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Process intensification technology-assisted deep eutectic solvent pretreatment for fractionation of lignocellulosic biomass: a review

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Lignocellulosic biomass pretreatment has become a prerequisite for the efficient conversion of lignocellulosic components into high-value chemicals and materials as sustainable alternatives to fossil-based products. In recent years, deep eutectic solvents (DESs) have emerged as promising green and versatile solvents for biomass fractionation. However, their relatively limited treatment efficiency and the necessity for multi-component recovery have driven the development of intensified DES pretreatment strategies. This review first briefly summarizes the performance of various DES systems when applied alone to biomass pretreatment, and then systematically highlights recent advances in intensified technologies integrated with DES processes. These intensification strategies include physical approaches, such as microwave irradiation, ultrasonic treatment, pulsed electric fields, and mechanical activation, as well as chemically driven processes, including hydrothermal treatment, steam explosion, and catalyst-assisted DES pretreatment. The advantages, limitations, processing outcomes, and underlying mechanisms of these strategies are comparatively analyzed. To reduce the overall cost and environmental footprint of DES-based processes, current developments in DES recovery technologies are comprehensively reviewed. Finally, the existing challenges and future perspectives are discussed to provide guidance toward the development of efficient and sustainable DES-based biomass pretreatment technologies.

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1. Deep eutectic solvents (DESs) are promising green solvents for biomass pretreatment. To enhance their efficiency, this work reviews environmentally friendly intensification technologies applied to DES pretreatment. These intensified processes are critical for improving the fractionation and recovery of biomass components, which facilitate their subsequent high-value conversion.
2. Existing reviews on intensified DES pretreatment primarily focus on microwave and ultrasound technologies. However, this work comprehensively summarizes various intensified technologies, including microwaves, ultrasound, pulsed electric fields, mechanical activation, hydrothermal treatment, steam explosion, and catalysis. Relevant characteristics and underlying mechanisms of these strategies are analyzed, offering valuable guidance to researchers. Meanwhile, solvent recovery strategies are also discussed.
3. Future efforts need to incorporate artificial intelligence to accelerate the optimization of DES pretreatment processes, promote component separation, deeply reveal the separation mechanism, and determine application scale expansion from environmental and cost perspectives.

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1. Introduction

The energy and chemicals that are ubiquitous and indispensable in modern society mainly originate from non-renewable fossil feedstocks. With excessive exploitation of fossil resources and the growing concerns about environmental issues (*i.e.*, greenhouse gas emissions and waste accumulation), developing renewable and clean resources to replace fossil products has become a very promising research direction.[1] Lignocellulosic biomass, such as forestry residues, energy crops, and agricultural residues, is a low-cost, widely distributed, naturally abundant, carbon-neutral, and renewable

resource on Earth.[2] It is reported that the global annual production of such biomass is approximately 181.5 billion tons, yet only about 8.2 billion tons are utilized, leaving the vast majority to be discarded as waste.[3] Lignocellulosic biomass is mainly composed of cellulose (30–40%), hemicellulose (20–30%), and lignin (10–25%), and their content varies depending on the type of biomass (Fig. 1a).[4] Both cellulose and hemicellulose are carbohydrates. Cellulose is a linear polymer consisting of glucose units linked by glycosidic bonds, whereas hemicellulose is a complex polymer of pentoses and hexoses, such as xylose, mannose, and galactose.[5] Lignin is a three-dimensional cross-linked natural aromatic polymer, mainly composed of three phenolic units (*p*-hydroxyphenyl, guaiacyl, and syringyl). These units are connected by carbon–carbon bonds (such as β-5, β–β, and 5-5) and ether bonds (such as β-O-4, α-O-4, and 4-O-5).[6] The three major components derived from the fractionation and refining of lignocellulosic biomass can be further valorized into fuels, chemicals, and biomaterials as alternatives to petrochemical-based products (Fig. 1b).[7] The high-value utilization of biomass is of great value in alleviating current social and environmental problems. Nevertheless, the specific content of these lignocellulosic components varies depending on the type and source of the biomass. The compositional diversity introduces greater complexity and challenges to the overall conversion processes. Furthermore, cellulose, hemicellulose, and lignin are naturally cross-linked into a complex matrix *via* covalent and hydrogen bonds, along with the crystallinity of cellulose and the hydrophobicity of lignin, resulting in an extremely sturdy structure of the lignocellulosic biomass.[8] These structural characteristics pose the main bottleneck in biorefining technology, severely impeding the efficient conversion of lignocellulose into high-value bioproducts.[9] Therefore, in order to achieve subsequent efficient conversion, it is necessary to employ effective and economical pretreatment methods to break down the raw materials into their main components.

