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Advancements and Applications of Microwave-Assisted Deep Eutectic Solvent (MW-DES) Lignin Extraction: A Comprehensive Review

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Nomenclature

MW-DES: microwave assisted-deep eutectic solvent
LCB: lignocellulosic biomass
ILs: ionic liquids
HBD: hydrogen bond donor
HBA: hydrogen bond acceptor
Kamlet-Taft (K-T)
ChCl: choline chloride
LA: lactic acid
AA: acetic acid
GA: glycolic acid
FA: formic acid
OA: oxalic acid
H-unit: paracoumaryl alcohol
S-unite: sinapyl alcohol
G-unit: coniferyl alcohol
LCCs: lignin-carbohydrate complexes
GBG: guaiacylglycerol-β-guaiacyl ether
Mn: average molecular weight
Mw: weight-average molecular weight
DESL: lignin extracted with DES
MWL: milled wood lignin

Abstract

Lignocellulosic-derived biorefineries present an environmentally friendly avenue for generating biofuels and bioproducts, curbing emissions, and advancing environmental stewardship. Yet, the intricate structure of biomass poses obstacles to its efficient conversion into bio-derived products while conserving the native bonding motifs, especially for lignin. The limitations of conventional methodologies stimulated the exploration of innovative solvents and processes. Deep eutectic solvents (DES), a class of solvents comprised of mixtures of hydrogen-donor and hydrogen-acceptor compounds, boasting low toxicity, remarkable solubility, adaptability in synthesis, and selectivity, have garnered increasing attention as sustainable solvents for lignin extraction. The incorporation of microwave-assisted heating can further enhance DES-based lignin extraction efficiency and potential for value creation.

This comprehensive review underscores the potential of the MW-DES technique in harnessing lignin—a prized renewable resource—for the sustainable production of energy and materials. From dissecting DES's elemental composition to elucidating DES-microwave-biomass interactions, scrutinizing the MW-DES lignin extraction process factors, and delving into extracted lignin characterization, this review aims to thoroughly evaluate the MW-DES approach's promise in leveraging lignin's potential across diverse industrial sectors.

Keywords: microwave, deep eutectic solvents, DES, lignin, extraction, pulping

1. Introduction

Global energy consumption has expanded due to population expansion in the 20th century, which has also encouraged the manufacture of fuels, chemicals, and materials that significantly rely on fossil resources [1]. The overconsumption of fossil resources has led to severe climate and environmental issues, as well as concerns regarding energy security and sustainable development due to the vulnerability of oil prices to fluctuations and dependence on imported fuels [2,3]. To tackle these issues, the energy transition to renewable resources like solar, wind, hydro, and geothermal is more imperative than ever. However, this transition alone won't be enough as the demand for platform chemicals from oil refineries continues to rise along with global economic expansion [4]. Lignocellulosic biomass (LCB) is a renewable organic material sourced from vegetation, including forest residues, agricultural waste, energy crops, and organic fractions of solid wastes. LCB has gained interest due to its sustainability, renewability, and carbon neutrality, making it a potential alternative energy source. LCB-based biorefineries have emerged as a promising approach, in which biomass is utilized to produce biofuels and valuable bioproducts to replace those produced in traditional oil refineries. Biorefineries are also anticipated to decrease greenhouse gas emissions and ease the energy crisis [5,6], while offering economic opportunities for agriculture and forestry industries, organic waste management, and production of liquid fuels, platform chemicals, and carbon-neutral energy [7]. Global annual production of LCB is estimated at 181.5 billion tons with potential supplies being contributed by various sectors [8,9].

LCB is a heterogeneous organic matrix with a three-dimensional structure that is primarily composed of lignin, cellulose, and hemicellulose, as well as a few other minor components, such as minerals and extractives [10]. The three major components in LCB are inherently interconnected resulting in distinctive chemical and physical properties, thereby establishing a sturdy structural matrix within the plant cell wall [11]. In contrast to cellulose and hemicellulose, which primarily consist of sugars, lignin distinguishes itself by its distinctive three-dimensional structure and highly heterogeneous characteristics. Lignin is a heterogeneous polymer of various phenylpropanols, such as coniferyl, sinapyl, and p-coumaryl alcohols depending on the plant species, type, or part. The cross-linked network and branched arrangement of the phenylpropanols are the main reasons why LCB is challenging to break down during processes like conventional pulping or biomass conversion. Moreover, the heterogeneity of lignin in terms of both variability in bond chemistry and between plant species, not only limits upgrading and advanced applications for chemicals or materials, but also hinders further development of hemicellulose and cellulose applications [12]. Lignin has always been industrially generated as a byproduct waste in biorefinery processes and had a relatively low utilization rate among the main components of LCB as Fig. 1 shows. As a natural aromatic biopolymer, lignin offers a potential as a renewable supplier for phenol, an aromatic precursor of polymers derived from petroleum [13]. Research development focused on harnessing lignin's distinctive properties for energy and chemicals is vital for sustainability, maximizing lignin utilization, and potentially enhancing the profitability and competitiveness of biorefinery.

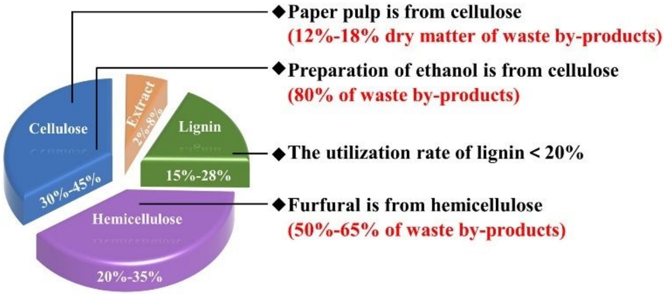

Fig. 1 The usage ratio of three major components in lignocellulosic biomass [14]

To effectively use lignin, it is crucial to extract it with qualities that allow for further downstream conversions and upgrading. Widely used methods include organosolv fractionation, acid hydrolysis, alkaline pulping, steam explosion, dilute acid pretreatment, as well as enzymatic hydrolysis [15,16]. These methods have been applied individually or in combination to achieve specific outcomes. However, each method has its limitations such as selectivity issues, degradation of lignin, high energy requirements, solvent cost and safety, lignin recovery efficiency, and so on. Common solvents used in the lignin extraction process including dilute acids, alkali solvents, and organic solvents, may reduce commercial profitability and the process's overall applicability because they are toxic, corrosive, volatile, or require high temperatures and pressures [17]. Although the capacity of ionic liquids (ILs) to extract lignin in high yields has lately gained a lot of interest, its high cost, complex synthesis procedure, poor biodegradability, toxicity, and poor recoverability prevent further application in lignin extraction [18].

To avoid the drawbacks of ILs while keeping their desirable properties, researchers have studied DES as a distinctive and green designer solvent. DESs are non-aqueous solvents created by combining two or more elements, commonly a hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), in a predetermined ratio. These components undergo a eutectic phase transition at a relatively lower temperature than each component's melting point [19]. Because of low toxicity, broad liquid range, versatility, and improved solubility, DESs have been explored in diverse areas like green chemistry, extraction, and catalysis. Following the initial introduction of DESs by Abbott et al. as IL alternatives [20], many studies have investigated and succeeded in lignin extraction in DES [21–23]. Despite the potential of DES, several challenges and limitations remain in its use for this purpose, particularly concerning extraction efficiency. For example, DES-based lignin extraction often demands longer extraction times than the traditional methods to achieve the same efficiency [24,25]. Microwave (MW)-assisted heating is a prominent solution to enhance reaction efficiency and heating speed in the extraction medium. In comparison to conventional heating, microwave-assisted heating provides swift and volumetric heating, energy efficiency, and precise temperature control for DES-driven lignin extraction. This novel approach enables researchers to enhance extraction efficiency, shorten processing time, and attain superior lignin extracts [26].

The objective of this review is to provide a comprehensive overview of studies on the application of DES in conjunction with the MW-DES method for lignin extraction. Our exploration is guided by three key dimensions: (1) an examination of ongoing research on lignin extraction through MW-DES; (2) an exploration of potential mechanisms associated with MW-DES; and (3) a systematic discussion on the structural modifications of extracted lignin by MW-DES. Furthermore, this review presents insights into the prospects and challenges associated with environmentally friendly and efficient lignin extractions, highlighting the existing issues in the field.

2. The effects of different reactants (biomass and DES) for lignin extraction

2.1 Different DES for lignin extraction

The composition of DES plays a crucial role in defining the characteristics and effectiveness of these solvents for various applications. DESs can be categorized based on their components and the interactions that give rise to their eutectic properties. Broadly, DESs are classified into two main types: hydrogen bond donor-acceptor DES and metal-containing DES. These primary categories can be further subdivided based on the specific combinations of hydrogen donors, acceptors, and metal components as shown in Fig. 2.

(1) Type I DESs: These DESs are produced from the combination of quaternary ammonium salt (e.g., choline chloride) and non-hydrated metal halide (e.g., $AlCl_3$). The use of Type I DES in the processing of lignocellulose has not been widely adopted because of the high melting temperatures of non-hydrated metal halides.

(2) Type II DESs: In contrast, one hydrated metal halide, such as $AlCl_3 \cdot 6H_2O$, and a quaternary ammonium salt are the main components of Type II DESs, which make them more practical for industrial applications since they are inherently resistant to air and moisture.

