different properties of the feedstock to achieve efficient delignification without compromising the structure of the feedstock to some extent. Biomass that is not recalcitrant, such as herbaceous biomass, can be treated in comparatively low-temperature, monocarboxylic acid-based systems [46]. In contrast, systems of dicarboxylic and tricarboxylic DESs and multicomponent DES systems have multiple interaction sites and might be attractive to treat the dense woody biomass, particularly G-type softwoods with softwood lignin [59].

3.1.2. Polyol-Based DESs

The use of polyol-based DESs is gaining popularity for lignin-first fractionation because of their ability to regulate lignin reactions and preserve structural integrity [60]. A key advantage is their ability to provide nucleophilic stabilization. In acidic conditions, hydroxyl-

containing polyols can capture the reactive intermediates that are generated at the lignin α-position and generate more stable α-etherified structures in situ. This helps reduce C–C coupling with active lignin fragments and minimize the number of irreversible condensation products [61,62]. Protection does not prevent acidolytic cleavage of the β-O-4 linkages, but it will reduce a high degree of rearrangement of the lignin skeleton, and the recovered lignin will be closer to the original lignin and have a higher percentage of native ether bonds and less condensation [63,64].

There is, however, a trade-off between this structural benefit and process efficiency. Polyol based DESs have relatively high viscosity and low acidity, which may affect mass and heat transfer. For instance, it took 15 h to delignify 74% of rice straw treated with ChCl–Gly at 150 °C [51]. Length of treatment and the increased temperature may result in increased energy and therefore treatment costs.

Considering the low reactivity and mass transfer of binary polyol-based DESs, a large number of multifunctional ternary systems involving an acidic component/Lewis acid center have been investigated during the last few years [65]. It is possible to reduce the eutectic temperature and viscosity and promote mass transfer by changing the proportions of the components [49,54,66]. The design of the currently used ternary DESs uses the following main approaches, which are complementary to each other. One is a combination of carboxylic acid Brønsted acidity and the polyol nucleophile protection. Pretreatment of eucalyptus with a ChCl–Gly–maleic acid system combined with microwave irradiation achieved sugar yields of up to 90.9% [66]. The other strategy is the incorporation of a small amount of Lewis acid (e.g., $AlCl_3$, $FeCl_3$ and $ZnCl_2$) in a polyol-based DES to enhance lignin separation. Mechanistic studies have shown that the Lewis acid centers produced by $AlCl_3 \cdot 6H_2O$ can react with hydroxyl groups of glycerol, forming complexes that are active and promote the disruption of the hydrogen-bonding network and breaking of the ether bonds of LCCs. Meanwhile, glycerol can act as a nucleophile and react with benzylic intermediates generated during β-O-4 cleavage, thereby decreasing the probability of irreversible C–C condensation reactions. This controlled depolymerization may also release or retain the phenolic hydroxyl groups, and the resulting lignin retains good antioxidant activity [31,67].

Hence, the role of polyols in DESs extends beyond that of a solvent component to include protective and structure-regulating functions in multifunctional formulations. With appropriate use of cosolvents and microwave irradiation, ternary polyol-containing DESs could be useful for obtaining lignin with high structural reactivity while maintaining acceptable fractionation efficiency.

3.1.3. Emerging Non-Conventional and Lignin-Derived DESs

Towards addressing the limitations of conventional ChCl-based DESs in terms of viscosity, feedstock adaptability and recycling stability, there has been increasing attention paid to DESs, which do not involve ChCl, but rather other HBA and HBD components like guanidinium salts and betaine [68]. Besides macroscopic transport properties, the other merits of guanidinium-based DESs are related to unique molecular interactions. The relatively low viscosity of the guanidine hydrochloride–LA system may be associated with the unique structural characteristics of the guanidinium cation, which could influence the intermolecular interactions within the DES system. For instance, the viscosity of the guanidine hydrochloride–LA system was 8.73 cP at 120 °C, which was lower than that of the ChCl–LA system (10.68 cP) under the same conditions [30]. More importantly, guanidinium hydrochloride can act as a chaotropic agent. In combination with the dipolar polarization induced by microwave irradiation, it can perturb hydrogen-bonding networks within lignin and weaken hydrophobic interactions among aromatic structures, thereby destabilizing the

lignin matrix. Such systems have also shown a degree of structural selectivity toward lignin containing S units [55].

Another emerging approach is the use of lignin-related aromatic compounds, such as vanillin, p-coumaric acid, and guaiacol, to construct bio-derived DESs. Because these components share structural features with native lignin, they may exhibit favorable molecular compatibility with lignin aromatic units, including π–π interactions, and thereby enhance the solvation of aromatic fractions [57,69]. However, strongly associated hydrogen-bonding networks in some of these systems may also limit their deconstruction activity. To address this problem, Lu et al. introduced $AlCl_3 \cdot 6H_2O$ into a ChCl–guaiacol (GG) system. At a ChCl–GG–$AlCl_3 \cdot 6H_2O$ molar ratio of 1:1:0.07 and 120 °C for 3 h, lignin and hemicellulose removal reached 73.22% and 93.05%, respectively, markedly improving component separation [70].

However, further research is needed on these emerging DES families, and solvent design based on an understanding of DES structure and lignin type should be encouraged rather than empirical screening of different formulations [71]. Future systems will be targeted at the integration of low viscosity, high mass transfer and in situ stabilization of the reactive lignin intermediates. Use of appropriate stabilizing groups will be even more important when translating the systems to lignin-first biorefining processes and knowledge about drift and evolution of the solvent over repeated recycles will become important.

3.2. Synergistic Effects of DESs with Other Methods

Many DESs exhibit relatively high viscosity, resulting in poor solvent penetration, high mass-transfer resistance, and prolonged treatment times. Combining DESs with other physical fields like ultrasound and microwave irradiation or chemical and biological catalysts to fractionate and convert lignocellulose could be effective in two ways: enhancing the transfer of heat and mass and regulating the reaction pathways. Most physical fields increase contact between the solvent and biomass and increase the energy input to the system. Selective bond cleavage, lignin modification and controlled depolymerization can also be accomplished using catalytic systems. Examples of DES-based synergistic systems with ultrasound, microwave irradiation, and catalytic strategies are summarized in Table 2, highlighting their effects on fractionation efficiency and lignin structural regulation. The following sections discuss the synergistic effects of ultrasound, microwave irradiation, and catalytic technologies with DESs.

Table 2. Synergistic strategies combining DESs with physical fields, catalytic systems, and biological treatments for enhanced lignocellulose deconstruction.

Route	Synergy Approaches	Biomass	DES (HBA:HBD)	Conditions	Lignin Removal (%)	Proposed Mechanism and Key Outcome	Reference
Physical field	Intermittent ultrasound	Durian husk	ChCl–LA (1:1)	80 °C, 1.5 h, 900 W ultrasound	99.44	Cavitation-induced disruption of biomass structure and improved DES penetration; CNF yield of 58.22%.	[72]

Table 2. *Cont.*

Route	Synergy Approaches	Biomass	DES (HBA:HBD)	Conditions	Lignin Removal (%)	Proposed Mechanism and Key Outcome	Reference
	Sweeping frequency ultrasound	Sugarcane bagasse	ChCl–LA (1:2)	120 °C, 3 h, sweeping-frequency ultrasound (40 kHz, 60 min)	85.6	Reduced acoustic dead zones and improved cavitation distribution.	[73]
	Microwave irradiation	Trans-genic poplar	ChCl–EG–$AlCl_3{\cdot}6H_2O$ and ChCl–Gly–$AlCl_3{\cdot}6H_2O$ (1:2:0.1)	110 °C, 10 min, 400 W microwave irradiation	93.0–95.1	Microwave dielectric heating enhanced DES activation and fractionation; aliphatic OH groups were partially preserved.	[74]
	Microwave irradiation	Moso bamboo	GH–Gly–$FeCl_3{\cdot}6H_2O$ (1:2:0.1)	120 °C, 350 W for 2 min followed by 150 W for 10 min	~81.0	Promoted LCC cleavage while maintaining lignin structural integrity.	[16]
Chemical catalysis	Lewis acid-assisted DES	Moso bamboo	ChCl–Gly (1:2)	140 °C, 3 h, 0.01 mol L^{-1} $AlCl_3$	89.7	Enhanced acidity; promoted β-O-4 cleavage and generation of lignin fragments.	[15]
	Acid-assisted DES	Poplar wood	ChCl–Gly (1:2) + H_2SO_4 catalyst	140 °C, 2–4 h	85.33	Water content affected DES performance; higher water content reduced lignin removal.	[28]
	Alkali-assisted DES	Poplar powder	ChCl–EG–CBSA (1:2:0.7) + KOH additive	90 °C, 30 min	97.01	KOH addition enhanced biomass swelling and accessibility.	[75]

Table 2. *Cont.*

Route	Synergy Approaches	Biomass	DES (HBA:HBD)	Conditions	Lignin Removal (%)	Proposed Mechanism and Key Outcome	Reference
	Lewis acid-assisted DES	Abaca	ChCl–EG–$AlCl_3$ (1:2:0.1)	120 °C, 30 min	94.61	High saccharification rate (9.72 times).	[76]
	Single-atom catalyst-assisted DES	Corn straw	ChCl–LA (1:2) + Nb/CN catalyst	120 °C, 6 h	96.5	Atomically dispersed Nb sites promoted LCC cleavage; DES environment may facilitate catalyst stability and recyclability.	[77]
Biological coupling	Laccase-enzyme Coupling	Rice straw	ChCl–Gly (1:2)	110 °C, 3 h DES pre-treatment followed by laccase treatment (pre-MW)	NR (focus on ethanol production)	Laccase-assisted oxidation of residual lignin; ethanol conversion reached 72.5%.	[78]

Abbreviations: ChCl, choline chloride; LA, lactic acid; Gly, glycerol; EG, ethylene glycol; GH, glycine hydrochloride; CBSA, chlorobenzene sulfonic acid; MW, microwave; CNF, cellulose nanofiber; LCC, lignin–carbohydrate complex; NR, not reported.