The pretreatment of lignocellulosic biomass is a critical step for structural deconstruction and component separation, which contributes significantly to the overall cost of the biorefinery process.[11] Conventional pretreatment technologies primarily include mechanical milling, acid/alkali treatment, organosolv treatment, hydrothermal treatment, and biological treatment.[12] They can be classified into physical, chemical, biological, or combined treatment processes. As illustrated in Fig. 2a, these pretreatment technologies contribute to the destruction of the biomass structure and the separation of major components to varying degrees, thereby facilitating subsequent fermentation and high-value conversion. However, the challenges inherent in these processes, such as high energy demand, prolonged treatment durations, poor selectivity, chemical consumption, the associated economic and environmental burdens, as well as equipment corrosion, can substantially compromise process profitability and pose a significant obstacle to sustainable industrial-scale application.[13] Furthermore, these treatments disrupt the native structure of the separated components, particularly lignin and hemicellulose, thereby constraining the potential for further high-value conversion of the biomass. Thus, researchers have been dedicated to developing sustainable and efficient green methods for biomass pretreatment.

In recent years, novel environmentally friendly solvent pretreatment methods have emerged as a popular pretreatment strategy for the fractionation of lignocellulosic biomass. This approach not only reduces the environmental impact of the process but also enhances the structural preservation and separation selectivity of the biomass components. In contrast to conventional organic solvents (*e.g.*, methanol, ethanol, and acetone), these novel solvents overcome the inherent draw-

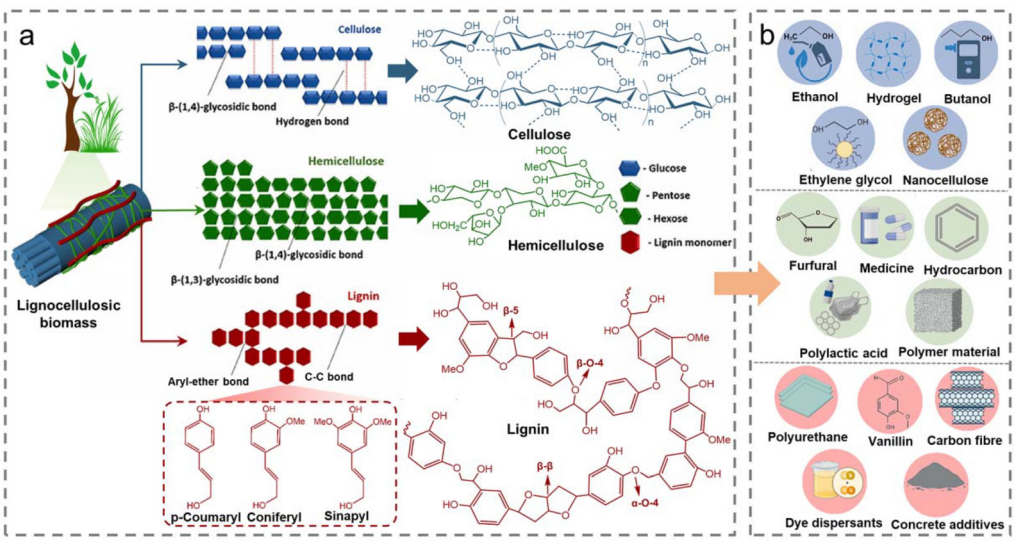

Fig. 1 (a) Schematic structure of lignocellulosic biomass.[4,10] Adapted from ref. 10. Copyright 2021, Elsevier. (b) Conversion of biomass components into biomass-based products.[7] Adapted from ref. 7. Copyright 2025, Elsevier.