(3) Type III DESs: The main components of type III DESs are quaternary ammonium salt and other HBDs, like carboxylic acids. Due to their affordable starting components, simple production, interaction with water, low viscosity, and excellent biodegradability, these kinds of DESs are frequently used in the processing of biomass [27].

(4) Type IV DESs: Inorganic transition metals and HBDs (such as urea) are used in Type IV DESs even though metal salts are often unable to ionize in non-aqueous conditions.

(5) Type V DESs: Frequently hydrophobic, Type V DESs are made entirely of non-ionic molecules. Making the distinction between HBAs and HBDs for Type V DESs can be difficult. However, it has been found that the preparation of Type V DESs relies heavily on an extraordinarily strong interaction resulting from the differential in acidity between phenolic and aliphatic hydroxyl (OH) groups [28].

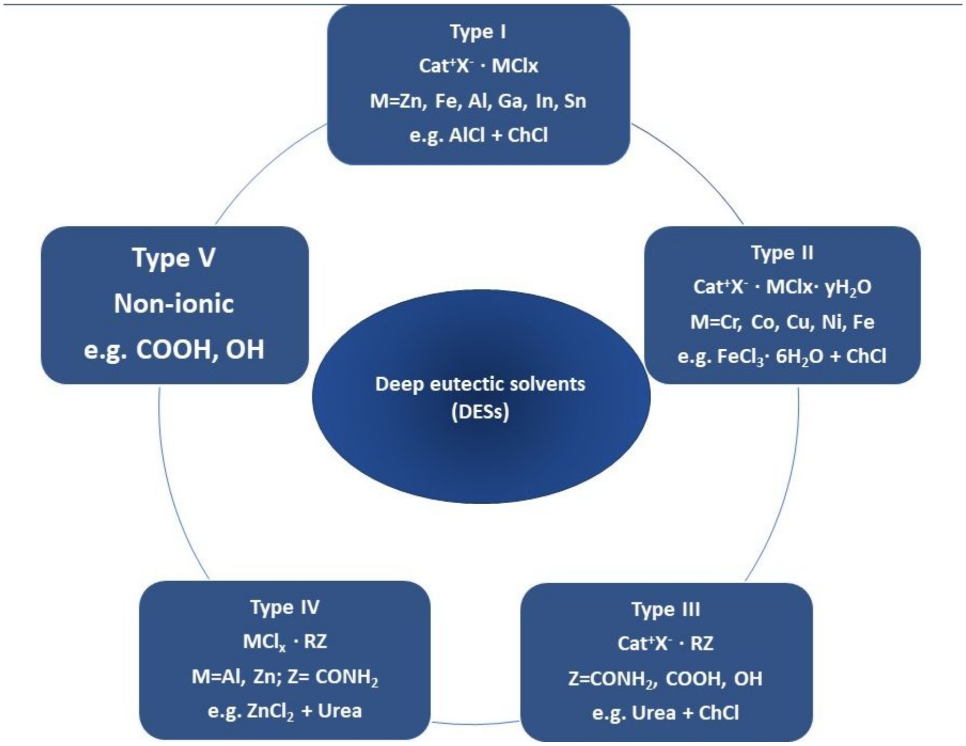

Fig. 2 The formulation for categorizing deep eutectic solvents (DESs) (this figure has been adapted/reproduced from ref [28] with permission from ELSEVIER copyright 2023).

While numerous research endeavors have explored the realm of delignification and lignin extraction, it’s worth noting that not all DESs prove equally effective in cleaving LCCs with lignocellulose and achieving efficient lignin fractionation. For efficient lignin extraction using DES, a synergistic interaction between HBDs and HBAs in the DES is essential. Typically, HBDs donate protons, facilitate hydrogen bonding, and interact with lignin's functional groups. HBAs, on the other hand, weaken the intermolecular forces holding lignin and other biopolymers in biomass. In Table 1, we summarized various DES and their effects on lignin extraction.

Table 1 Lignin extraction with various DES

Feedstock	Temp (℃)	Time (h)	DES: feedstock	HBD	HBA	HBD: HBA	Yield (%)	Reference
Douglas fir	145	6	10:1	LA	ChCl	1:1	78.5	[29]
Sugarcane bagasse	160	14.1	17:1	Urea	ChCl	2:1	82	[30]
Rice straw	60	12	20:1	LA	ChCl	5:1	60	[31]
Eucalyptus	130	6	10:1	LA	ChCl	10:1	64	[32]
Poplar wood	130	6	49:1	LA	ChCl	9:1	61.5	[33]

peach pit (Prunus persica)	145	6	9:1	LA	ChCl	2:1	70.2	34
walnut shell (Juglans nigra)	145	6	9:1	LA	ChCl	2:1	64.3	34
Akebia' herbal residues	120	8	10:1	FA	ChCl	2:1	40.7	35
Akebia' herbal residues	120	8	10:1	AA	ChCl	2:1	33.8	35
Akebia' herbal residues	120	8	10:1	GA	ChCl	2:1	58.4	35
Akebia' herbal residues	120	8	10:1	Levulinic acid	ChCl	2:1	20.2	35
Corncob	150	15	16:1	GA	ChCl	2:1	59	36
switchgrass	110	1	10:1	GA	ChCl	2:1	18.73	37
wheat straw	90	12	20:1	Monoethanolamide	ChCl	6:1	81	38
wheat straw	90	12	20:1	Diethanolamine	ChCl	8:1	73.5	38
wheat straw	90	12	20:1	Methyl diethanolamine	ChCl	10:1	44.6	38
wheat straw	90	12	20:1	Acetamide	ChCl	2:1	3.4	38
wheat straw	90	12	20:1	Urea	ChCl	2:1	27.7	38
wheat straw	90	12	20:1	Glycerol	ChCl	2:1	24.7	38
Corncob	140	2	n.d.	Benzyl trimethylammonium chloride	LA	2:1	70	39
Corncob	140	2	n.d.	Benzyl triethylammonium chloride	LA	2:1	68	39

2.1.1 Different HBDs

Common HBDs applied for lignin extraction include carboxyl-containing HBDs, Hydroxyl-containing HBDs, and Amine/amide-containing HBDs. The functional groups in various HBDs have important effects on their interactions with lignin, affecting both lignin extraction efficiency and the resulting chemical structure.

According to Table 1, most research works have adopted ChCl-based DES and carboxyl-containing DES with acidic HBD such as LA, AA, FA, and levulinic acid. Carboxyl-containing HBDs remarkably perform well in biomass pretreatment and delignification, outperforming HBDs with other functional groups. Their ability to remove over 90% of lignin from various lignocellulose sources [40,41] is attributed to the presence of active protons supplied by carboxylic acids, which catalyze the cleavage of chemical linkages in lignocellulose. The number of carboxyl groups within an HBD positively correlates with delignification efficiency, but an excessive number of carboxyl groups may impair interactions between DESs and lignin. Regarding acidic DES, its functional acidic sites can support proton-catalyzed bond cleavages, including those of glycosidic bonds, ether bonds, and carbohydrate/lignin interactions. In the lignin extraction process, these reactions are crucial processes. [42]. Consequently, the pKa value of the DES can serve as a gauge for estimating its delignification capability. A lower pKa value indicates higher acidity, translating to enhanced performance in lignin extraction. Moreover, the Kamlet-Taft (K-T) solvatochromic parameters (α, β, π*) can be employed to predict the attributes of the DES. In this context, α signifies H-bond acidity, β denotes basicity, and π* reflects the solvent's polarity and polarizability. DES with elevated α and β values exhibit improved lignin extraction performance, where higher α values denote superior H proton donation capacity, and higher β values indicate enhanced H-bond acceptance capacity [43]. The values of some DES can be obtained in Table 2. Mankar et al. also found that DES (made with ChCl and OA) yielded the highest lignin extraction of 37.8%, mainly attributed to its high α value of 1.32 [44]. Mattonai et al. also compared four different HBDs including FA, AA, propanoic acid, and LA for their ability to extract lignin and found FA (followed by LA) provided the best yield (16% in weight, equivalent to 64% of the total Klason lignin) at 130 °C. Their rationale was rooted in the strength of the hydrogen bond network, with formic acid's small size and lactic acid's hydroxy group enhancing bond cleavage efficiency and DES solvation power, respectively [45].

Table 2 The Kamlet-Taft (K-T) solvatochromic parameters (α, β, π*) of some DES [44]

DES	α	β	π
ChCl: OA	1.32	0.62	1.09
ChCl: LA	1.17	0.51	1.12
ChCl: AA	0.92	0.54	1.10

ChCl: BA	0.81	0.53	0.96

2.1.2 Different HBAs

HBAs form a synergy with HBDs in the DES. Hou et al. proved that the introduction of ChCl to HBDs (lactic acid, acetic acid, glycolic acid) helped enhance the lignin dissolution compared to pure acid [35]. Common HBAs are different forms of sulfonium, phosphonium, and ammonium salts and ChCl is one of the most often used HBAs for creating DESs because of its nontoxicity, affordability, and biodegradability. According to earlier studies, lignin removal was enhanced by the highly electronegative Cl− in ChCl's tendency to form H-bonds with the hydroxyl groups in lignin [46]. Additional investigations have demonstrated that the halide counterion present in the HBA promotes β-O-4′ bond breaking and inhibits lignin self-condensation [17,47]. Hou et al. also conducted research on rice straw with DES composed of different HBAs and HBDs and found that when ChCl was chosen as the HBA, a weaker pretreatment efficiency was observed for most of the DESs, regardless of the kinds of HBDs [17] compared to the acidic Lac-based DESs. However, regardless of the HBD used, the biomass dissolving efficiency of the DESs was higher when lactic acid was used as the HBA than when ChCl-based DESs were used. This demonstrates that the degree of DES pretreatment and biomass fractionation efficiency are mostly determined by the appropriate choice of HBA and HBD. Therefore, the first step in effectively utilizing DESs is to determine the best possible combinations.