3.2.1. Ultrasound-Assisted Treatment

Ultrasound is an effective approach for alleviating the mass-transfer limitations associated with the high viscosity of DESs [79,80]. As illustrated in Figure 3a, the growth and rapid collapse of cavitation bubbles generate shock waves, high-velocity microjets, and local shear forces near solid–liquid interfaces. These effects disrupt the compact biomass structure, improve DES penetration, and increase effective contact between the solvent and lignocellulosic components [73,81].

Under moderate acoustic conditions, improved mass transfer can shorten treatment time or reduce the temperature required to achieve a comparable degree of fractionation. This may limit secondary lignin condensation associated with prolonged high-temperature treatment and help preserve the aromatic framework and some labile ether linkages [82]. Excessive sonication, however, may intensify acid-catalyzed hydrolysis in strongly acidic DESs and increase subsequent reactions of lignin-derived intermediates. Optimizing the ultrasonic pulse interval has been shown to improve delignification efficiency, indicating that ultrasound-assisted DES treatment requires a balance between intensified mass transfer and suppression of undesirable side reactions [72].

In addition to the sonication intensity and time, the control of the spatial distribution of the acoustic field also provides another approach to improve the performance of the process. This is due to the formation of standing waves, irregular cavitation regions and local overheating, which can result in non-uniform treatment using conventional fixed-frequency

ultrasound [83]. To solve this issue, Ji et al. applied a ChCl–LA system to handle the bagasse and preactivated it with periodic sweep-frequency ultrasound. By periodically changing the operating frequency, persistent standing waves were reduced and acoustic dead zones were eliminated, which led to a more uniform distribution of cavitation throughout the reactor. Mass transfer was then improved in the viscous DES using the bagasse that had been pretreated by ultrasound. Thus, the sweeping frequency treatment further enhanced the effectiveness of ultrasound and DES pretreatment: the lignin-removal rate was raised from 80.13% to 85.62% [73].

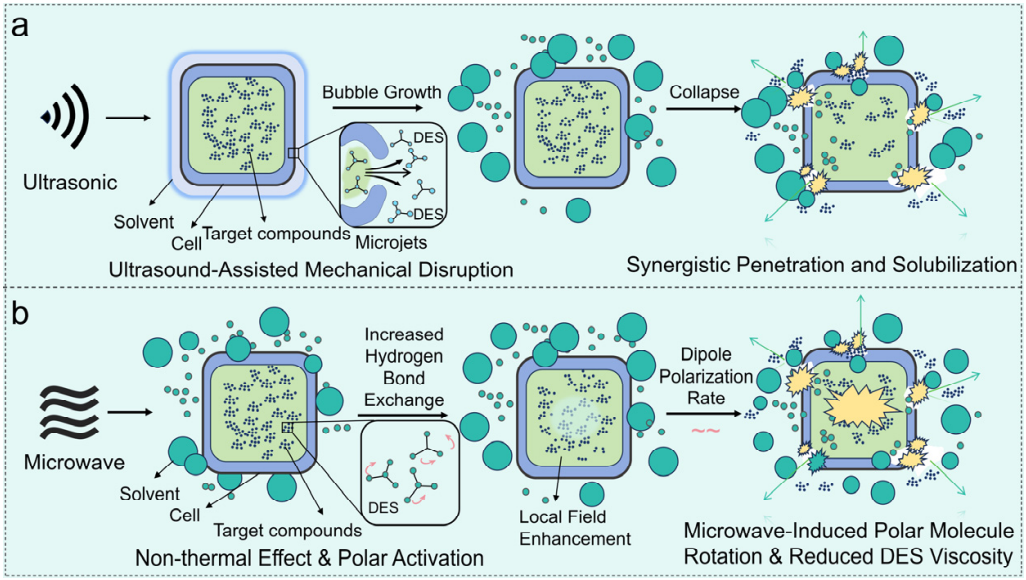

Figure 3. Mechanisms of physical-field-assisted DES pretreatment for lignocellulosic biomass fractionation. (**a**) Ultrasonic-induced cavitation enhancing cell wall disruption, DES penetration and mass transfer. (**b**) Microwave-assisted dielectric heating promoting volumetric heating, molecular motion, DES penetration, and lignin solubilization.

The concepts of physical chemical sequential strategies developed outside DES systems also are useful for future ultrasound-assisted DES processes. Liu et al., for instance, applied visible-light photocatalysis to oxidize the benzylic hydroxyl groups (α-OH) in lignin side chains into carbonyl groups, thereby decreasing the bond dissociation energy of β-O-4 linkages. The next applications of the ultrasound-assisted ethanolysis resulted in depolymerization of lignin and enhanced the conversion of lignin, light-oil yield and production of phenolic monomers in comparison to untreated lignin [84]. Although DESs were not tested in that study, the idea of chemical preactivation followed by physical-field-assisted depolymerization is a helpful framework to consider when designing future photocatalysis ultrasound DES systems [85].

3.2.2. Microwave-Assisted Treatment

Considerable attention has been paid to microwave-assisted pretreatment due to the capability of boosting the speed of DES-based fractionation. When an object is heated by microwave electromagnetic fields, the result is fast heating of the material throughout (volumetric heating), which is due to the increase in molecular motion and the exchange of internal energies from dipolar polarization and ionic conduction. These effects can facilitate DES penetration and acid-catalyzed reactions and promote the dissociation and dissolution of lignin, as shown in Figure 3b [86,87]. Under proper dielectric conditions, laboratory experiments demonstrate that microwave heating can significantly reduce treatment time [37].

Microwave-assisted polyol-based DESs could be used in lignin-first processing with high efficiency of delignification, but the structural preservation of lignin seems to be highly dependent on the HBD. Ma et al. studied the effect of a ChCl–Gly–$AlCl_3$ system and ChCl–EG–$AlCl_3$ system on the transgenic poplar. Both systems have been delignified with an efficiency of 92.98–95.13% under microwave irradiation at 110 °C. The increased thermochemical conditions, however, also led to a very high degree of cleavage of the β-O-4 ether bonds. The content of native lignin was 52.69–57.77 β-O-4/100 aromatic units (100 Ar), but only 1.17–3.92/100 Ar was detected after treatment with the EG-based DES, and almost none with the Gly-based system. The generated benzylic and phenolic intermediates reacted through cross-condensation, resulting in a change in the distribution of aromatic units and decreased selectivity in subsequent conversion of the lignin [74].

With careful consideration of microwave conditions and DES chemistry, such structural degeneration can be minimized. In a particular fractionation process, Xie et al. showed that diol-type DES treatment can be carried out simultaneously to in situ-modify reactive lignin intermediates by etherification reaction to suppress further condensation reactions. An abundance of 39.29/100 Ar of β-O-4 was obtained after treatment at 120 °C for 30 min and 84.19% structural retention was obtained for the fuel produced from peanut shells [88]. The outcome shows that DESs can be used not only as solvents and reaction media in the microwave treatment of lignin, but also as chemically active environments, which are able to guide the reaction pathways of the lignin.

Though microwave-assisted DES reactions have excellent lab-scale efficiency, many challenges are still associated with their scale-up [16]. The extremely polar DESs absorb microwave energy very efficiently, but this prevents the microwave energy from penetrating deeply when the reactor is large. Longer irradiation can also cause local overheating, non-uniform heat distribution, and thermal damage to the DES constituents, which can cause solvent performance to wane gradually over time. Moreover, the complexity of multiphysics control and relatively high operating costs are also important barriers to industrial implementation [89].

3.2.3. Chemical and Biological Catalysis

Introducing chemical or biological catalytic centers into DES media provides a route to integrating solvation, component fractionation, and selective bond cleavage within a single reaction system. Such coupled processes are increasingly considered as a means of improving both lignin separation efficiency and downstream utilization potential [90,91].

As discussed above, the introduction of Lewis acids can increase the effective acidity and electron-accepting ability of DESs [92]. Metal centers can coordinate with lone-pair electrons on oxygen atoms in β-O-4 and α-O-4 linkages, polarizing and weakening the corresponding C–O bonds. Within an appropriate acidity range, delignification generally increases with the number and strength of accessible acid sites. Lignin condensation and even carbonization, however, can be promoted by excessive acidity [15].

At atomically dispersed metal sites on solid supports, metal utilization is higher and separation and recycling of the catalysts easier than those of soluble metal salts. In the corn stover fractionation process in a ChCl–LA system, DES acts as an acidic, solvating and competitive hydrogen-bonding agent which can swell the biomass and induce part dissociation of LCC initially. Then, these cleavages occur on the interface, which is further promoted by an atomically dispersed Nb/CN solid acid. Structural characterization showed that Nb was mainly anchored to the carbon nitride support in an Nb–N_4 coordination environment, providing both weak and strong acidic sites. Treatment at 120 °C for 6 h resulted in 96.5% lignin removal. Importantly, the isolated lignin-rich fraction underwent only limited depolymerization and retained much of its structural integrity. The main

advantage of this system therefore lies in selective fractionation and lignin release under relatively mild conditions rather than extensive lignin depolymerization [77].

Biocatalysts such as laccases have also been investigated for the oxidation and removal of residual lignin and phenolic compounds. Sawhney et al. combined a ChCl-based DES with microwave irradiation and laccase treatment for rice straw pretreatment. DES solvation and microwave volumetric heating first disrupted the compact lignocellulosic structure, after which laccase further acted on residual lignin and phenolic fractions. Under optimized conditions, the reducing sugar yield reached 421.5 mg/g and the saccharification efficiency reached 72.6%. The selected laccase also showed good compatibility with ChCl-based DESs, retaining substantial residual activity after 72 h of pre-incubation in most of the DES formulations tested [78,93].