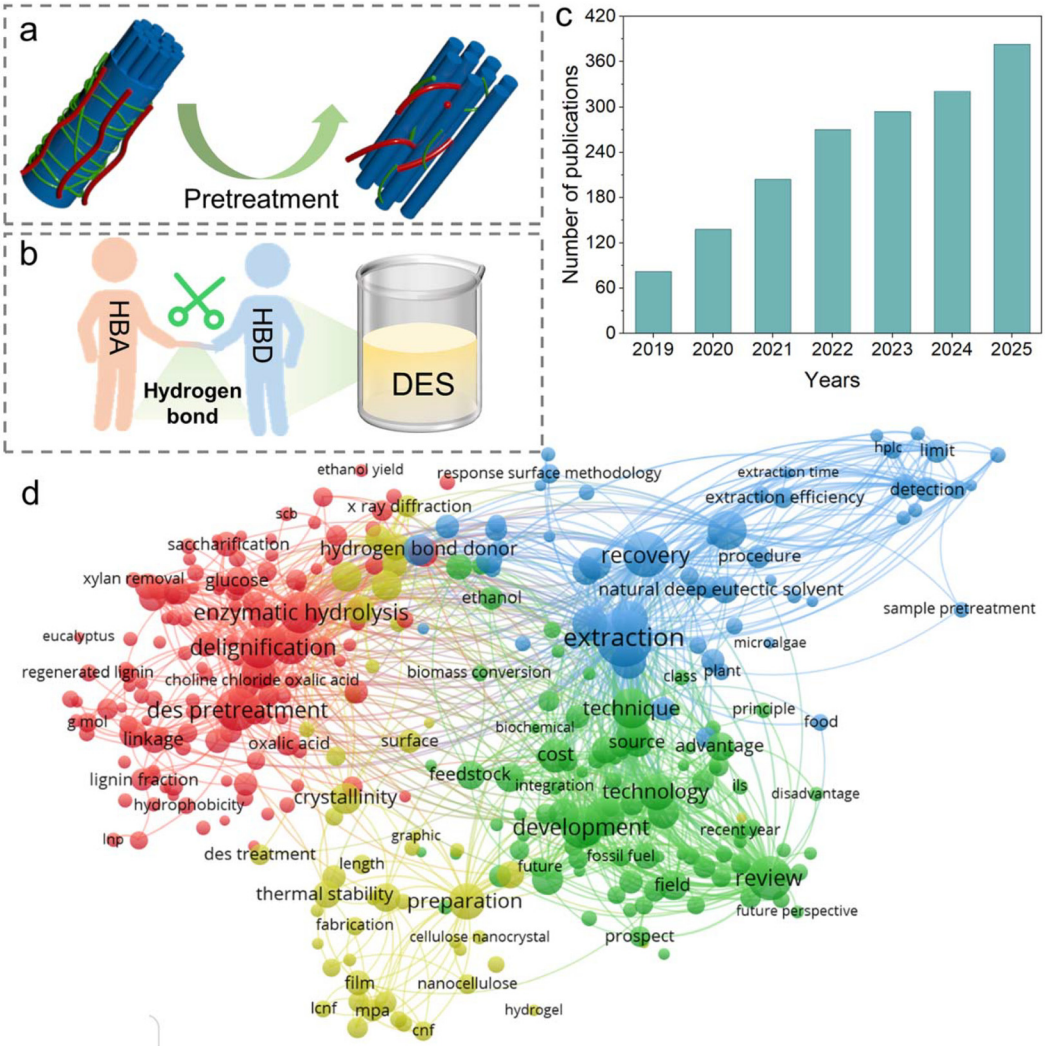

Fig. 2 (a) Schematic diagram of lignocellulosic biomass pretreatment. (b) The characteristics of the DES system. (c) The number of publications related to biomass pretreatment. (d) Keywords co-occurrence network analysis using VOSviewer software.

backs of high volatility, flammability, toxicity, and poor sustainability.[14–16] Ionic liquids (ILs), for instance, have been widely studied for biomass pretreatment due to their high stability and strong dissolution capacity toward lignocellulosic components.[17,18] Nevertheless, ILs have been widely criticized for their high synthesis cost, toxicity, and poor biodegradability. By contrast, deep eutectic solvents (DESs), while sharing similar physicochemical properties with ILs, have attracted growing interest owing to their cost-effectiveness, relatively low toxicity, biodegradability, and recyclability.[19] DESs are composed of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD), which exhibit high viscosity and strong hydrogen bonding interactions (Fig. 2b).[20] In particular, choline chloride-based DESs are generally considered green solvents, demonstrating advantages over ILs in both environmental and technical aspects.[21] Furthermore, DESs can effectively deconstruct biomass, selectively extract lignin and hemicellulose, and enhance the saccharification efficiency of cellulose.[5] For example, the study by Cheng *et al.* reported that a diol-based DES pretreatment removed 63% of the lignin and 73% of the xylan from bamboo at 110 °C, leading to a glucan saccharification yield of up to 95%.[22] Importantly, more than 90% of the recovered lignin maintained a relatively intact structure, which is highly advantageous for subsequent high-value utilization. Additionally, DES pretreatment is superior to traditional methods in terms of energy efficiency. For instance, Gunny *et al.* examined alcohol-based DES and NaOH-pretreated rice husk for saccharification and found that the former consumes approximately 20% less energy than the latter.[23] Li *et al.* also reported similar results on the low energy consumption of DES pretreatment.[24] Procentese *et al.* further compared the energy consumption per unit mass of biomass between DES pretreatment and other common methods (*e.g.*, acid/alkali treatment and steam explosion), and similarly showed that DES pretreatment offers a clear advantage in terms of low energy consumption.[25]