Hydroxyl-containing groups are also commonly used for DES synthesis including polyalcohol-based HBDs (e.g., ethylene glycol, propylene glycol, and glycerol) and carbohydrate-based HBDs (e.g., glucose, fructose, and xylitol). When combined with a harmless HBA (such as betaine or ChCl), this kind of DES often shows high biocompatibility with enzymes and microorganisms at nearly neutral pH degrees [48]. Most studies have demonstrated that, even under harsh pretreatment conditions, polyalcohols, or carbohydrate-based DESs have poor efficiency during lignin dissolving and separation because of the neutrality of the hydroxyl-containing HBDs. Grass, with its weaker covalent link, is a good candidate for a hydroxyl-containing HBD pretreatment.[37] To illustrate, the ChCl/glycerol DES stands as an instance where potent lignin fractionation during biomass pretreatment isn’t readily apparent. This lack of efficacy is attributed to the DES’s limited presence of active protons and acidic sites. In the ChCl–glycerol system, chloride ions (Cl^-) are encapsulated by an arrangement of mutual anionic hydrogen bonds ([Cl(glycerol)]−) and cationic H-bonds ([Ch(glycerol)]+). This structure thus reduces the occupied-site anions' capacity to absorb H-bonds, which results in a dearth of protons and inactive acidic sites and, ultimately, subpar performance [43]. A higher number of hydroxyl groups in HBDs can reduce lignin removal due to the formation of extensive hydrogen bonds between HBA and HBD, weakening the ability of HBA to compete with intra-molecular bonding in biomass components[43]. The position and type of hydroxyl groups in HBDs can influence their performance in lignin extraction [49]. To improve the DES, some researchers also tried to introduce the third constitute in DES to form a ternary system. Xia et al. integrated $AlCl_3·6H_2O$ into the ChCl/glycerol DES using the framework of acidic multisite coordination theory. This novel DES was then employed for lignin extraction. They discovered that supramolecular complexes were created by the synchronized competition of anionic H-bonds and unidentate aluminum ligands, which allowed multisite bridging ligands to cleave both H-bonds and ether bonds in LCCs. Therefore, a remarkable 95.46% increase in lignin fractionation efficiency was achieved. The lignin's purity also impressively reached 94 ± 0.45%. A unique ternary DES system was developed by Wang et al. in a different investigation 63. It consists of ChCl and glycol, plus OA or trifluoromethanesulfonic acid (HOTf). The results showed that both solvent solutions successfully integrated EG (80–85%) into the remaining enzyme lignin. The recovered lignin fragments also showed an impressive linkage concentration, consisting of 60-80% aryl ether bonds.

HBDs with amine/amide groups, such as urea, imidazole, and ethanolamine, were explored for their lignin fractionation effects, too. More intermolecular H-bonds between HBDs and HBAs can be formed by HBDs with more amines, amides, or hydroxyls. This decreases the amount of free and active groups that can interact with lignocellulose and lowers the efficiency of lignin formation during DES processing.

The process for removing lignin from biomass when utilizing chlorine-based DES is based on the development of an H-bond (hydrogen bond) between the lignin and the halogen anions, such as Cl-, of the

DES. With the -OH groups found in lignin; those halogen anions can form hydrogen bonds. This contact encourages the extraction of aromatic chemicals as well as the lignin's breakdown. The ability of the electronegative halogen anion in the DES to establish an H-bond with lignin is therefore intimately related to the effectiveness of lignin extraction [50].

2.2 Different biomass for lignin extraction

2.2.1 Interactions between main biomass fractions and DES

In the lignin-carbohydrate complexes (LCCs) found in LCB, natural lignin is closely bound to cellulose and hemicellulose [51]. To effectively use DES in lignin extraction, it is crucial to comprehend the basic interactions between it and the key components of biomass.

Lignin is structured from phenolic monomers (H, G, and S units) interconnected predominantly by aryl ether bonds such as β-O-4 and α-O-4, and carbon-carbon bonds (C-C bonds) such as 5–5 or β-β. The strength of C-C bonds, owing to their elevated bond dissociation energies, usually results in greater resistance to cleavage when contrasted with C-O bonds, as depicted in Fig. 3. Alongside aryl ether and C-C linkages, DES also breaks down lignin via various chemical reactions, encompassing hydroxylation, demethoxylation, and crosslinking [52,53].

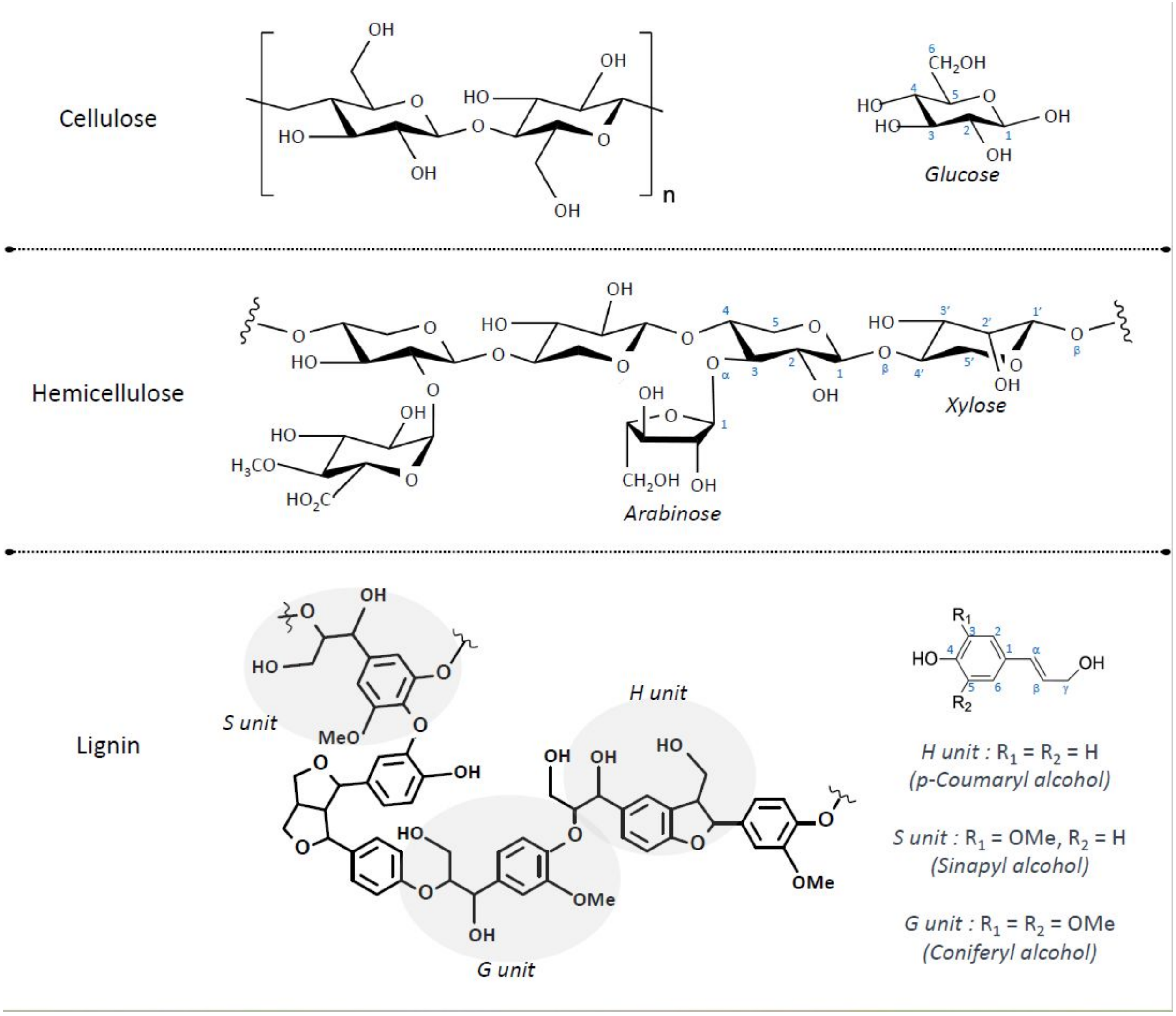

Fig. 3 Chemical compositions of cellulose, lignin, and hemicellulose.