Overall, the design of DES-based synergistic systems involves three closely related considerations. First, mass-transfer limitations associated with high viscosity should be reduced by improving solvent penetration and energy transfer, thereby increasing the accessibility of lignocellulosic components. Second, Brønsted/Lewis acidity, hydrogen-bond competition, and interfacial activation should be controlled to promote cleavage of LCC linkages and lignin ether bonds. Third, irreversible condensation of reactive lignin intermediates should be minimized through nucleophilic protection by polyols, catalytic selectivity, and appropriately mild reaction conditions. Future process development should therefore move beyond maximizing delignification alone and instead optimize fractionation efficiency, lignin structural preservation, catalyst and solvent recyclability, and overall process economics. These selective fractionations and in situ stabilization strategies also provide a structural basis for the subsequent controlled depolymerization and functional utilization of lignin.

4. Lignin Depolymerization

In the following discussion, mechanistic statements are differentiated according to the supporting evidence: direct experimental observations are distinguished from model-compound studies, computational simulations, and proposed mechanistic interpretations.

For clarity, four distinct roles of DESs are differentiated throughout the following sections: (i) DES as a pretreatment or fractionation medium, after which lignin is converted in another medium; (ii) DES as the direct reaction medium or electrolyte during lignin depolymerization; (iii) DES as a catalyst-synthesis or material-synthesis medium, where the subsequent lignin reaction occurs outside the DES; and (iv) DES-derived lignin or DES-derived materials, where the DES affects upstream structure, but is not present during the final application. These categories represent different technological concepts and should not be attributed to the same DES-mediated mechanism.

DESs have been proposed to stabilize reactive intermediates. More commonly, however, they are used to promote the selective separation of lignin from the lignocellulosic matrix while preserving structurally reactive motifs through controlled fractionation conditions. However, the efficient conversion of lignin into value-added chemicals remains a major bottleneck in the comprehensive utilization of lignocellulosic biomass. Unlike the fractionation stage, which emphasizes structural preservation, lignin depolymerization requires selective cleavage of key interunit linkages while minimizing the recondensation and over-conversion of reactive aromatic fragments. This function of DESs is related to the microenvironment control of the reaction and stabilization of the reactive species generated.

DESs may play various roles in different depolymerization processes. DESs used for thermochemical conversion mainly serve to precondition lignin and facilitate subsequent bond cleavage. They can also serve as reaction media and modify the catalytic interface and local solvation environment of photocatalytic systems. DESs can play multiple roles in

electrochemical processes such as solvents, electrolytes and interface reaction regulators. Despite these differences among the three routes, activation of lignin linkages, solvation of fragments and control of reactive intermediates are all common features and the ultimate goal in each case is to maximize lignin conversion while maintaining high selectivity toward desirable products.

This section presents three types of depolymerization with the aid of DESs—thermochemical depolymerization, photocatalytic depolymerization, and electrochemical depolymerization—their respective reaction mechanisms, product distributions, and some issues to be considered in practical applications, as illustrated in Figure 4. Tables 3 and 4 provide some additional characteristics of each of these.

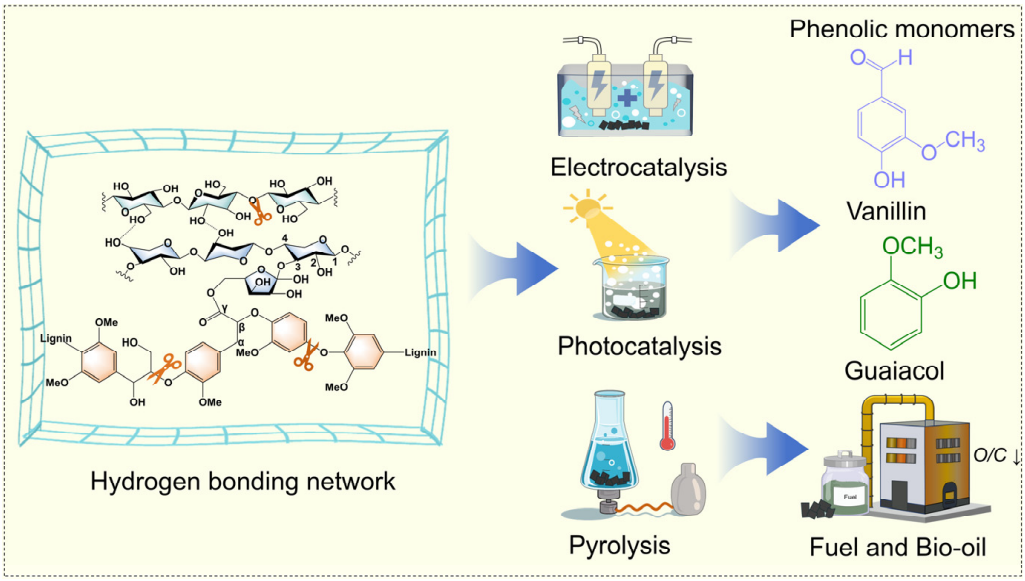

Figure 4. Representative lignin depolymerization strategies for the production of value-added chemicals and fuels. Electrocatalytic, photocatalytic and thermochemical approaches enable lignin conversion into products such as vanillin, guaiacol and bio-oil.

The lignin substrate is specified throughout this section because conversion results are strongly dependent on lignin origin and isolation history. Native-like or biomass-derived lignin retains a comparatively high proportion of structural motifs present in the original plant cell wall; technical lignin is a broader category of industrially isolated lignins that have undergone process-induced structural changes; Kraft lignin is a sulfur-containing technical lignin obtained from alkaline Kraft pulping and is typically more condensed; enzymatic-hydrolysis lignin is the lignin-rich residue remaining after enzymatic carbohydrate hydrolysis; and lignin model compounds are simplified molecules representing selected linkages, such as β-O-4. Conversion percentages obtained for model compounds should therefore not be directly compared with those of native or technical lignins.

Table 3. Comparison of selected DES-assisted lignin depolymerization pathways.

Depolymerization Method	Typical Reaction Conditions	Main Products	Core Advantages	Key Disadvantages and Challenges	Potential Applications	Reference
Pyrolysis	300–800 °C, seconds to minutes, inert/H_2 atmosphere	Bio-oil, guaiacol-type phenols, biochar	Mature industrial route, high throughput, wide feedstock adaptability	High energy cost, poor monomer selectivity, irreversible lignin recondensation and coking	Large-scale bio-fuels and carbon materials production	[94,95]
Photocatalysis	25–30 °C, visible or simulated sunlight, hours to days	Aromatic monomers (e.g., vanillin, guaiacol)	Mild conditions, low energy input, DES hydrogen-bond interactions may stabilize reactive intermediates	Limited light penetration in viscous DES, difficult catalyst recovery	Lab-scale synthesis of high-value aromatic platform chemicals	[96,97]
Electrocatalysis	25–30 °C, constant potential/current, hours	Vanillin, syringaldehyde, p-hydroxybenzoic acid	Controllable product distribution, no toxic oxidants/reductants, compatible with renewable energy integration	Electrode surface fouling, mass transfer limitations, poor long-term electrolyte recyclability	Precise preparation of bio-based fine chemical intermediates	[98]

Table 4. In-depth analysis of DES-mediated lignin conversion: mechanisms and performance.

Route	Substrate Type/Source	DES (HBA:HBD)	Process Conditions	Specific Role of DES in the Process	Key Findings/Merits	Limitations/Challenges	Reference
Pyrolysis	Technical lignin/Softwood enzymatic hydrolysis lignin	ChCl–LA (1:2)	DES pretreatment: 80–120 °C, 16 h; Pyrolysis: 550 °C, 8 min, N_2	DES pretreatment agent	Pretreated lignin obtains 2.59 times higher monophenol yield than raw lignin; bio-oil yield reaches 63.4 wt%	Severe aromatic condensation at high temperature; DES recovery requires energy-intensive water evaporation	[95]

Table 4. *Cont.*

Route	Substrate Type/Source	DES (HBA:HBD)	Process Conditions	Specific Role of DES in the Process	Key Findings/Merits	Limitations/Challenges	Reference
	Technical lignin/Softwood enzymatic hydrolysis lignin	K_2CO_3-Gly (1:5)	DES pretreatment: 80–120 °C, 16 h; Pyrolysis: 550 °C, 8 min, N_2	Alkaline DES pretreatment agent	Altered phenolic product distribution; bio-oil yield 52.1 wt%	Strong condensation tendency at high temperature; Lower monophenol selectivity compared with acidic DES under the investigated conditions	[95]
	Technical lignin/Kraft lignin	ChCl–4-Cl–BSA (1:0.7)	DES pretreatment: 130–170 °C, 1–7 h; Depolymerization: 150 °C, 3 h	Dual-function reactive solvent and homogeneous catalyst	Achieved 52.46% lignin depolymerization and highlighted the competition between depolymerization and recondensation	Limited efficiency for complex lignin substrates; extra measures required to suppress repolymerization	[99]
	Technical lignin/Softwood kraft lignin	ChCl–EG (1:2)	DES pretreatment: 120 °C, 2 h; Pyrolysis: 550 °C, 30 s, He	DES pretreatment agent	Enhanced p-hydroxyphen-yl-derived (H-type) phenolic fractions	High pyrolysis temperature demand; additional DES recovery after pretreatment may increase process complexity	[100]
	Technical lignin/softwood kraft lignin	$ZnCl_2$-EG (1:2)	DES pretreatment: 120 °C, 2 h; Pyrolysis: 550 °C, 30 s, He	DES pretreatment agent	Promoted catechol-type (C-type) phenolic products	Potential Zn residue and downstream purification issues; DES recovery remains challenging	[100]
	Technical lignin/softwood kraft lignin	ChCl–acetic acid (1:2)	DES pretreatment: 120 °C, 2 h; Pyrolysis: 550 °C, 30 s, He	DES pretreatment agent	Altered oxygenated aromatic product distribution	Acid-induced lignin condensation risk; DES recycling and long-term stability require further investigation	[100]