According to the search results from the Web of Science (WOS) database, the number of published research articles and reviews on the DES pretreatment of biomass has been growing year by year from 2019 to 2025, demonstrating the increasing interest in biomass pretreatment using DES methods (Fig. 2c). To further visualize the current research on DES pretreatment of lignocellulosic biomass, the relevant literature retrieved over the past six years (*i.e.*, 2019–2025) was analyzed using VOSviewer software, which excels at constructing and visualizing bibliometric networks. Fig. 2d presents the co-occurrence network of keywords related to "deep eutectic solvent pretreatment" or "DES pretreatment" in combination with "biomass". In this network, distinct color-coded clusters represent semantically related research themes. The node size corresponds to the frequency of occurrence, while the interconnecting lines reflect the strength of associations between the terms.[26] As illustrated by these interconnected clusters, research on DES pretreatment mainly focuses on delignification, component extraction efficiency, recovery technologies, development of related pretreatment technologies, and applications of pretreated biomass. This indicates the broad scope and increasing depth of DES research in biomass pretreatment. Furthermore, this trend has also led to the emergence of various reviews on DES pretreatment in recent years. For example, Wang *et al.* focused specifically on lignin extraction and saccharification enhancement in their summary of advances in DES pretreatment of biomass, along with a systematic analysis of the mechanism of biomass deconstruction by DES.[13] Xiao *et al.* reviewed the composition and classification of DES, analyzed the critical parameters governing the DES pretreatment process, and explored the roles of functionalized DES in lignocellulose valorization.[5] Similarly, in order to further guide DES pretreatment to promote biomass conversion, Xu and colleagues comprehensively outlined the synergistic effects of various parameters in DES pretreatment, including biomass particle size and crystallinity, solvent components, temperature, reaction time, and liquid–solid ratio.[27] In addition, converting biomass treated with DES into functional materials has also become a recent research hotspot. Shen *et al.* summarized the emerging applications of DES in the production of biomass-derived carbon materials, and highlighted challenges related to solvent recoverability and cost control.[28] Tan *et al.* systematically reviewed lignocellulosic biomass fractionation using DES and the subsequent conversion of DES-derived saccharides and lignin into biomass-based products, with particular emphasis on the performance of diverse DES systems and pretreatment strategies.[29]

The existing reviews on DES pretreatment have mainly focused on summarizing various DES-based biomass pretreatment strategies, optimizing processing parameters, elucidating the pretreatment mechanisms, and developing functional biomass-based materials mediated by DES. However, an important drawback of the DES pretreatment process is that its high viscosity hampers mass transfer efficiency, resulting in low overall efficiency. Moreover, this result also causes difficulties in solvent recovery. The viscous DES tends to adhere to the pretreated solid biomass, creating a physical barrier that obstructs enzymatic access to cellulose and consequently restricts its hydrolysis into fermentable sugars. For example, the study by Dong *et al.* showed that extracting lignin from eucalyptus using a diol DES still required 48 h at 120 °C.[30] This significantly restricts the large-scale application of this pretreatment approach. Moreover, different biomass feedstocks such as hardwoods, softwoods, and grasses exhibit significant differences in the contents of cellulose, hemicellulose and lignin, which makes it extremely difficult to adopt a universal treatment method. In response to these limitations, the integration of DES pretreatment with various intensified technologies has been increasingly explored in recent years. For instance, Xia *et al.* reported that microwave-assisted acid DES pretreatment of reed achieved approximately 65% lignin removal within only 40 s, while attaining a cellulose saccharification yield of 88%, far surpassing the performance of conventional DES pretreatment.[31] According to the research from Sharma *et al.*, ultrasound-assisted pretreatment of sugarcane bagasse with ethylene glycol (EG)-based DES for 7.7 min resulted in a 1.2-fold higher cellulose sugar yield.[32]

Nevertheless, current reviews on intensified DES treatment of lignocellulosic biomass have merely discussed the microwave- and ultrasonic-assisted technologies, which leads to insufficient coverage.[33–35] In fact, beyond the aforementioned approaches, various emerging strategies for enhancing DES pretreatment have been developed in recent years, including physical methods such as pulsed electric fields and ball milling, as well as chemical methods like hydrothermal treatment and catalytic processes. These methods not only improve the overall performance of DES pretreatment but also enhance the value-added potential of biomass. Therefore, it is essential to comprehensively analyze diverse intensification technologies for DES pretreatment and compare their process characteristics. Such an analysis will facilitate a deeper understanding of the principles and application scopes of different intensified DES processing strategies, thereby promoting more efficient DES-based biomass processing.