According to previous studies [40,55], the DES-based lignin extraction is summarized in three steps as illustrated in Fig. 4. The initial phase involves the solubilization of lignin, wherein the lignin present in the lignocellulosic biomass is dissolved within the DES solution. To engage in composition with the links in the LCC network, the ions in the DES form strong hydrogen bonds with the hydroxyl (OH) groups in the polysaccharides. As a result, the ester and ether connections within the inherent lignin break down, leading to the separation of the lignin macromolecules from the LCC structure. Because a substantial proportion of lignin remains insolubilized at this stage, the lignin yield is low but results in a relatively high molecular weight, comprising a notable quantity of breakable ether connections. The subsequent phase involves the depolymerization of lignin, wherein further fractionation occurs, leading to the breakdown of lignin macromolecules into oligomers characterized by reduced molecular weight. Since ether links account for a sizable fraction (45–65%) of the interunit bonds in natural lignin, they are specifically the β-O-4 connections that break during depolymerization. The exploration of the DES-driven lignin extraction mechanism involved subjecting a lignin dimer model compound, guaiacylglycerol-β-guaiacyl ether (GBG), to ChCl-Lac DES at a temperature of 145°C. Complete hydrolysis of GBG resulted in the generation of guaiacol (G1) and a Hibbert's ketone (HK)-type compound (G2), with the presence of an intermediate, G3, observed (as shown in Fig. 5). This process resembles lignin acidolysis catalyzed by HCl. Notably, DES treatment exhibited limited formation of by-products or phenolic re-condensation products compared to lignin acidolysis. Interestingly, DES treatment of hydroxymatairesinol (HMR), a dimeric model compound linked by a β–β (C–C bond), revealed no fragmentation products even after a three-hour reaction. This underscores DES's capacity for selective ether bond cleavage without affecting the C-C linkages in lignin.

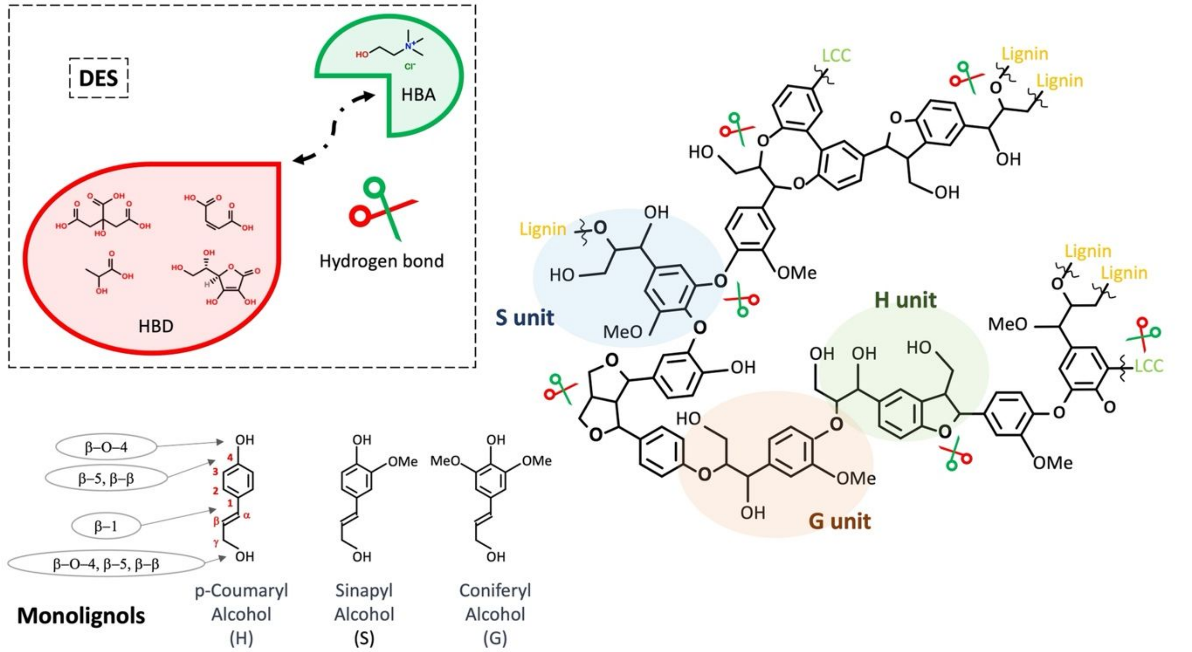

Fig. 4 The extraction of lignin and the predicted breakage sites for common intramolecular linkages and LCC benzyl ester structures using DES processing.

The elucidation of the mechanism steps during this stage of the acidic cleavage of aryl ether bonds in lignin model compounds offers insights into tuning processing methods. These steps encompass: (i) protonation of the α-carbon hydroxyl group; (ii) α-carbon dehydration and β-carbon deprotonation; (iii) the formation of carbocation and/or enol-ether intermediate; (iv) β-carbon hydroxylation; and (v) cleavage of β-O-4 ether bond cleavage [56,57]. Lastly, the concluding phase involves lignin condensation. Lignin oligomers may interact with unsaturated reactive intermediates post-hydrolysis, leading to the formation of higher molecular weight complexes, particularly under severe reaction conditions. The repolymerized lignin oligomers generated in this stage are anticipated to be unreactive due to the formation of stable C-C bonds [58].

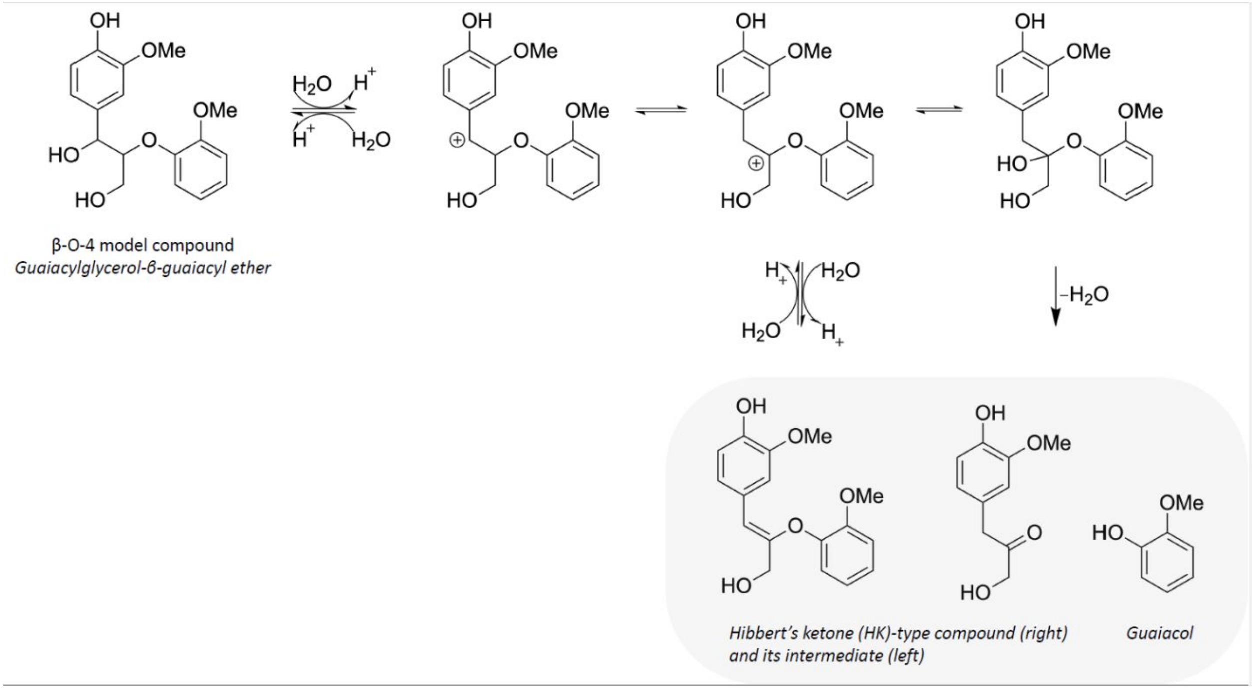

Fig. 5 The main mechanisms driving the breakdown of β-O-4 linkages in lignin during DES treatment were identified via investigations involving the model compound (this figure has been adapted/reproduced from ref [29] with permission from ROYAL SOCIETY OF CHEMISTRY, copyright 2023).

The most common biopolymer in the world, cellulose, is a linear polysaccharide made of D-glucose subunits joined together by -(1,4)-glycosidic linkages, as seen in Fig. 3. Hydrogen bond connection between the parallel chains increases the durability of the glycosidic link in cellulose, making it less soluble in common solvents.

Due to its disorganized structure, DES has a more limited capacity to dissolve cellulose than ILs. This reduced capacity limits the rise in entropy that results from interacting with cellulose, which results in lower solubility toward cellulose [59,60]. To target lignin extraction while reducing the dissolution of cellulose and hemicellulose, it is best to choose a DES with low attachment to cellulose.

The dissolution of cellulose entails a significant disruption of both its intermolecular and intramolecular hydrogen-bond networks. Like ILs, DES works to dissolve cellulose by breaking the original hydrogen connections between molecules and forming new ones between the -OH groups of cellulose and the DES. The intermolecular and intramolecular hydrogen bonds in cellulose are weakened by a solvent's capacity to serve as a hydrogen bond acceptor. A significant link between cellulose solubility and the hydrogen bond basicity (β) of ILs or DESs has been shown in earlier studies [61]. It was suggested that β can be used as an indicator to estimate cellulose dissolution [62]. Higher β values are associated with better cellulose dissolution, and the type of anions strongly influences β. Anions like Cl-, OAc-, HCOO−, $(MeO)_2PO_2^-$, morpholine, or imidazole, which act as favorable hydrogen bond acceptors, are promising options for forming DESs that facilitate cellulose dissolution [63].