Table 4. *Cont.*

Route	Substrate Type/Source	DES (HBA:HBD)	Process Conditions	Specific Role of DES in the Process	Key Findings/Merits	Limitations/Challenges	Reference
	Biomass-derived lignin/oil palm lignin	ChCl–OA–EG (1:1:4)	DES pretreatment: 90 °C, 6 h, oil bath; Py-GCMS: 500 °C, 10 s, He	Structural protective agent	EG component protected lignin integrity; generates diverse phenolic products	Strong substrate specificity; complex multi-step reaction mechanisms	[101]
Photocatalysis	Lignin model compound/ β-O-4 lignin model	BT-CA (1.2:1, 60 vol% H_2O)	Full-spectrum visible light (238 W), 8 h, Bi_2O_3/ Bi_2WO_6 heterojunction photocatalyst	DES reaction medium and radical stabilizer	85.62% model depolymerization; generates guaiacol and p-hydroxyb-enzaldehyde.	Light penetration in viscous DES.	[102]
	Biomass-derived lignin/rice straw lignin	ChCl–Hydroquin-one (2:1)	25–30 °C, visible light, pH = 5, 1 mL/L H_2O_2, catalyst loading 0.7 g/L, lignin concentration 50 mg/L, 4 h	Photocatalyst modification medium and bandgap regulator	Induced bandgap shift; enhanced photocatalyst efficiency by nearly 5 times.	Magnetic catalyst separation difficulty; poor long-term stability in DES medium	[97]
Electrocatalysis	Lignin model compound/ β-O-4 model compound (PPe)	ChCl–EG (1:10) + CH_3CN co-solvent	25 °C, constant current 80 mA cm^{-2}, 6 h, Ni-Co/C carbon electrode	DES conductive electrolyte and radical stabilizer	91.86% depolymerization; generates benzaldehyde, acetophenone, benzoic acid.	Electrode fouling; high viscosity restricts mass transfer.	[103]

Table 4. *Cont.*

Route	Substrate Type/Source	DES (HBA:HBD)	Process Conditions	Specific Role of DES in the Process	Key Findings/Merits	Limitations/Challenges	Reference
	Technical lignin/Kraft lignin	ChCl–LA and ChCl–EG systems (1:2) + 10 vol% H_2O additive	Room temperature, CV −1.8~+1.8 V, 50 mV/s, 5 cycles, glassy carbon, Pt and Ag/AgCl electrodes	Conductive DES electrolyte	Max syringaldehyde 234.03 mg/L in ChCl–LA; GRA confirms 5 CV cycles as optimal condition.	Phenolic over-oxidation; low monomer yield compared to thermal methods.	[104]

Note: Substrate types are classified according to lignin origin and structural complexity. Lignin model compounds represent simplified structures containing specific interunit linkages, whereas technical lignin and biomass-derived lignin contain heterogeneous aromatic units and diverse linkages. Therefore, reported depolymerization efficiencies should not be directly compared among different substrate categories. Abbreviations: DES, deep eutectic solvent; ChCl, choline chloride; HBA, hydrogen-bond acceptor; HBD, hydrogen-bond donor; LA, lactic acid; Gly, glycerol; 4-Cl–BSA, 4-chlorobenzenesulfonic acid; OA, oxalic acid; EG, ethylene glycol; K_2CO_3, potassium carbonate; BT, benzothiazole; CH_3CN, acetonitrile; GRA, grey relational analysis; CV, cyclic voltammetry; PPe, phenethyl phenyl ether; Py-GCMS, pyrolysis gas chromatography–mass spectrometry; N_2, nitrogen atmosphere; He, helium atmosphere.

4.1. Pyrolytic Depolymerization

Although pyrolysis is a relatively mature thermochemical process, it has some issues such as low product selectivity, high energy consumption and large-scale catalyst deactivation [94]. An approach to counter some of the disadvantages of such limitations is to pretreat DES prior to the thermal conversion. Acidic DESs can induce protonation and cleavage of the β-O-4 linkages, solvation of the lignin, chemical degradation of the lignin in terms of its average molecular weight, increase the amount of phenolic hydroxyl groups of lignin, and decrease the intermolecular cross-linking of the lignin network [101]. Such alterations in the structure can result in changes in subsequent pyrolysis reactions, and can reduce the reactivity of the reactive intermediates towards condensation and char formation at high temperatures. As a result, the liquid product fraction can be increased while solid char formation is suppressed. For example, acidic DES pretreatment increased the pyrolysis-oil yield of lignin from 46.2 wt% to 63.4 wt% and promoted the formation of phenolic monomers such as 4-methylguaiacol, guaiacol, and 4-vinylguaiacol [95].

The evolution of functional groups during DES pretreatment also influences the formation and transformation of intermediates during pyrolysis, while different HBDs can shift the resulting product distribution [105]. Lignin pretreated with ChCl–EG and $ZnCl_2$–EG exhibits distinct product selectivity. ChCl–EG favors the formation of p-hydroxyphenyl-derived (H-type) compounds, whereas $ZnCl_2$–EG promotes the formation of catechol-type (C-type) products [106]. These differences may arise from the different effects of the two DES systems on dehydration of γ-hydroxyl groups and demethoxylation pathways during lignin conversion.

Further improvement in pyrolysis selectivity may require coupling upstream DES-mediated structural regulation with downstream catalytic upgrading [107]. Metal–organic frameworks (MOFs) and MOF-derived metal–carbon materials possess tunable pore structures and highly dispersed metal sites that can facilitate deoxygenation, hydrogenation, and aromatization of pyrolysis vapors [108]. Previous studies have shown that DES-derived functional groups can interact with ZIF-67 to construct bifunctional heterogeneous interfaces containing both Lewis acid sites and hydrogen-bonding sites. Although such systems have so far been investigated mainly for small-molecule reactions such as CO_2 cycloaddition, their interfacial design offers a potentially useful concept for lignin conversion [109].

On this basis, a staged strategy combining DES-mediated lignin preconditioning, pyrolysis, and confined catalytic upgrading with MOF-derived materials can be envisioned. In such a scheme, DES pretreatment would first reduce lignin polymerization and regulate interunit linkages, after which MOF-derived catalysts could promote deoxygenation and aromatization of the resulting pyrolysis vapors within confined pore environments [99,110]. This concept remains largely prospective, however, and its feasibility will depend on issues including DES residues, thermal transformation of MOFs, pore-scale mass transfer, and catalyst deactivation by coke deposition [111,112].

4.2. Photocatalytic Depolymerization

Photocatalytic depolymerization utilizes light energy to drive redox reactions and offers the advantage of selective cleavage of specific lignin interunit linkages under relatively mild conditions [96]. In recent years, DESs have been increasingly explored not only as alternative media for photocatalyst preparation but also as reaction environments for lignin photocatalytic conversion, providing new opportunities for catalyst design and regulation of the local reaction microenvironment.

DESs can act as solvents or structural modifiers during photocatalyst synthesis, influencing crystal phase formation, morphology, dopant incorporation, and optical properties of the resulting materials [113]. Mittal et al. employed a ChCl–hydroquinone DES as a

synthesis medium to prepare γ-Fe_2O_3/N and Fe co-doped Fe TiO_2 magnetic photocatalysts. The combined effects of N and Fe doping, together with the coupling between γ-Fe_2O_3 and TiO_2, narrowed the bandgap to 1.93 eV and enhanced visible-light absorption. The obtained catalyst promoted the conversion of straw-derived lignin into vanillin and guaiacol [97]. However, it should be noted that in this study DESs were mainly involved in photocatalyst synthesis, while subsequent lignin depolymerization was conducted in an aqueous medium.

Beyond catalyst preparation, DESs can also serve as reaction media to improve lignin dissolution and facilitate interfacial interactions between lignin molecules and heterogeneous photocatalysts [114]. For example, Suo et al. coupled a betaine–CA system (molar ratio 1.2:1, water content 60%) with a Bi_2O_3–Bi_2WO_6 heterojunction photocatalyst. Under visible-light irradiation at room temperature, this system achieved 85.62% depolymerization of a β-O-4 lignin model compound. When applied to spruce-derived native lignin, the depolymerization efficiencies of Klason lignin, dioxane lignin, and alkali lignin were 24.74%, 26.43%, and 32.25%, respectively [102]. These results demonstrate that the high bond-cleavage efficiency observed for model compounds cannot be directly extrapolated to native or technical lignins.

Mechanistic analysis reveals that the major merits of the Bi_2O_3–Bi_2WO_6 heterojunction are the effective separation and migration of photogenerated charge carriers, while the water in the DES regulates substrate dissolution, adsorption, and local proton reactions involving radicals. Real-time EPR analysis revealed phenoxy radical signals before irradiation, which may provide evidence for carbon-centered lignin radicals in the DES environment. The synergistic effect between DES-mediated microenvironment regulation and heterojunction photocatalysis resulted in $\cdot O_2^-$ being identified as the predominant active species following light activation [102].

Traditional photocatalytic systems, however, have issues with the quick recombination of electron hole, limited lifetime of the active oxygen species and poor selectivity of the radical induced reaction [115]. It is also suggested that both the competition between the bond cleavage pathway and the over oxidation pathway, and the recondensation pathway, can be affected by solvation environment of the DESs which can also affect the local stability, diffusion behavior and reaction probability of the reactive oxygen species and radicals that are formed during the lignin degradation process [96,114]. Thus, combining photocatalytic systems with a DES-controlled reaction environment may provide a promising route toward more selective lignin depolymerization.