In the context of DES-based biomass pretreatment, process intensification refers to strategies that enhance mass and heat transfer and intensify solvent–biomass interactions, thereby improving the efficiency of lignocellulosic fractionation and cellulose saccharification. This review surveys and analyzes the literature published since 2019 concerning intensified DES pretreatment of biomass. It offers a critical overview of the process characteristics and mechanisms from chemical and physical standpoints, along with their corresponding performance outcomes. The review is structured as follows. Firstly, the conventional DES pretreatment process of lignocellulosic biomass is briefly introduced based on the different types of DES. Furthermore, this review systematically examines the intensified DES pretreatment strategies applied to the fragmentation of lignocellulosic biomass, with an in-depth analysis of physical intensification methods (*i.e.*, microwave irradiation, ultrasonication, pulsed electric fields, and mechanical milling) and chemical approaches (*i.e.*, hydro-

thermal treatment, steam explosion, and catalytic modification). These technologies synergistically enhance DES performance by optimizing solvent–biomass interactions, thereby improving the delignification efficiency and enzymatic saccharification of recalcitrant lignocellulosic substrates. Meanwhile, the costs and environmental implications associated with the potential scale-up of these technologies are also briefly analyzed. Besides, the process of one-pot biomass pretreatment based on DES is also introduced. In addition, considering the significant impact of cost, the strategies for solvent recovery and reuse reported in the literature are also discussed. Finally, this study discusses the current challenges and potential perspectives regarding enhanced DES pretreatment for the valorization of biomass. Against the backdrop of the rapid development of environmentally friendly DES in biomass pretreatment, this study provides insights and guidance for enhancing the overall efficiency of lignocellulosic biomass pretreatment. It offers a comprehensive understanding of the mechanisms and process characteristics underlying various DES intensification strategies, as well as their respective advantages and limitations, thereby supporting the rational selection of pretreatment approaches for specific applications. From the perspective of process intensification, this work clarifies the principles governing enhanced DES-based fractionation of lignocellulosic components and promotes the broader implementation of DES in biorefinery systems. Ultimately, these advances will contribute to the high-value utilization of biomass waste resources, reduced reliance on fossil resources, and the sustainable development of the bioenergy industry.

2. DES pretreatment overview

DES was firstly synthesized by Abbott *et al.* in 2001 by simple heating, serving as a promising solvent alternative to IL.[36] Compared to traditional organic solvents, DES possesses unique advantages such as high stability, lower toxicity, and biodegradability.[22,37] DES is a mixed solution system typically composed of HBAs and HBDs in a specific molar ratio, with a melting point lower than that of each individual component.[38] This reduction in melting point is attributed to the presence of ions with low lattice energy and charge delocalization effects during hydrogen bond formation.[39] When HBAs and HBDs are mixed to synthesize DES, the strength of the hydrogen bond network formed is significantly influenced by the type, size, and ratio of the DES components, which in turn affects the physicochemical properties of the DES. Therefore, DES is recognized as a designer solvent whose properties can be tailored by adjusting the composition and ratio of the constituents.[40] Most DESs have relatively high viscosity (>100 cp) at room temperature, which reduces the mass transfer efficiency of the DES system. This high viscosity arises from the extensive hydrogen bond networks formed among all the components, as well as additional intermolecular interactions such as van der Waals forces and electrostatic forces.[41] The polarity of DES, which is influenced by variations in HBDs, has a significant impact on the solubility of biomass components. For example, polyol-based HBDs make DES exhibit high polarity by forming extensive hydrogen bonding networks. Furthermore, the increased alkyl chain length of HBDs reduces the polarity of DES.[41] Generally, the density of DES is greater than that of water (approximately 1.0–1.35 g cm^{-3}), which is affected by the DES components and reaction temperature.[42] An increase in the hydroxyl content of HBDs often leads to an increase in DES density. The change in DES density may alter their interaction with solute molecules, thereby affecting their solubility. Furthermore, it plays a crucial role in extraction and separation processes. Compared to commonly used solvents, DES generally exhibits low volatility and relatively high thermal stability, which are influenced by their composition and hydrogen bonding. Unlike ILs, the thermal decomposition of DESs often requires overcoming hydrogen bonding first, followed by the decomposition of components with poor thermal stability.[43]