Hemicellulose is a heterogeneous branched polymer comprising diverse sugar units. It generally exhibits higher solubility in DES compared to cellulose. However, hemicellulose extraction is regarded as less attractive in biomass conversion compared to cellulose or lignin extractions, and the studies on the reaction mechanism between hemicellulose and DES are limited. Xylan is a type of hemicellulose commonly used to study hemicellulose in lignocellulosic biomass. Researchers found that xylan exhibits good solubility in DES as a result of hydrogen bonding interactions between DES molecules and the polysaccharide [64]. This interaction disrupts the intermolecular hydrogen bonding of the xylan solute. Investigations have indicated that DES, with potent electron-withdrawing groups, aids in the efficient removal of xylan. Furthermore, an inversely proportional correlation between the removal of xylan and the pKa value (acid dissociation constant) of the HBD was observed, with temperature dependence [49].

2.2.2 Different biomass types

Although the ideal biomass for lignin extraction seems to be biomass with high lignin content, high lignin content is also correlated with the degree of recalcitrance in feedstock since it represents the amount of lignin and carbohydrate linkage. In the study of Wan et al. ultrafast microwave-assisted ChCl:LA pretreatment was developed for fractionating switchgrass, corn stover, and *Miscanthus* and corn stover showed the highest lignin removal (about 80%) because the structure of corn stover is less recalcitrant [65]. Kohli et al. investigated six DESs for lignin extraction from miscanthus and birchwood, they discovered that ChCl-FA and ChCl-OA DESs, respectively, extracted the most lignin from the miscanthus and birchwood. Furthermore, it takes longer to remove lignin from birchwood than from miscanthus. Additionally, the structure of lignin differs depending on the feedstock; lignin from birchwood displayed greater structural alterations [66]. This can be due to the more complex and denser structure of birchwood than miscanthus.

Besides, different feedstock also requires different solvents for lignin extraction. In the study of Lynam, the AA: ChCl was the most effective DES in lowering molecular weight and raising PDI of lignin extracted from rich husks and sugarcane bagasse, while LA: ChCl enhanced these characteristics for coffee chaff, and the best DES for lignin extraction from corn stover is FA: ChCl[67]. When DES with acetic acid is chosen to extract lignin, it may be able to dissolve components that can be acetylated in biomass which affects the extracting result of different biomass [68].

Table 3 lignocellulose and lignin composition for softwoods, hardwoods, and grasses ([69]).

	Lignocellulose composition (wt.%)			Monolignol distribution in lignin (wt.%)		
	Cellulose	hemicellulose	Lignin	H	G	S
Softwoods	46-50	19-22	21-29	<5	>95	0
Hardwoods	40-46	17-23	18-25	0-8	25-50	45-75

Grasses	28-37	23-29	17-20	5-35	35-80	20-55

3. The influence of process parameters for lignin extraction with DES

3.1 Common process for lignin extraction with DES

While specific details may vary depending on the DES formulation and the kind of biomass being treated, the general steps are shown in Fig. 6. (1) First, preparing the biomass and DES, usually biomass should be pretreated to remove impurities and decrease the biomass particle size. At the same time, DES is prepared by mixing the appropriate HBD and HBA in a specific ratio. The selection of the DES components can influence the efficiency and selectivity of lignin extraction. (2) The pretreated biomass is then mixed with the DES to ensure proper contact and interaction between the DES and the lignocellulosic material. The mixture is typically heated to an appropriate temperature to enhance lignin solubility and improve extraction efficiency. Microwave-assisted heating may be used for faster and more uniform heating. (3) During the heating and mixing process, the DES penetrates the biomass and solvates the lignin, causing it to dissociate from the lignocellulosic matrix. The DES selectively extracts lignin from the biomass while leaving cellulose and hemicellulose largely intact, as long as the type of DES does not have a strong solubilization effect on them. (4) Once the extraction process is complete, the lignin-DES solution is separated from the remaining biomass components. Various separation methods can be used, such as filtration, centrifugation, or decantation. (5) Following this separation, an antisolvent is usually added to the lignin-DES mixture that changes the partition coefficients and allows the solubilized lignin to precipitate. The recovered lignin is then characterized to determine its purity, molecular structure, and properties. DES is recovered and potentially reused in subsequent extraction processes, which helps reduce the overall solvent consumption and waste generation.

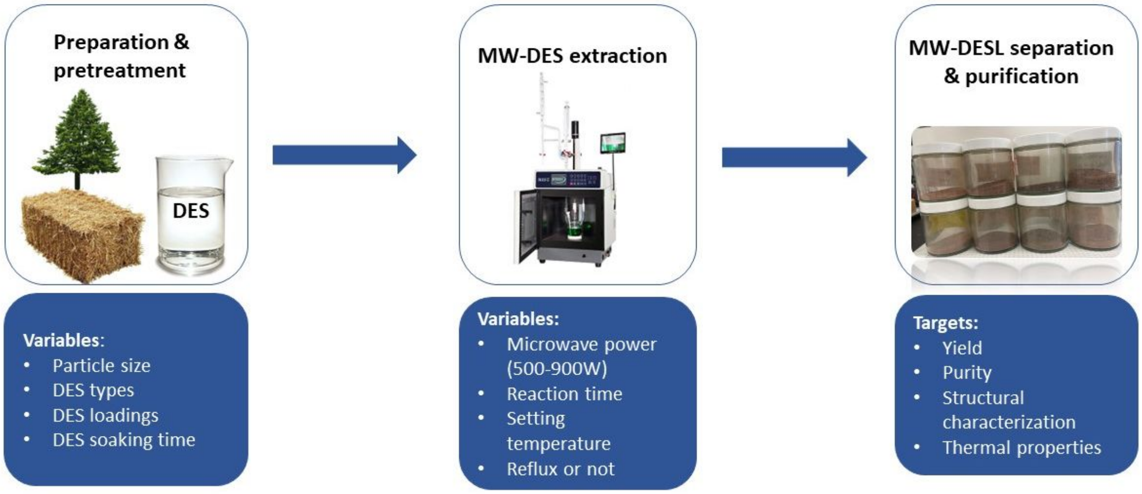

Fig. 6 Common process for lignin extraction from LCB with DES.

3.2 Severity of extraction reactions

Reaction time and temperature are the common factors affecting lignin extraction. The severity of the reaction can be measured by the H factor (Equation 1), which is a measurement that evaluates the severity of a certain chemical pulping pretreatment technique for lignin removal by taking temperature and duration into consideration.

$$H = \int_0^t \exp\left(43.2 - \frac{16115}{T}\right) dt \qquad (1)$$

where T is the temperature in Kelvin (K) and t is the time in hours (h). Common extraction of lignin needs a temperature range from 100°C to 150°C (212°F to 302°F) as Table 1 shows. Although some studies can perform the extraction at temperatures lower than 100 ℃, a long reaction time is required as compensation [70]. At the appropriate temperature range, the lignin extraction efficiency increases with the elevated temperature. For all DESs, higher temperatures weaken the attractive forces by promoting molecular dynamics and increasing the kinetic energy, therefore, the viscosity of DES can be decreased and the heat and mass transfers get improved. For instance, it was found that as the temperature climbed from 50 to 100 °C, the shear viscosity of DES Gly:ChCl (1:1) decreased by a factor of ten [71]. However the best temperature varies from DES types and biomass types.

Reaction time is another factor that matters for lignin extraction efficiency. Longer DES soaking/reaction time will decrease the ether bonds and certain monomers. There is a greater reduction in the number-average molecular weight (Mn) and weight-average molecular weight (Mw) of lignin with longer treatment times at higher temperatures [51]. Usually, a higher temperature or longer reaction time will lead to a much lower percentage of β-O-4 bonds in the extracted lignin, and mild treatment conditions give a higher content of preserved ether bonds in DES lignin [72].

High pressure is not necessary for lignin extraction with DES, normally, the extraction is conducted under atmospheric pressure. However, due to some closed extraction systems, the vapor pressure of DES itself can form during the extraction process. In general, DESs showed higher vapor pressure compared to common ionic liquids. The vapor pressure-temperature relationship of DESs seems to be more complex than that of molecular liquids as well as that of most ionic liquids [73]. The change in pressure can influence the density, viscosity, phase behavior, and dissolution capacity, which results in the lignin extraction. However, there are not enough studies on the effect of pressure on lignin extraction with DES. Future studies are needed to understand the extraction system and the DES properties.

4 The introduction of the microwave (MW) heating method in lignin extraction

While the effectiveness of DES in lignin extraction has been demonstrated in many studies, one significant challenge is the extended duration of reaction, often spanning hours or even days, resulting in substantial energy consumption and diminished economic gains. The introduction of MW heating is a good method due to its heating mechanism, and due to several compelling advantages of the combination of MW heating and DES:

(1) Rapid and Efficient Heating: MW heating offers fast and efficient heating compared to conventional heating methods. The microwaves directly interact with the polar molecules in the DES, causing rapid molecular rotation and agitation, leading to efficient energy transfer to the solvent. This rapid volumetric heating can significantly reduce the extraction time and increase the overall efficiency of the process. The H-factor can be greatly reduced with MW heating in comparison to conventional heating. At

150 °C for 20 minutes of pre-treatment, with a slightly lower H factor of 55.5, Mankar et al.'s trials produced the highest lignin extraction yield of 73.9% [21,44]. Liu et al. found that the combination of microwave irradiation and DES effectively breaks down LCCs and permits speedy separation of wood lignin. MW heating proved crucial for achieving efficient lignocellulose fractionation with the solvent, as it only required 3 minutes of heating at 80°C under 800 W microwave irradiation. In contrast, achieving similar results without MW heating would take significantly longer, approximately 9 hours, using a conventional bath oil heating method [40]. Muley et al. [12], also found that FA-based DES can efficiently fractionate lignin from biomass in as little as 1 min at a temperature of 150°C, with 85.8% yield.