4.3. Electrochemical Depolymerization

With the use of renewable electricity and the tuning of the applied potential, one should be able to selectively convert electrochemically depolymerized lignin under relatively mild conditions [98]. In these types of systems, the DESs can be used as medium to control the reaction at interfaces, as reaction solvent and as ionic conducting medium (Figure 5).

During electrolysis, the ionic constituents of DESs can form electrical double layers at electrode surfaces that differ substantially from those formed in dilute aqueous electrolytes. These interfacial structures may influence lignin-fragment adsorption, charge transfer, intermediate diffusion, and competing reaction pathways. But, the interfacial regulation in DES does not always result in the decrease of the resistance of the reaction. Their actual effects are a function of the different factors of viscosity, ionic conductivity, water content, materials of electrodes and applied potentials [104]. Zhang et al. employed a NiCo/C catalyst with a DES electrolyte system to study β-O-4 lignin model compounds. The in situ generation of reactive oxygen species, which was a key step in the process, accounted for almost 90% of the substrate conversion, while aromatic compounds, including benzaldehyde, benzoic acid, and phenol, were formed as products [103]. Mechanistic analysis showed that

the primary pathways of action were radical oxidation type of action with the involvement of both ·OH and $\cdot O_2^-$. As for the case of DES, the solvation environment around the substrates, the interfacial microstructure formed by DES, the adsorption of substrates, the diffusion of the reactive species, and the stabilization of the products can be affected, although the effect of DES on the suppression of intermediate recondensation is not understood.

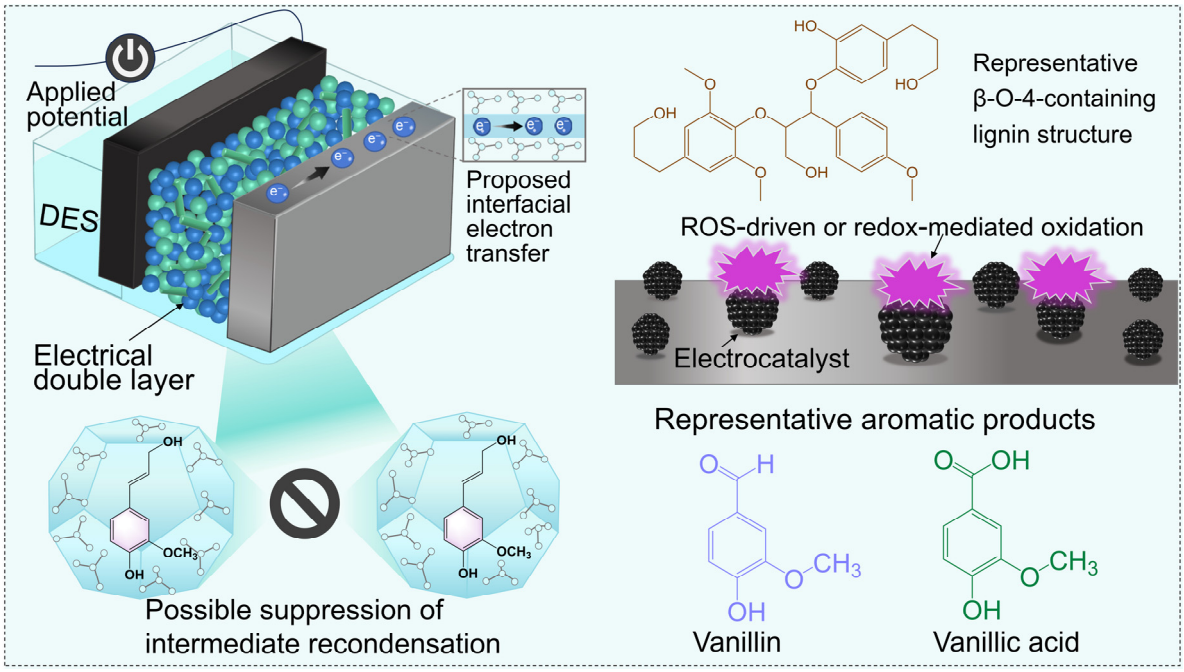

Figure 5. DES-assisted electrocatalytic lignin depolymerization toward selective aromatic products. DESs can serve as reaction medium and electrolytes to facilitate lignin activation, electron transfer and selective oxidation.

Polyoxometalate (POM)-based oxidation systems also show the ability of DESs to act as electrolyte-regulating media and reaction microenvironment modifiers in the case of electrochemical lignin transformation. Sun et al. designed a bimetallic-site POM/Ni foam electrode and selectively oxidatively cleaved the β-O-4 linkages in model compounds of lignin in a DES medium. In this system, DESs are not only used to offer the reaction environment but also to control the ion transportation, interfacial charge distribution, local solvation structure, hydrogen-bonding network and adsorption behavior of the substrate. In the meantime, it is possible that the ionic environment of DESs can affect the interfacial interactions between the POM active sites and the species derived from lignin. The POM-mediated interfacial electron-transfer process opens up possibilities for controlling the depth of oxidation as well as for tuning the selectivity for aromatic products. However, for DES–POM coupled systems, the compatibility between the electrolyte properties and catalytic activity has a significant influence on the performance of the system. Parameters such as DES viscosity, water content and ionic conductivity can affect the redox cycling of POM/bimetallic sites, electron transfer at the interface, and substrate and intermediate diffusion [116].

The effect of the DES structure in electrochemical lignin depolymerization is not the same for all the DES systems [90]. In general, DESs containing carboxylic acid are more efficient in swelling and dissolving lignin, while polyol-based DESs might be superior in electrochemical stability and intermediate regulation. Mass-transfer resistance is, however, a significant challenge for many highly viscous DES systems, especially in diffusion of macromolecular lignin fragments towards electrode surfaces. Besides the traditional methods

like increasing temperature, optimizing water content, and adding low-viscosity cosolvents, other methods like lignin-based self-supported integrated electrodes can be used [117]. Slurry-based catalytic reactors and reactors with two or more phases may help increase the utilization of the active sites and the mass transfer between the different phases [118].

While macroscopic transport can be enhanced by mass transfer, the molecular-level evolution of electrochemical interfaces mediated by DES remains not well understood. DESs have different solvation environments than conventional aqueous electrolytes and the interfacial processes underlying the operation of non-noble metal catalysts and long-term electrochemical stability of the catalysts need to be studied [119,120]. Furthermore, the high conversion and selectivity that has been achieved with lignin model compounds cannot be directly used to describe the performance of native lignin conversion. New indicators, such as aromatic monomer yield, carbon yield, product selectivity, Faradaic efficiency, energy consumption per unit product, and long-term recyclability of DESs and electrodes should therefore be taken into account for future assessment.

4.4. Summary

Considering the characteristics of different lignin depolymerization pathways discussed above, future developments may increasingly focus on integrated photoelectrochemical depolymerization strategies. In these systems, DESs may be used as electrolytes and reaction media, which may help dissolve the substrates and transport the ions between the interfaces as well as regulate the reaction at the interface [98]. The light irradiation could decrease the externally applied bias for the electrochemical conversion and the applied potential might be used to drive the separation and utilization of the photogenerated charge carriers in a preferred direction. DESs may provide a tunable microenvironment to stabilize the reactive species and modulate the interfacial electron-transfer processes under coupled energy fields.

However, practical implementation still faces challenges, including maintaining DES structural stability and ensuring efficient solvent recovery under complex multiphysics conditions. In general, the combination of DES-controlled reaction environment with advanced energy-input strategies could unlock the potential for further developing lignin depolymerization processes that are more pathway-selective and efficient in energy use.

5. DES-Based Lignin Functionalization and Applications

Lignin has various structural motifs—the aromatic backbone, the phenolic hydroxyl groups, and the reactive side chains—that enable its utilization in numerous applications, including UV shielding, radical scavenging, interfacial adhesion, and chemical derivatization [121]. However, because of the wide range of its molecular weight and the complex distribution of functional groups that are present in lignin, it is difficult to predict what properties and applications a given lignin will have. Thus, lignin separation and depolymerization should not be considered the ultimate objective of biomass valorization; rather, retaining and controlling lignin reactivity is a prerequisite for high-value utilization.

In addition to their use as tunable fractionation media, DESs also have the ability to modify lignin microstructure and reactivity by hydrogen-bond interactions, acid–base catalysis and in situ stabilization effects [25]. Recent developments in DES-mediated lignin modification and functionalization are summarized, with a focus on three main application areas: smart and functional materials, bio-based platform chemicals, and bioenergy conversion. Representative applications of DES-derived lignin toward smart and functional materials are illustrated in Figure 6. Further discussion of the potential for industrial implementation and environmental benefits is carried out from the techno-economic analysis (TEA) and life-cycle assessment (LCA) points of view.