Common HBAs include quaternary ammonium salts, guanidine hydrochloride, and proline, while HBDs primarily include amides, carboxylic acids, and polyols (Fig. 3a).[44] Choline chloride (ChCl) is the most widely used HBA, owing to its biodegradability and non-toxicity.[45] Another reason is that Cl^- ions can form strong hydrogen bonds with hydroxyl groups in polysaccharides, leading to greater disruption of chemical bonds within the lignin–polysaccharide complex.[46] The pioneering work of Francisco *et al.* in applying a carboxylic acid-based DES to wheat straw pretreatment rapidly spurred extensive research into DES pretreatments for the separation and refining of lignocellulosic biomass.[47] The strong hydrogen bonding network endows DES with the capacity to compete with the inherent linkages within lignocellulose, which facilitates the deconstruction of labile ether bonds between the phenylpropane units of lignin, along with the hydrogen and covalent bonds between lignin and hemicellulose.[5] In this process, DES anions interact with electron-deficient sites in lignin and hemicellulose molecules, thereby effectively disrupting the lignin–carbohydrate complex (LCC) linkages at the sites marked by the arrows (Fig. 3b).[48,49] After pretreatment, the dissolved lignin and hemicellulose fractions remain in the DES solvent, whereas the cellulose-rich solids are retained due to the hindrance of the more robust hydrogen bonding networks. DES in the filtrate can subsequently be recovered through methods such as anti-solvent addition.

According to the different properties of HBDs, DES-mediated pretreatment can be categorized into acidic, neutral, and alkaline strategies. They are comparatively summarized in Table 1. Acidic DESs are widely applied in biomass pretreatment, with their HBD typically being organic acids such as lactic acid (LA), oxalic acid (OA), and formic acid (FA). The carboxylic groups can release active protons (*i.e.*, acid catalysis) in the DES system with strong hydrogen bond interactions, which catalyze the breakage of chemical bonds such as ester, ether, and glycosidic bonds, as well as LCC linkages in lignocellulosic biomass.[50] This process primarily promotes the depolymerization of lignin and hemicellulose to disrupt the structure of the biomass.[51] For instance, research by Su *et al.*

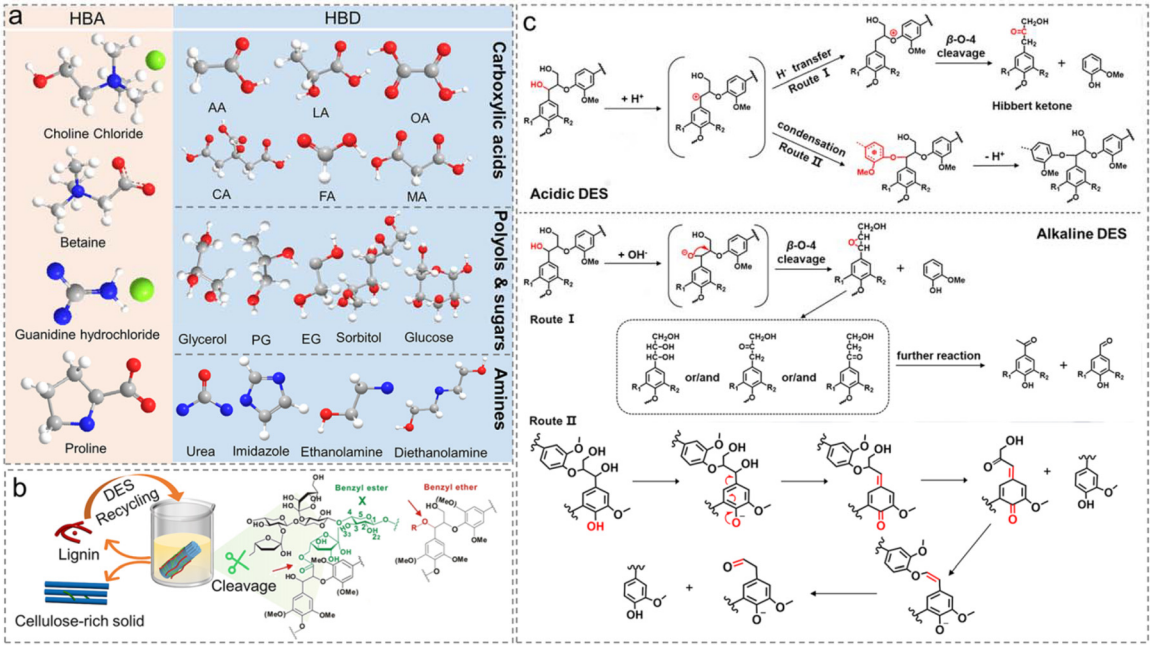

Fig. 3 (a) Representative HBAs and HBDs in the synthesis of DESs.[44] (b) Schematic diagram of DES destroying lignocellulosic biomass.[48] Adapted from ref. 48. Copyright 2025, Springer. (c) Possible lignin separation mechanism during acidic and alkaline DES pretreatment.[55,65] Adapted from ref. 55. Copyright 2025, Elsevier.