(2) Selective Heating: Microwaves selectively heat polar molecules, such as water, which is often present in biomass and DES formulations. By targeting the polar parts of the biomass with selective heating given by microwaves, lignin can be extracted and dissolved more easily while being mostly unaffected by other parts of the biomass. The inherently charged nature of the DES mixture also allows it to directly interact with the oscillating electric field component of the microwaves, leading to a non-random increased mobility (as opposed to the random movement in conventional heating).

(3) Enhanced Solvent-Solute Interactions: The biomass's DES and lignin interactions are improved by MW heating. The better extraction efficiency is produced by the enhanced agitation and molecular mobility inside the DES, which creates a more suitable environment for lignin solubilization and increases the chances of solvents' active moieties encountering a target bond for breakage.

(4) Improved Mass Transfer: The microwave-induced agitation and mixing at the molecular scale within the DES-biomass mixture improve mass transfer rates, enabling better contact between the solvent and lignin. This efficient mass transfer enhances the extraction of lignin from the biomass matrix.

(5) Lower Energy Consumption and Environmental Sustainability: Due to its ability to bypass the reactor wall and interact directly with the biomass-DES substrate, MW heating is often more energy-efficient compared to conventional heating methods. It can lead to reduced energy consumption, making

the extraction process more environmentally friendly. The thermal lags associated with conventional heating are eliminated, as microwaves simply turn on and off on demand, and, as an electric-heating method, its energy source can be produced via solar, wind, or nuclear sources, leading to a de-carbonized processing method and reducing the associated environmental costs.

(6) Versatility: MW heating with DES is a versatile approach that can be applied to various lignocellulosic biomass sources and different DES formulations. It can be optimized and tailored for specific biomass types, making it applicable to a wide range of lignin extraction processes.

4.1 MW-assisted heating mechanism

Microwaves are part of the electromagnetic spectrum, ranging mainly from 300 MHz to 300 GHz in frequency [74]. Microwave-induced heating effect in materials is due primarily to two mechanisms: dipolar polarization and ionic conduction [75,76]. When a high-frequency electric field (the electric field components of the microwaves) interacts with charged particles or ions within a material, such as dissolved salts (e.g., sodium, potassium, and calcium chlorides), the ions experience an alternating force that alternates billions of times per second (depending on the microwave frequency) in a direction parallel to the electric field lines [74]. The oscillating electric field accelerates these ions, leading to collisions with neighboring particles and the transfer of kinetic energy, resulting in increased agitation and heat within the material. This process converts energy from the microwave field into heat, facilitating microwave-induced heating [77]. The second interaction that contributes to MW heating involves polar molecules, particularly water, commonly found in liquid materials [78]. In polar molecules like water, the separation of positive and negative charges creates a dipole, which tends to align itself with the direction of the electric field component of the microwaves. As the field direction changes rapidly, the dipolar molecules either lag behind the field changes, dissipating heat as it always trying to catch up with its resting state, or, if the molecule's relaxation times are within a certain range vs the period of field oscillations, the dipoles start rotating rapidly, generating molecular friction and subsequent heat. The combined effects of ionic interaction (in the presence of charged particles in solvents) and dipolar rotation serve as the fundamental heating mechanisms that make microwave-assisted extraction rapid and efficient.

The uniform and rapid heating facilitated by these mechanisms make this process an exceptional choice for lignin extraction, particularly when employed alongside DES. Because of the way in which they transfer heat, MW heating is generally quicker and more effective than traditional heating, which reduces the amount of energy and reaction time needed. In terms of the lignin extraction process, studies also prove the high efficiency of microwave-assisted heating. Sun et al. adopted microwave-based heating for switchgrass pretreatment, followed by hydrolyzing with cellulase enzymes, and found that microwave pretreatment resulted in a greater sugar yield than normal heating due to the disruption of recalcitrant structures [79]. Kumar et al. [80] also obtained higher glucose yields from switchgrass biomass pre-treated with DES in the presence of microwaves for 40 min (5.06 g/L) compared to conventional heating for 3 hours (4.66 g/L).

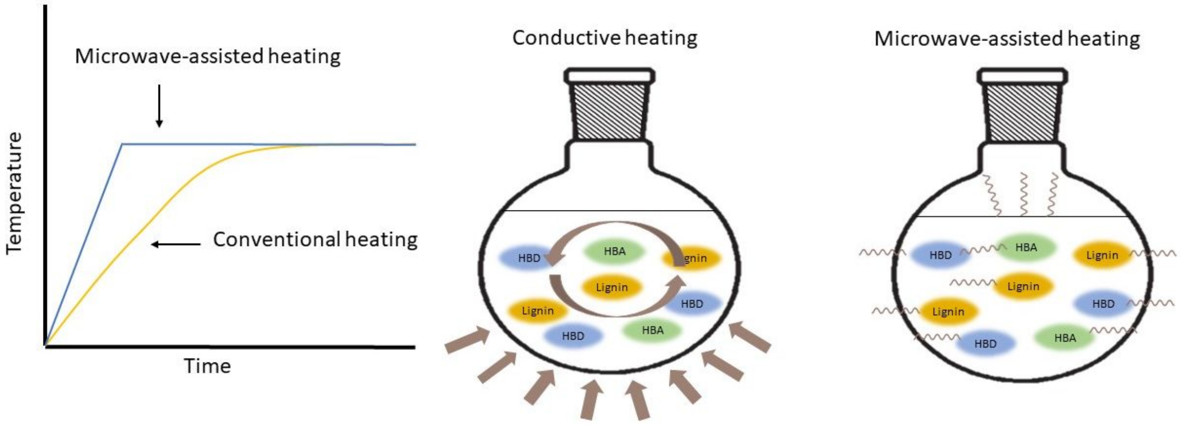

Fig. 7 Comparison between conventional heating and microwave heating mechanisms.

4.2 Interactions between microwave, DES, and biomass

When determining if a material is suitable for MW heating, dielectric parameters including the dielectric constant (DC), loss factor (LF), and loss tangent (*tan δ*) are very important. DC refers to the material's ability to maintain charge, whereas LF refers to the electrical energy loss in dielectrics. Tan δ, or the ratio of LF to DC, is a material's ability to convert electromagnetic energy into heat at a particular frequency and temperature. The efficiency of MW heating greatly depends on the material's dielectric properties, with low dielectric loss materials exhibiting poor MW absorption characteristics and high dielectric loss materials permitting surface heating. Therefore, it is crucial to understand how dielectric properties affect MW processing in order to build an efficient system. [81].

As discussed above, microwave-assisted processes using DESs have gained popularity in research due to the unique characteristics of both MW heating and DESs' physicochemical properties which are conducing to bond breaking. Recent investigations have revealed that DESs demonstrate a stronger thermal heating response to microwaves compared to water. Published literature indicates that DESs' dielectric properties are very favorable to microwave absorption and conversion into heat [12], with *tan δ* values at 2450 MHz (one of the FCC allotted frequencies for industrial applications) of 0.9 for a 2:1 mixture of formic acid: ChCl, 0.54 for 1:1 mixture of oxalic acid: ChCl, and 0.505 for 1:1 mixture of lactic acid: ChCl. For reference, the *tan δ* for water at the same frequency is approximately 0.085 [78]. This response is influenced by various factors, such as the ability to form hydrogen bond networks, the presence of hydroxyl groups, the ionic nature of the HBA component (including ChCl), and the increased polarity of DESs upon exposure to an electromagnetic field. Thermal decomposition represents a crucial constraint for the MW heating response, as it disrupts the hydrogen bond network and leads to the breakdown of the HBD. In addition, in such applications, other substances in the reaction mixture may absorb microwave energy and initiate desired reactions. Thus, DES plays a crucial role not only in the heating process, but also in enhancing the reaction rate and overall efficiency by providing a suitable environment for the reactants and facilitating their interaction.

Temperature, frequency [82], moisture content, density [83], and composition affect the dielectric characteristics of the biomass itself [84,85]. Among the three main components of biomass, hemicellulose generally has the best dielectric properties. Due to the amorphous nature and the presence of polar functional groups, such as hydroxyl groups, hemicellulose is more susceptible to dielectric heating. Compared to hemicellulose, the strong hydrogen bonding and crystalline structure of cellulose limit the interaction with electromagnetic waves, including microwaves. While lignin can be a good microwave absorber, its dielectric properties may vary depending on its chemical composition and degree of polymerization. The presence of aromatic rings and polar functional groups contributes to its microwave-absorbing ability to some extent, but it may not match the dielectric properties of hemicellulose [86]. Additionally, when biomass is treated, the dielectric characteristics of the material change continually. As the biomass is relatively intact (in terms of cellulose-hemicellulose-lignin network) at the beginning of the process, there is a lack of mobility of these compounds and therefore the biomass components themselves contribute relatively little to the overall heating process. However, as the dissolution process progresses and lignin and hemicellulose are being liberated from the matrix, they can contribute to the dielectric heating effects. If small particles are charred as well in the process (or are included on purpose to act as additional microwave absorbers), these dielectric properties also change. For example, the process of pyrolyzing biomass, either in microwave cavities[87] or conventional reactors might result in the formation of some char or tar, which can alter the dielectric characteristics of the biomass and function as a catalyst [88].