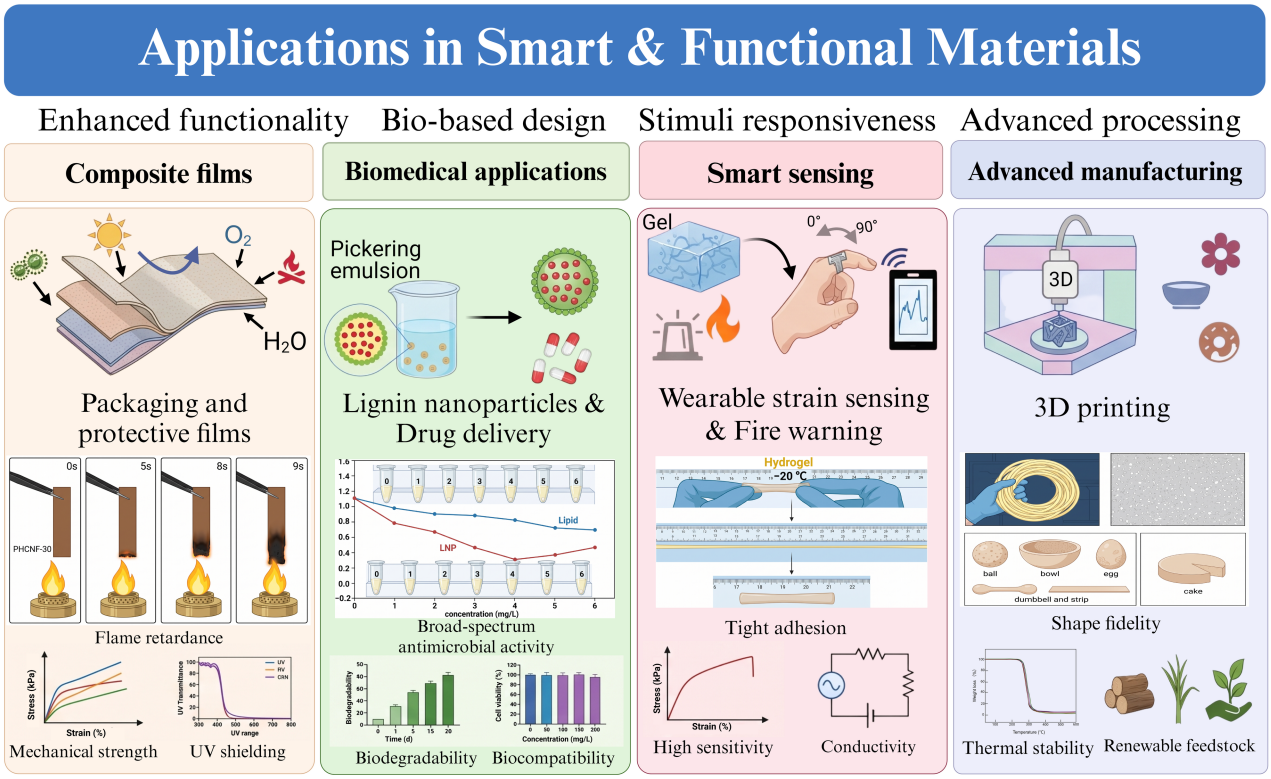

Figure 6. Representative applications of DES-derived lignin toward smart and functional materials, including composite films, biomedical materials, smart sensing system and advanced manufacturing. This figure has been redrawn and adapted from [122–125].

5.1. Targeted Chemical Modification of Lignin in DESs

The high and broadly distributed molecular weight of lignin, together with the heterogeneous distribution of its functional groups, contributes to variable chemical reactivity and inconsistent material performance [7,126]. DESs offer a platform that can be used to tune the interactions between molecules and the reaction environment to modify lignin [127].

Two-dimensional heteronuclear single quantum coherence (2D-HSQC) analysis has shown that certain DES systems promote cleavage of β-O-4 linkages through hydrogen-bond competition, acid–base activation, and nucleophilic interactions. These processes can also be responsible for the partial demethoxylation and ether-bond transformation which leads to higher exposure of the phenolic hydroxyl groups. For example, a ChCl–EG system achieved an H-type phenolic product yield of 38.39%, whereas a $ZnCl_2$–EG system favored C-type phenolic products with a yield of 34.02% [100]. By regulating the abundance and distribution of functional groups at the molecular level, DES-mediated structural modification can improve the subsequent conversion efficiency and material performance of lignin.

Phenolic hydroxyl groups serve as key reactive sites for lignin functionalization. Conventional lignin modification generally follows a two-step process involving lignin isolation followed by chemical derivatization [128]. Reported modification strategies include grafting phenolation [129], DDQ-assisted pre-oxidation [130], radical polymerization/cross-linking [131], esterification [132] and multiple fatty-chain modification [133]. For instance, introducing long-chain aliphatic groups into lignin side chains can reduce surface polarity, adjust hydrophilic–hydrophobic balance, and improve compatibility between lignin and nonpolar polymers [133]. However, conventional modification routes often rely on organic solvents, strong acid/base catalysts, or multiple separation and purification steps, resulting in increased solvent consumption, processing time, and purification requirements [134].

To overcome the limitations of conventional multi-step modification, coupling DES-mediated solvation with in situ functionalization has emerged as an alternative one-step strategy. Reactive amino acid-derived DESs have been developed to achieve targeted lignin amination directly during the modification process (Figure 7). These DESs simultaneously promote lignin dissolution and β-O-4 cleavage while enabling amino acid components to participate in subsequent functionalization reactions. Mechanistic studies revealed that a lysine–formic acid DES can increase lignin phenolic hydroxyl content by approximately 50% through enhanced bond cleavage. The amino acid moiety can undergo nucleophilic reactions with reactive lignin side chains or Schiff-base condensation with carbonyl groups generated during oxidative depolymerization, introducing amino and carboxyl functionalities into the lignin backbone and producing amphoteric functionalized lignin [135].

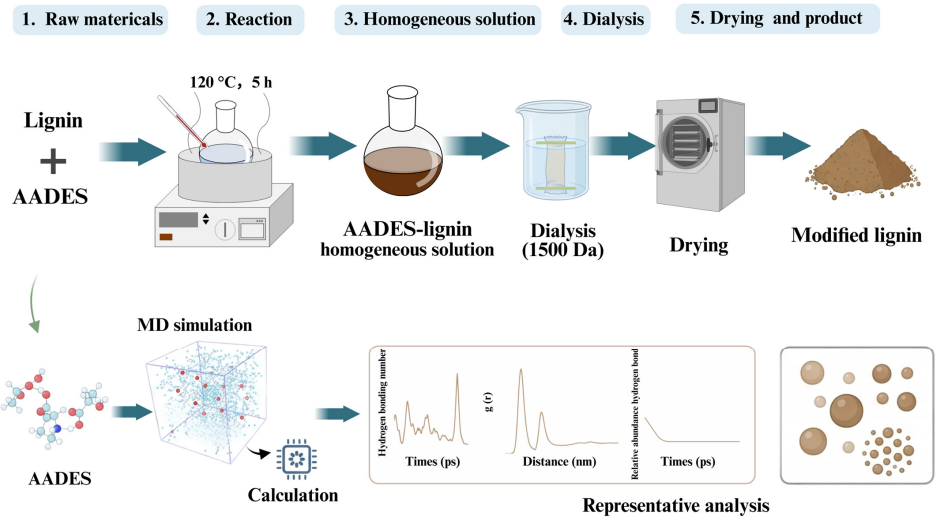

Figure 7. Schematic illustration of AADES-mediated lignin dissolution and in situ functionalization redrawn (adapted from [135]).

However, the reproducibility of the process and purification costs are the main concerns in the scale-up of lignin modification with DES. Inconsistency of functional-group substitution efficiency and modification can be affected by variation in biomass feedstock. Furthermore, the majority of the existing literature employs laboratory grade lignin with only purified lignin samples studied and the impact that impurities (including ash and residual carbohydrates) in the crude lignin have on the lignin modification is not sufficiently known. Research in the future therefore should aim for robust DES-based functionalization with increased tolerance to heterogeneous lignin feedstocks.

5.2. High-Value Functional Materials

As discussed in the previous section, the solvation effect and the regulation of structure of DESs can be used to prepare high-performance, lignin-based functional materials. The tunable properties of DESs can be used to assemble and integrate lignin structure at multiple structural scales to form a functional composite, such as UV shielding and flame retardant composites or intelligent composites with a sensing function. Three representative systems of applications, namely lignin nanoparticles (LNPs), lignin–cellulose nanofiber (LCNF) composites, and smart responsive materials, are described below.

5.2.1. LNPs and Colloidal Systems

Controlled morphology of LNPs can be achieved by using tunable and mild DES systems as media [136]. In antisolvent precipitation, DESs affect the dissolution behavior of

lignin, its interactions among molecules and exposure of functional groups on the surface which affects the nucleation and aggregation of LNPs [122].

The HBD structure and acidity of DESs define the morphology and surface chemistry of LNPs. Acidic ChCl-based DESs can help to decrease the solubility of lignin, and also help to promote homogeneous nucleation to ensure the formation of nanoparticles with several tens nanometers and relatively narrow size distribution. In situ acid-induced demethoxylation can be used to change particle surfaces and enhance the surface charge density, the absolute value of the zeta potential of some systems is over 30 mV [122,137].

Due to their small size, numerous phenolic hydroxyl groups and high surface charge, these active LNPs have the potential to be used as functional fillers in biodegradable polymer films [138]. Due to the numerous hydroxyl groups on the LNP surface, there are hydrogen bonds formed at the interface between LNP and polymer matrices (3D network) [139]. For instance, Li et al. added a walnut-shell-derived LNPs which were extracted using a ternary DES in PVA films. With the help of mechanical analysis, it was found that both tensile strength (33.32 MPa) and elongation at break (45.52%) of the samples improved simultaneously owing to improved stress transfer and energy dissipation properties. Moreover, the aromatic lignin structures were evenly distributed contributing to the UV-shielding property, which was higher than 80% for both UVA and UVB region [139–141].

In the case of cellulose-based composites where the interfacial integrity is not so great, other DESs with heteroatoms like phytic acid with sulfamic acid and urea, can promote in situ esterification and phosphorylation of LNPs. These modified nanoparticles exhibit improved interfacial bonding with cellulose matrices and promote compact char-layer formation during thermal degradation, thereby enhancing flame retardancy and oxidation resistance of composites [125].

Beyond solid-state composite applications, DES-regulated wettability and surface charge endow LNPs with amphiphilic characteristics. Electrostatic repulsion prevents droplet coalescence and improves colloidal stability, making LNPs suitable as bio-based Pickering emulsion stabilizers [142,143]. These systems show potential applications in cosmetics, drug delivery, bio-based coatings, and active packaging [121,122,144,145].