Table 1 Comparison of common acidic, neutral and alkaline DES pretreatment

Strategy	DES types	Biomass	Conditions	Lignin removal	Hemicellulose removal	Cellulose retention	Features	Ref.
Acidic DES	ChCl–LA	Poplar sawdust	130 °C, 1.5 h	89.3%	76%	90.5%	High dissociation efficiency, high viscosity, corrosiveness, lignin condensation, excessive degradation	52
	ChCl–LA	Eucalyptus	130 °C, 6 h	93%	94.5%	82.5%		53
	ChCl–OA	Moso bamboo	100 °C, 3 h	73.4%	84%	94.1%		69
	ChCl–OA	Rape straw	130 °C, 1 h	83.6%	89%	55.1%		70
	ChCl–CA	Bamboo	130 °C, 1 h	78.8%	57.5%	98.2%		71
	ChCl–AA	Rice straw	126 °C, 2.5 h	83.1%	82.1%	98.8%		72
Neutral DES	ChCl–Gly	Corncob	150 °C, 12 h	55%	47%	—	Environmental friendliness, maintenance of component structure integrity, high dosage usage, low efficiency	62
	ChCl–EG	Switchgrass	130 °C, 0.5 h	24%	1%	97%		73
	ChCl–Gly	Rice straw	150 °C, 15 h	52.2%	29.6%	96.5%		59
	ChCl–EG	Rice straw	150 °C, 15 h	30.7%	41.0%	82.2%		59
	ChCl–xylitol	Rice straw	150 °C, 15 h	21.4%	26.3%	84.5%		59
	ChCl–BDO with $AlCl_3$	Bamboo	120 °C, 1 h	85.5%	91.1%	~95%		61
Alkaline DES	ChCl–imidazole	Populus	115 °C, 15 h	26.4%	34.8%	77.1%	Selective removal of lignin, substantial lignin removal, high saccharification yields, complex separation, strict reaction conditions	74
	ChCl–urea	Rice straw	120 °C, 6 h	48.5%	19.7%	85.0%		75
	ChCl–MEA	Wheat straw	90 °C, 12 h	81.0%	47.3%	90.8%		66
	K_2CO_3–Gly	Oil palm empty fruit bunch	120 °C, 8 h	51%	36%	75%		76

LA – lactic acid; OA – oxalic acid; CA – citric acid; AA – acetic acid; Gly – glycerol; EG – ethylene glycol; BDO – 1,4-butanediol; MEA – monoethanolamine.

revealed that the LA-DES removed 76.0% of hemicellulose and 89.3% of lignin from poplar sawdust at 130 °C.[52] Similarly, Shen *et al.* reported that when treated with acidic DES from 90 °C to 130 °C, lignin removal increased from 36% to 93%, while the cellulose content remained almost unchanged, suggesting rapid lignin depolymerization and cellulose stability.[53] As illustrated in the depolymerization mechanism (Fig. 3c), acidic DES preferentially cleaves susceptible β-O-4 linkages to form Hibbert's ketones, promoting the dissociation of lignin.[54,55] Moreover, the side chains of lignin units generate a large number of free radicals under such conditions, leading to the formation of recalcitrant C–C linkages between adjacent lignin units and resulting in lignin condensation.[56] The condensed lignin not only adheres to the surface of cellulose, reducing the efficiency of enzymatic hydrolysis, but also diminishes the conversion value of lignin itself. As for hemi-

cellulose, it is hydrolyzed into sugars under strong acidic DES pretreatment at temperatures above 120 °C, whereas its degradation is less pronounced under milder conditions.[57] However, the possible excessive degradation of carbohydrates during acidic DES pretreatment leads to a decrease in product yield.[58] Additionally, the corrosive nature of acidic systems further challenges the application of acidic DES.