The MW-DES extraction system for lignin involves interactions between microwaves and both biomass and DES. Recent studies showed that DES pretreatment with MW assistance performed better and consumed less energy. With ChCl:LA and ChCl:OA and MW-assistant heating, more than 70% lignin had been extracted within minutes [40,65]. Microwave irradiation in this process enhances the ion properties and raises the molecular polarity of DESs, which might be one route for improved lignin extraction efficiency.

Table 4 Literature review of lignin extraction with the MW-DES method

	Reaction condition				DES composition			Results		
Feedstock	Temp (℃)	Time (min)	Power (W)	DES: feedstock	HBD	HBA	HBD: HBA	Yield (%)	Purity (%)	**Reference**
Fir (Abies alba)	110	30	600	20 : 1	FA	ChCl	5 : 1	10	n.d.	[45]
	120	30	600	20 : 1	FA	ChCl	5 : 1	11	n.d.	
	130	30	600	20 : 1	FA	ChCl	5 : 1	16	n.d.	
	110	30	600	20 : 1	AA	ChCl	5 : 1	2	n.d.	
	120	30	600	20 : 1	AA	ChCl	5 : 1	3	n.d.	
	130	30	600	20 : 1	AA	ChCl	5 : 1	7	n.d.	
	110	30	600	20 : 1	propanoic acid	ChCl	5 : 1	1.5	n.d.	
	120	30	600	20 : 1	propanoic acid	ChCl	5 : 1	2	n.d.	
	130	30	600	20 : 1	propanoic acid	ChCl	5 : 1	8.5	n.d.	
	110	30	600	20 : 1	LA	ChCl	5 : 1	3.5	n.d.	
	120	30	600	20 : 1	LA	ChCl	5 : 1	15	n.d.	
	130	30	600	20 : 1	LA	ChCl	5 : 1	12.5	n.d.	
Southern pine	150	15	n.d.	6: 1	FA	ChCl	2: 1	89.6	n.d.	[12]
	150	15	n.d.	6: 1	LA	ChCl	1: 1	72.4	n.d.	
	130	15	n.d.	6: 1	oxalic acid dihydrate	ChCl	1: 1	83.8	n.d.	
Rice straw	155	30	n.d.	10: 1	FA	ChCl	2: 1	36.1	n.d.	[80]
Poplar wood flour	81	3	800	20 : 1	oxalic acid dihydrate	ChCl	1 : 1	15.4	80	

	80	5	800	20 : 1	oxalic acid dihydrate	ChCl	1 : 1	15.8	93	40
	80	10	800	20 : 1	oxalic acid dihydrate	ChCl	1 : 1	15.1	96	
	80	9h	n.d	20 : 1	oxalic acid dihydrate	ChCl	1 : 1	~5	85	
	110	9h	n.d	20 : 1	oxalic acid dihydrate	ChCl	1 : 1	17.5	90	
coconut coir	125	20	n.d	30 : 1	Butyric acid	ChCl	2 : 1	7.5	n.d.	44
	125	20	n.d	30 : 1	AA	ChCl	2 : 1	16	n.d.	
	125	20	n.d	30 : 1	LA	ChCl	2 : 1	36	n.d.	
	125	20	n.d	30 : 1	oxalic acid dihydrate	ChCl	2 : 1	37	n.d.	
	90	20	n.d	30 : 1	LA	ChCl	2 : 1	10.9	n.d.	
	110	20	n.d	30 : 1	LA	ChCl	2 : 1	28.5	n.d.	
	130	20	n.d	30 : 1	LA	ChCl	2 : 1	35.1	n.d.	
	150	20	n.d	30 : 1	LA	ChCl	2 : 1	73.9	n.d.	
	170	20	n.d	30 : 1	LA	ChCl	2 : 1	71.2	n.d.	
	150	5	n.d	30 : 1	LA	ChCl	2 : 1	35.1	n.d.	
	150	10	n.d	30 : 1	LA	ChCl	2 : 1	42.4	n.d.	
	150	30	n.d	30 : 1	LA	ChCl	2 : 1	56	n.d.	
	150	40	n.d	30 : 1	LA	ChCl	2 : 1	53	n.d.	
	150	20	n.d	30 : 1	LA	ChCl	1:00	16.9	n.d.	
	150	20	n.d	30 : 1	LA	ChCl	4 : 1	82	n.d.	
	150	20	n.d	30 : 1	LA	ChCl	6 : 1	50	n.d.	
	150	20	n.d	30 : 1	LA	ChCl	8 : 1	40	n.d.	
switchgrass	152	0.75	n.d	10 : 1	LA	ChCl	2 : 1	48.39	87.42	65

corn stover	152	0.75	n.d	10：1	LA	ChCl	2：1	70.84	84.96	
miscanthus	152	0.75	n.d	10：1	LA	ChCl	2：1	42.67	86.01	
Cocoa Bean Shell (CBS)	90	30	200	20：1	PTSA-Gly	ChCl	2:1:1	6.4	n.d.	89
	110	30	200	20：1	PTSA-Gly	ChCl	2:1:1	29.2	n.d.	
	130	30	200	20：1	PTSA-Gly	ChCl	2:1:1	95.5	n.d.	
	90	30	200	10：1	PTSA-Gly	ChCl	2:1:1	3.5	n.d.	
	110	30	200	10：1	PTSA-Gly	ChCl	2:1:1	16.3	n.d.	
	130	30	200	10：1	PTSA-Gly	ChCl	2:1:1	57.5	n.d.	

n.d.: not defined in the literature, LA: lactic acid, AA: acetic acid, FA: formic acid

5 Exploration pathways for chemical transformation of lignin

Except for determining the yield and purity of lignin, the characterization of lignin is crucial for unraveling the mechanism and optimizing the process of lignin extraction with DES. It provides detailed insights into the structural and chemical changes such as the molecular weight, polydispersity, degree of polymerization, and functional groups during the extraction process.

Common methods for lignin characterization include elemental analysis, Fourier Transform Infrared Spectroscopy (FTIR), and Nuclear Magnetic Resonance (NMR) Spectroscopy for determining functional groups and lignin's molecular structure, Gel Permeation Chromatography (GPC) for identifying the molecular weight distribution, Ultraviolet-Visible (UV-Vis), Spectroscopy, Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS), Thermogravimetric Analysis (TGA) for the thermal stability, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and X-ray Diffraction (XRD).

5.1 Lignin modification with DES extraction

Pan et al indicated that lignin with more phenolic hydroxyl groups, less aliphatic hydroxyl groups, low molecular weight, and narrow polydispersity showed high antioxidant activity [90]. Lignin extracted with DES often displays a narrower molecular weight distribution, improved purity, better structural integrity, and more functional groups. Those samples that underwent this procedure showed improved thermal stability and exceptional antioxidant activity [91]. Zhang et al. compared the Douglas Fir lignin (DESL) extracted with DES, milled wood lignin (MWL), and other typical software lignin and they found that DESL had a narrower and lower molecular weight range, ranging from 490-2600 g/mol with a peak molecular weight of roughly 890 g/mol [29]. Wen et al. conducted a series of characterizations of lignin extracted with DES (lactic acid- ChCL) under 60-140℃. They discovered that during DES treatment, the primary change involved the selective dissociation of the aryl ether linkage (β-O-4) without affecting the C-C bonds. This conclusion is consistent with our previous work that when subjected to DES treatment (ChCl/lactic acid) at 145°C, the β-O-4 dimeric model (guaiacylglycerol-β-guaiacyl ether) was completely converted, leading to the stoichiometric release of Hibbert's ketone and guaiacol, with no cleavage observed for the β-β-linked dimeric model (hydroxymatairesinol, HMR) [29]. The cleavage of ether linkage resulted in the increased phenolic hydroxyl groups in lignin, while aliphatic hydroxyl groups decreased, possibly due to DES-induced dehydration or acylation reactions. Besides, in the aromatic region (Fig. 8), DES primarily catalyzed the degradation of G-type lignin units at lower temperatures (60-100°C) and, at higher temperatures (120-140°C), S-type lignin was more readily removed than G-type lignin [92]. Besides, the oxidation and demethoxylation reactions also occurred during the DES treatment process, leading to the condensations of G and S-types lignin. This will cause an increase in the S/G ratio. [93,94]The oxidation and demethoxylation reactions that occurred during the DES treatment process, led to the condensations of G and S subunit lignin, which also contributed to an increase in the S/G ratio (Ma et al., 2021, Ma et al., 2020).