5.2.2. LCNF Composites

DES systems can simultaneously promote cellulose fibrillation while retaining an appropriate amount of lignin, thereby providing nanofibers with multifunctional properties [146]. For example, fractionation of straw using an $FeCl_3$-modified ChCl–EG system produced lignin-rich LCNFs [147]. During this process, DES-induced moderate demethoxylation increases phenolic hydroxyl content, facilitating interactions among lignin, cellulose, and polymer matrices.

Compared with pure cellulose nanofibers, LCNFs exhibit enhanced hydrophobicity and UV-shielding ability [148]. For instance, ChCl–OA combined with surface modification using oxazolidinone generated lignin-enriched outer layers on fibers, reducing surface energy and improving dispersion within hydrophobic PLA matrices [149]. Only 3.7 wt% addition was sufficient to increase composite flexural strength by 153% through efficient interfacial stress transfer. Furthermore, ChCl–LA combined with ultrasonic treatment of alkaline peroxide mechanical pulp achieved a high LCNF yield of 68.23% [150].

The three-dimensional lignin–cellulose framework provides LCNFs with shear-thinning behavior and low yield stress, making them promising candidates for sustainable 3D printing materials. Residual lignin acts as a natural compatibilizer, improving interfacial adhesion between LCNFs and PLA and facilitating high-precision extrusion-based manufacturing [124]. DES-based one-pot pretreatment combined with surface grafting strategies further enables regulation of rheological and mechanical properties, offering potential for

complex bio-based materials in applications such as tissue scaffolds, active food packaging, and optical films [151].

5.2.3. Flexible Electronics and Smart Responsive Materials

DESs can serve as reaction media for constructing flexible polymer networks. A ChCl–EG–H_2O ternary DES system can disrupt aggregation of external alkali lignin through strong hydrogen-bond interactions. Free radicals generated on liquid gallium–indium alloy surfaces interact with lignin through hydrogen bonding, enabling in situ polymerization and formation of flexible functional materials. The resultant sensor has high electrical conductivity (0.33 S m^{-1} at room temperature), a quick response time (milliseconds) and long durability (more than thousands of times stretching), which enables the sensor to detect the pulse signal and minor changes in the human body [123].

Current hydrogels have limitations such as water loss and low-temperature brittleness. Ionogels, however, fabricated using ChCl–Gly DESs and lignin–hemicellulose complexes, have long-term water-holding capabilities and antifreeze properties [152,153]. The hydrogen-bond network of DESs makes it difficult to evaporate the solvent [154]. At the same time, lignin–hemicellulose complexes reform hydrogen-bonding network in the nanocell, inhibit water crystallization and facilitate dissociation and release of bound Cl^- ions. These mechanisms give the materials flexibility at low temperatures as well as a high ionic conductivity (161 S m^{-1}), which enhances both mechanical and electrical performance. Furthermore, the materials are thermoresponsive, meaning that when the temperature is above a certain point, the DES ions migrate faster, drastically reducing resistance and thus allowing second level fire warning actions [152].

5.3. Platform Chemicals and Bioenergy Conversion

DESs can also control the pathway of lignin depolymerization by controlling bond-cleavage pathways and facilitate the conversion of the aromatic framework to value added platform molecules. Combined with external energy fields, DESs can tune the thermodynamic stability and local chemical environment lignin molecules, thereby controlling product distributions and improving conversion efficiency.

5.3.1. Selective Depolymerization Toward Aromatic Monomers

This section emphasizes the unique effect of DES in combination with external energy inputs to control lignin functional groups and reaction intermediates to facilitate the selective formation and enrichment of phenolics with the other routes of lignin depolymerization summarized in Section 4.

The matching of HBA and HBD plays a decisive role in determining monomer yields and product selectivity. In acidic ChCl–LA systems, weakening of β-O-4 linkages and the formation of Hibbert's ketone intermediates favor the production of 4-methylguaiacol during pyrolysis, increasing its yield to 2.59 times that obtained from native lignin. In contrast, alkaline and transition-metal-based DESs show greater selectivity toward platform compounds such as acetophenone derivatives and aromatic aldehydes [95].

DES-assisted photocatalytic strategies may involve either DES-mediated photocatalyst synthesis or the direct use of DESs as reaction media. In the former case, a ChCl–hydroquinone DES can be used as a precursor for photocatalyst synthesis, whereas the subsequent lignin depolymerization was performed in an aqueous medium. Under visible-light irradiation, lignin depolymerization of up to 97.1% has been achieved, accompanied by the enrichment of value-added phenolic products such as vanillin and guaiacol. These products are attractive feedstocks for green flavor and fragrance production as well as pharmaceutical intermediates [97].

DESs are also advantageous in electrocatalytic conversion because they reduce side reactions associated with aqueous electrolysis while suppressing uncontrolled secondary repolymerization of the products [90]. In a ChCl–OA system, hydrogen-bond interactions stabilize reactive intermediates and facilitate efficient conversion of lignin model compounds, resulting in markedly improved selectivity and yields of acetophenone, phenol, and benzoic acid [116]. For the electrolysis of industrial kraft lignin, DESs such as ChCl–LA and ChCl–EG can serve as alternative ionic electrolytes. Grey relational analysis showed that after five cyclic voltammetry scans, the syringaldehyde concentration reached a maximum of 234.03 mg/L, demonstrating a potentially robust route for the selective production of phenolic compounds from industrial lignin [104].

5.3.2. Liquid-Fuel Precursors and Bio-Oil

Unlike chemical-production routes that prioritize monomer purity and yield, DES treatment can improve the fuel properties of lignin by restructuring its elemental composition and molecular-weight distribution, thereby increasing the energy density and quality of the resulting bio-oil.

Pretreatment of softwood kraft lignin with a ternary ChCl–CA–EG DES promotes chemical deoxygenation and increases the relative carbon and hydrogen contents, raising the higher heating value from 22.67 to 25.92 MJ/kg. DES treatment can also remove impurities such as residual hemicellulose and ash, reducing the formation of non-energy products such as CO_2 and H_2O during pyrolysis and consequently improving the energy density and storage stability of the resulting bio-oil [106].

Manipulation of lignin's molecular-weight distribution can make further changes in its behavior during high-temperature processing. Lignin is very prone to producing highly reactive radicals when exposed to heat, which drive dehydrogenative cross-linking and extensive char formation if not treated. With the DES, the overall radical concentration has been reduced from 3.84×10^{17} to 1.61×10^{17} spins/g, which prevents excessive cross-linking, char formation and likewise other side reactions, but still leaves enough radical activity for depolymerization. In the meantime, the ratio of value added catechol-type compounds and light monocyclic aromatics in the bio-oil rises and can be used as valuable feedstock for fine-chemical–pharmaceutical synthesis [100,155].

5.4. Comprehensive Assessment of Industrialization Pathways

Lignin is both technically interesting from an industrial point of view and at the same time naturally a structural limitation from a feedstock point of view. It is widely available, has a distinctive aromatic structure and possesses a variety of reactive functionalities that can lead to the production of platform chemicals, functional materials and biofuels. However, because of the diversity of botanical sources and isolation techniques, the S/G/H composition, abundance of β-O-4 linkages, degree of condensation, molecular weight, and impurity content can vary considerably, making selective conversion and continuous processing challenging. Thus, the main challenge for lignin industrialization lies not in feedstock availability, but in achieving consistent conversion of structurally heterogeneous lignin. DESs can improve lignin fractionation, dissolution, and selective bond cleavage through their tunable solvation environments, although large-scale implementation remains constrained by economic viability, environmental impacts, solvent recyclability, and process control. This section therefore evaluates DES-mediated lignin utilization from the perspectives of techno-economic performance, life-cycle impacts, and structure–performance relationships.

5.4.1. TEA and LCA

A key consideration in evaluating DES-mediated lignin processing is the overall efficiency of resource recovery and recycling throughout the process [156]. Techno-economic studies of specific DES-based biomass processes indicate that solvent recovery can substantially influence process economics. For example, in a DES-based crystalline nanocellulose production process using an oil palm empty fruit bunch, solvent recovery reduced the estimated production cost from USD 4.75 to 3.56 kg^{-1} CNC [157]. However, such results are process-specific and should not be interpreted as universal recovery requirements for DES-mediated lignin refining. During scale-up and repeated recycling, biomass-derived ash components, including K^+ and Na^+ ions, together with degraded oligosaccharides, can accumulate in the solvent phase. These impurities disrupt the equilibrium structure of DESs and progressively impair their rheological properties and dissociation capacity [158].

Available TEA and LCA studies indicate that solvent recovery can influence both process economics and environmental performance; however, the magnitude of these effects is highly system-specific. Reported outcomes depend on the DES composition, feedstock, product slate, recovery method, allocation procedure, functional unit, and system boundary [157,158]. Direct TEA/LCA data for DES-mediated lignin refining remain comparatively limited, and quantitative findings from broader biomass-processing systems should therefore be identified explicitly as case-specific rather than directly extrapolated to lignin refining [157,158].

Beyond production cost, life-cycle environmental impacts represent another major barrier to DES industrialization. Microwave-assisted DES treatment has been explored to reduce the energy demand associated with conventional high-temperature processing. Reaction times can be shortened from 1–3 h to 2–15 min, substantially reducing the duration of thermal exposure and thereby lowering the environmental burden of the pretreatment stage [159]. Nevertheless, such process intensification primarily reduces energy consumption and does not necessarily eliminate upstream environmental burdens associated with DES synthesis or emissions arising from other stages of the process.

Allocation among multiple product streams represents a potential source of uncertainty in TEA and LCA of integrated biomass-processing systems. However, standardized allocation approaches for high-value lignin products remain limited. Together with the lack of comprehensive inventory data for high-purity DES components, this introduces substantial uncertainty into coupled TEA–LCA assessments and limits direct comparison among different process configurations.