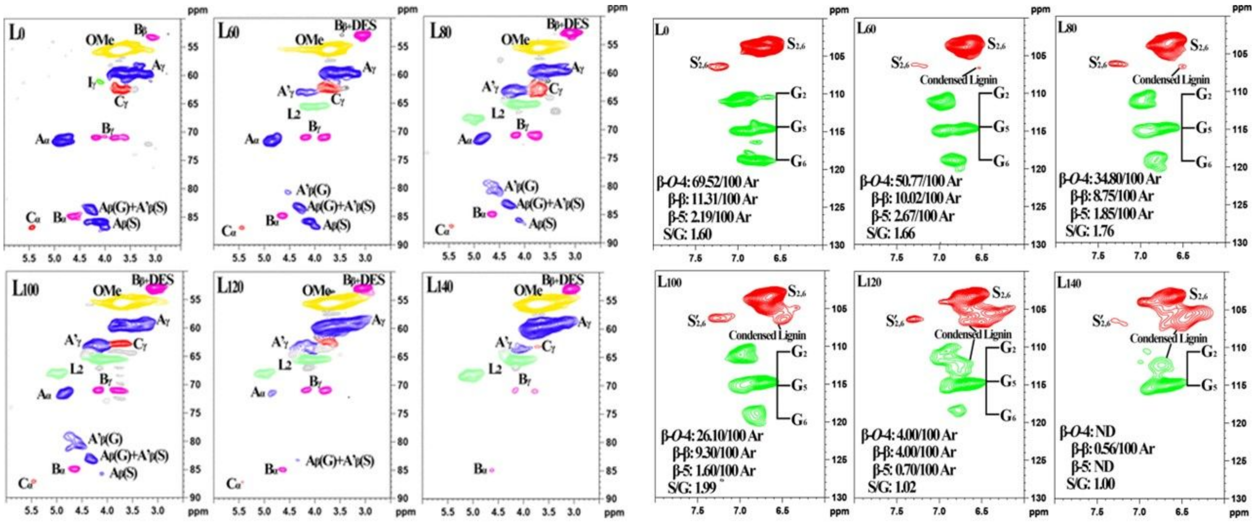

Fig. 8 2D-HSQC NMR spectra of the lignin side-chain region (left) and aromatic region (right) [92].

Apart from the depolymerization of lignin, the recondensation of lignin also occurred and resulted in more complex lignin compounds. But Pant's research showed that DES-extracted lignin compared with Kraft lignin had less condensed C-C linkages, which is favorable for further valorization to aromatics [44].

5.2 Differences of lignin with MW-heating and other heating methods

When utilizing DES under strict reaction circumstances, conventional heating that relies on conduction/convection-based methods causes heat dissipation because of temperature gradients [21]. In contrast, MW heating employs an electromagnetic field that induces rapid oscillation and rotation of polar molecules and charged moieties within the DES-lignocellulosic biomass mixture, accelerating heat generation [29]. This intensified heating facilitates lignin dissolution by breaking weak intermolecular forces, consequently enhancing lignin solubility in the solvent [12].

Research suggests that MW heating may also generate localized heat spots within the complex biomass structure, potentially leading to burst-like effects within particles. As a result, the biomass structure is disrupted, leading to a higher yield in lignin extraction. Molecular dynamic simulations also indicate that microwaves could stretch certain bonds within real lignin more compared to conventional heating, increasing the likelihood of bond breakage, and thus accelerating polymer breakdown [12]. Microwave-enhanced heating thus may lead to stressor effects in the microstructure, which breaks weak intermolecular forces and enhances lignin solubility in the solvent and can trigger specific reactions like additional dielectric heating and ionic conduction from the liberated small molecules. These reactions can selectively cleave crucial lignin bonds, such as ether linkages (β-O-4 bonds) [95], pivotal for lignin depolymerization and extraction. The cleavage of these linkages can elevate the phenolic hydroxyl content in the extracted lignin, potentially synergize with DES, and contribute to ether linkage cleavage during extraction. Multiphysics simulations of microwave heating of biomass [68] and lignin [87], the same one as above Nde et al] also indicate that the sample placement in the reactor also heavily influences the heating performance.

Furthermore, the combination of microwave and DES has been shown to efficiently cleave LCCs, yielding lignin with a low molecular weight (913), low polydispersity (1.25), and high purity (96%) [40]. The bound carbohydrate content and lignin molecular weight decreased when the severity of microwave-assisted extraction was increased. Increased extraction temperature and duration led to a greater release of OCH_3 groups in lignin as a result of more severe demethylation reactions [96]. Li et al. found that a lignin yield of 17.98% was reached by microwave-assisted extraction at 109°C for 60 minutes. The resultant lignin fraction has a low weight-average molecular weight of 6070 g/mol and a low bound sugar concentration of 1.81%. It also showed significant antioxidant activity (RSI 1.15), exceeding that of the common commercial antioxidant BHT but falling short of BHA [95]. Additionally, Zhou et al. demonstrated that the lignin recovered via MW-heating is a combination of the GS-type with the predominant inter-unit connection being the -O-4′ ether bond, but it is expected that the contributions of individual lignin monomeric subunits would be heavily dependent on the source of biomass as well. The radical scavenging index (RSI) of MW-assisted lignin was greater than that of milled wood lignin (0.53) in terms of antioxidant activity against DPPH, indicating that ML displayed significantly stronger antioxidant activity than milled wood lignin. [97].

However, the characteristics of extracted lignin can also vary depending on the composition of DES and the extracting conditions. There is a significant knowledge gap with respect to a wide range of DES types, microwave conditions, and extracted lignin properties, such as functional groups, molecular weight, and purity, and more investigations are needed to properly design unit operations targeting lignin separation via microwave methods.

6 Prospects and challenges

In summary, DES application in lignin extraction boasts appealing attributes: eco-friendliness, efficient extraction, selective cleavage, and synergy with MW heating for accelerated reaction rates and improved energy efficiency. However, integrating MW-DES into lignin extraction faces challenges such as the MW-assisted DES realm lacks comprehensive insights into mechanisms, MW-DES interplay, recovery strategies, and scalability summarized in Table 5. Future challenges include:(1) Complexity: Despite the vast range of uses and variety of DES types, insufficient study has been done on its characteristics, particularly its thermodynamic properties [98]. On this basis, the extraction of lignin involves multiple components, and multiple reactions, and is a complex system. Many experiments with different DESs, feedstocks, and conditions need to be conducted.

(2) Affordability: Although MW-assisted heating decreased the overall cost of the lignin extraction process, DES itself is not an economic-effective solvent. The effective recycling method for DES and the use of less expensive DES components to synthesize DES can be the potential solutions for reducing the cost. Besides, for a collaborative biorefinery, people also work on developing biomass-derived DES (bio-DES/green DES), which can add value to the whole industry. Further detailed investigation on these

research areas will provide the versatile uses of bio-DES for significantly lower cost and eco-friendly processes.

(3) Scaling Challenges: Lab-scale MW-DES success doesn't guarantee industrial scalability for lignin extraction. In larger-scale reactors, achieving uniform microwave heating throughout the entire volume can be difficult. Hotspots and temperature variations may occur, making it challenging to ensure consistent and controlled reactions. Besides, the potential for microwave leakage, especially in high-power systems, needs to be carefully managed to ensure the safety of personnel and the environment.

(4) Consistency: There are many factors that can affect the consistency of final lignin products. MW-DES process can be more sensitive to the biomass sample size and geometry exposed to microwave energy. Although addressing these challenges mandates concerted research initiatives, it is pivotal in fully harnessing lignin's potential as a valuable and renewable resource spanning diverse industrial sectors.

Table 5 Comparison between lignin extracted with MW heating and other heating methods.

	MW heating	Conventional heating
Extraction yield	Higher extraction yield (80-90%)	Lower extraction yield (50-70%)
Reaction condition	Lower temperature and shorter time (130-150℃，15-60 min)	Higher temperature and longer time (>140℃， hours)
Efficiency	Efficient and rapid, volumetric heating	Slower, temperature gradient-driven heating
Lignin properties	• Lower moisture content. • Lower Mw, Mn, and PDI (PDI (polydispersity (Mw/Mn) index) • Less char residue. • Minimal to no ether linkages. • Higher antioxidant activity. Formation of cross-peaks resembling Hibbert’s ketone (HK).	• Varying molecular weights. Varying polydispersity, and chemical properties
Lignin properties Solvent consumption	• Lower moisture content. • Lower Mw, Mn, and PDI (PDI (polydispersity (Mw/Mn) index) • Less char residue. • Minimal to no ether linkages.	• Varying molecular weights. • Varying polydispersity, and chemical properties • Larger volumes of solvent to ensure thorough penetration and

	• Higher antioxidant activity. • Formation of cross-peaks resembling Hibbert's ketone (HK). • Less solvent consumption	extraction from the lignocellulosic biomass.
Solvent recycles	The purity required for the recycled DES is important. MW heating might affect the purity differently from conventional methods.	• Thermal Degradation: conventional heating methods involve exposing the DES to high temperatures for extended periods. • Side Reactions: the elevated temperatures during conventional heating can trigger undesired side reactions between the DES and other components in the biomass matrix. • Solvent Loss: the use of high temperatures and prolonged heating times in conventional methods can lead to solvent loss through evaporation. Purity Issues: Exposure to high temperatures can cause the DES to pick up impurities or contaminants from the biomass.
Scale up potential	The infrastructure required for MW heating might differ from that of conventional heating methods. This could impact the feasibility of implementing microwave-assisted recycling on an industrial scale.	• Conventional heating methods that work well at small scales might face challenges when scaled up to industrial levels. Issues related to heat transfer, equipment design, and process control can arise.

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