5.4.2. DES Recovery, Regeneration, and Cycling Stability

Quantitative recycling performance is strongly formulation- and regeneration-dependent. For a ChCl–OA system used for corncob pretreatment, Yan et al. [160] showed that supplementing the depleted OA component and removing lignin from the recovered solvent enabled reuse for ten cycles. After the tenth cycle, glucan digestibility and glucose recovery were 66.23% and 64.43%, respectively, compared with 72.83% and 68.83% for the fresh DES treatment. These results demonstrate that replenishment of reactive components and impurity removal can be more important than cycle number alone.

More recent work on DES recycling after lignin extraction further demonstrates the importance of impurity management. Pasquet et al. [161] reported that continuous adsorption removed approximately 50% of lignin degradation products, while nanofiltration concentrated nearly 70% of hemicellulose-derived material in the retentate. The purified recycled DES restored lignin-extraction performance to a level approaching that achieved with fresh solvent. These studies show that cycling stability should be reported together with DES composition, recovery procedure, component loss or replenishment, impurity accumulation,

and retained fractionation performance rather than only as the number of reuse cycles. Quantitative data on regeneration energy, viscosity evolution, and composition drift remain unavailable for many published systems, which limits direct engineering comparison.

Future regeneration strategies may extend beyond conventional purification methods. Hydrophobic separation mechanisms developed in pharmaceutical and advanced-material systems could be adapted to facilitate DES recovery [27]. Another promising direction is the development of stimuli-responsive DESs, including thermoresponsive and pH-responsive systems [162]. By switching phase behavior or ionization states in response to external stimuli, these systems may enable controllable changes in solubility and thereby facilitate lignin–solvent separation while improving cycling stability.

5.4.3. Structure–Performance Relationships

A further challenge for continuous industrial processing arises from the intrinsic variability of lignin feedstocks. Lignin depolymerization and functionalization are governed by the interplay of multiple variables [163]. These include intrinsic lignin characteristics, such as the S/G/H ratio and initial β-O-4 abundance; DES-related parameters, including the HBD/HBA ratio, Hansen solubility parameters, and interfacial charge density; and operating conditions such as temperature, mass-transfer rate, and externally applied photonic or electric fields [24,164].

Current laboratory characterization relies largely on intermittent ex situ techniques such as 2D-HSQC NMR and FT-IR [43]. Although these methods provide useful qualitative and semi-quantitative structural information, they cannot capture in real time the dynamic evolution of DES hydrogen-bond networks and lignin structures during reaction. Existing predictive approaches are still dominated by relatively simple linear fitting models and are rarely supported by in situ or online spectroscopic monitoring within reactors. Their limited ability to accommodate impurity-rich industrial lignin results in poor batch-to-batch reproducibility and restricts reliable operation under continuous-processing conditions [165].

Overall, lignin offers a strong resource base and substantial potential for high-value utilization, but structural heterogeneity, process-induced condensation, and complex impurities continue to hinder stable continuous conversion. While DESs can remove some of the limitations that are related to lignin dissolution and selective depolymerization, the high viscosity of DESs, performance loss after recycling, energy requirements for regeneration, and environmental impacts remain unresolved issues. Future industrial process development will therefore require harmonized advances in feedstock fractionation, rational DES design, efficient solvent recovery and regeneration, process intensification, and online monitoring to ensure stable and cost-effective lignin conversion while balancing economic performance and environmental sustainability.

6. Conclusions and Outlook

6.1. Conclusions

Lignin utilization should be one of the main pathways to maximize the utilization of lignocellulosic biomass. The roles and underlying mechanisms of DESs in the lignin-refining process have been reviewed with a particular focus on lignin separation, catalytic depolymerization, and functional applications. The benefits of DESs are not limited to lignin dissolution/extraction. Their hydrogen-bond networks are tunable, which can change the solvation environment of lignin locally and affect bond-cleavage behavior. DESs can help to eliminate mass-transfer limitations and reduce reaction times along with maintaining structurally active moieties in lignin in combination with process-intensification techniques like ultrasound and microwave irradiation. In subsequent depolymerization, DESs may function as reaction media or interfacial modifiers. Available experimental, model-compound, and

computational studies suggest that their local solvation environments can influence intermediate stability, secondary condensation, and aromatic-product selectivity, thereby enhancing selectivity toward aromatic monomers such as vanillin and guaiacol. Lignin extracted by DES fractionation/deconstruction or chemically modified also has higher structural tunability to be incorporated in LCNFs, hydrogels, and stimuli-responsive composites. The molecular-weight distribution and thermal reactivity controlled by DESs can also decrease char generation during the pyrolysis process and enhance the quality of bio-oil. As a whole, DESs offer a partially connected pathway for lignin isolation and control of structure to subsequent materials/energy uses. Thus, their main advantage lies not simply in serving as alternatives to traditional solvents, but in their capacity to control multiple steps of the lignin conversion process.

6.2. Outlook

Although understanding of the roles of DESs in lignin refining has increased, their industrial application remains limited by solvent properties, feedstock variability, and scale-up challenges. High viscosity, associated mass-transfer resistance, and energy requirements for solvent recovery remain among the most pressing engineering constraints. Future DES development should therefore focus more on feedstock compatibility and recyclability. The impact of lignin-related compounds on the system and the possibility of using systems based on naturally occurring metabolites to reduce the reliance on petrochemical precursors should be studied, and the long-term changes in the composition of HBAs/HBDs and the buildup of ash, oligosaccharides, and other impurities during successive cycles should be systematically investigated. It is likely that in such cases the integration of membrane separation or selective adsorption or other low energy purification methods in the solvent regeneration will be more relevant to practical scale-up than maximization of extraction efficiency in one cycle.

The second limiting factor is the absence of good quantitative relationships between the composition of the DES and the structure of the lignin and the results of the reaction. A lot of the literature that exists is based on post-reaction, ex situ characterization, providing only limited information on the simultaneous evolution of hydrogen-bond network, lignin structure and reactive intermediates. Several experiments and simulations could be integrated together to establish more quantitative connections among the composition of DESs, the local reaction environment and product selectivity. Importantly, DESs should not be designed to pursue high acidity, alkalinity, or increased lignin solubility. An effective system should provide for intermediate stabilization, allowing for the cleavage of target linkages without high reactivity that could lead to grafting, condensation or further degradation. The creation of the relationships mentioned above would make it possible to shift DES screening gradually from the empirical trial-and-error mode to more specific design to specific lignin structures to obtain specific products.

From a process view, the majority of studies are still performed in batch reactors, and high conversion under laboratory conditions does not necessarily lead to stable operation under continuous conditions. Mixing, heat and mass transfer in this case should be considered in a new light, in the context of continuous-flow and process-intensified systems with high solids and high viscosities. Industrial feedstocks in particular should also be given greater attention. Limnic substances such as ash, residual carbohydrates, and different extents of condensation of the lignin can all affect the behavior of DES, but these effects are frequently overlooked when using model compounds as DES substrates or highly purified lignin.

Finally, the viability of lignin refining using DESs on a large scale will be determined by the feasibility of simultaneous technical performance, economic viability and environmental benefits. Future assessments should thus focus on the life cycle, from the procurement

of feedstock to the production of DESs and the recycling of solvents to the separation of products to waste treatment, and should involve adequate tools for allocating costs and environmental burdens to multiple products derived from lignin. Integrating reaction selectivity, solvent recycling, continuous processing, and TEA/LCA within the same process framework will provide a more realistic basis for assessing the industrial potential of DES-mediated lignin refining.

Author Contributions: H.W.: writing—original draft, investigation, conceptualization. A.M.: writing–review and editing, investigation. L.C.: writing—review and editing. X.Y.: writing—review and editing. M.R.: writing—review and editing. S.Z.: writing—review and editing. H.Y.: writing—review and editing. C.Z.: writing—review and editing, conceptualization, funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key R&D Program (2025YFF1107305), Jiangsu Provincial Frontier Technology R&D Program (Modern Agriculture BF2025319).

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article.

Acknowledgments: During the preparation of this manuscript, the authors used ChatGPT (OpenAI, GPT-5.6) solely for language polishing, including grammar correction, sentence refinement, and improvement of readability. All AI-assisted suggestions were carefully reviewed and revised as necessary by the authors, who take full responsibility for the final content of the manuscript.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript.

DES	deep eutectic solvent
HBA	hydrogen-bond acceptor
HBD	hydrogen-bond donor
LCC	lignin–carbohydrate complex
MW	microwave
CNF	cellulose nanofiber
LNPs	lignin nanoparticles
LCNF	lignin-containing cellulose nanofiber
TEA	techno-economic analysis
LCA	life-cycle assessment
ChCl	choline chloride
LA	lactic acid
OA	oxalic acid
CA	citric acid
Gly	glycerol
EG	ethylene glycol
EaCl	ethylammonium chloride
GH	glycine hydrochloride
TEG	triethylene glycol
TEBAC	triethylbenzylammonium chloride
VAN	vanillin
POM	polyoxometalate
MOF	metal–organic framework
CBSA	chlorobenzene sulfonic acid
EtOH	ethanol
BT	benzothiazole
CH_3CN	acetonitrile

K_2CO_3	potassium carbonate
$AlCl_3$	aluminum chloride
$ZnCl_2$	zinc chloride
$FeCl_3$	ferric chloride
CV	cyclic voltammetry
GRA	grey relational analysis
PPe	phenethyl phenyl ether
2D HSQC	two-dimensional heteronuclear single quantum coherence spectroscopy
Py-GCMS	pyrolysis gas chromatography–mass spectrometry
FTIR	Fourier transform infrared spectroscopy
NR	not reported
EFB	empty fruit bunch

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