Neutral DESs have also attracted growing interest for lignocellulosic biomass pretreatment due to their superior environmental benefits and biocompatibility. The HBD components in typical neutral DESs are primarily polyols (such as EG, glycerol, sorbitol, and butanediol) and certain sugars (such as glucose, sucrose, and fructose). The diffusion of small-molecule alcohols, combined with the synergistic effect of their multiple hydroxyl groups, enhances hydrogen bonding interactions with lignin and thereby promotes its dissolution. For instance, Hossain *et al.* reported that glycerol-based DES achieved 52.2% lignin removal from rice straw while retaining more than 90% of glucan. In contrast, sorbitol-based DES with more hydrogen bonding sites and thus higher viscosity removed only 30.8% lignin and resulted in a glucan digestibility of approximately 50%.[59] Similarly, glucose-based DES also has particularly high viscosity and poor fluidity, which impairs its mass transfer process.[60] In addition to facilitating lignin dissolution, polyols also provide structural stabilization effects. Recently, Cheng *et al.* reported that butanediol mitigated lignin condensation by introducing diol hydroxyl groups into the α-position of the β-O-4 linkages through etherification.[61] Specifically, the reaction of diols with Hibbert's ketones to form dioxane structures serves to suppress lignin condensation in acidolysis. Beyond their role in neutral DESs, polyols can also be incorporated into acidic DES to inhibit lignin condensation and preserve the structure of the liberated lignin. Despite their merits of low corrosivity, environmental benefits, and minimal damage to the lignin structure, neutral DESs generally exhibit relatively low removal efficiency for lignin and hemicellulose. For instance, Phromphithak *et al.* found that a glycerol-based DES treatment of corncob at 150 °C for 12 h yielded removal rates of merely 55% for lignin and 47% for hemicellulose, both of which were significantly lower than those achieved with acidic DESs.[62]

In contrast to the extensive investigation on acidic and neutral DES, studies on alkaline DES remain limited. Alkaline DESs are commonly constituted of components such as alcoholamines and urea.[44,63] They disrupt the lignin–carbohydrate linkages by deprotonating lignin phenolic hydroxyl groups, thereby facilitating the loosening of the structure and fractionation of biomass components.[64] The resulting highly nucleophilic anions attack the adjacent β-O-4 bonds, generating reactive quinone methide-type intermediates, which subsequently undergo either depolymerization into small fragments or repolymerization.[65] In addition to this pathway, the β-O-4 linkages in non-phenolic lignin subunits can also be cleaved under strong alkaline conditions to form epoxide intermediates. These intermediates then undergo further rearrangement and depolymerization reactions, yielding ketone and aldehyde fragments (Fig. 3c).[55,65] Owing to the inherent alkali solubility of lignin, alkaline DESs exhibit greater selectivity in lignin extraction compared to acidic DESs. For instance, Zhao *et al.* reported that ethanolamine-based DES treatment of wheat straw for 9 h resulted in the removal of 71.4% of lignin and 42.1% of hemicellulose, while 93.4% of cellulose was retained.[66] This selectivity promotes the retention of polysaccharides in the product and reduces by-product generation, enhancing the subsequent production of fermentable sugars. In addition, urea-DES releases ammonia as a nucleophile to accelerate the cleavage of LCC linkages. Furthermore, distinct from conventional alkaline pretreatments, mild alkaline DES suppresses the condensation of lignin fragments by capturing the carbocation intermediates generated from the cleavage of lignin ether bonds.[7,67] Reduced condensation is beneficial to maintaining a higher reactive group content in dissociated lignin, promoting high-value utilization such as the conversion of aromatic chemicals. However, alkaline DES pretreatment often requires acidic solvents to regulate the later separation of lignin, which inevitably increases subsequent costs and environmental issues. Recent reports have proposed a novel green recycling approach for separating components and recovering DES through the introduction of CO_2 into suitable alkaline DES systems.[68] In the future, more efforts will be needed to optimize the alkaline DES pretreatment strategy in order to enhance the effectiveness of biomass pretreatment.

Binary acid- or alkaline-based DES systems typically operate under relatively harsh conditions, which not only disrupt the structural integrity of biomass components but may also raise environmental concerns. In contrast, polyol-based DES systems suffer from low pretreatment efficiency. These limitations have constrained the broader application of DESs for high-quality biomass fractionation. Although ternary polyol-based DESs are emerging as promising solvents for biomass pretreatment, achieving a favorable balance among pretreatment efficiency, environmental sustainability, cost-effectiveness, and product quality remains an ongoing challenge that requires further development.

3. Intensifying technologies assisting DES pretreatment

Although DESs have shown significant potential in biomass pretreatment, their effectiveness still relies on relatively harsh reaction conditions, such as high temperature, prolonged duration, or strong acidity or alkalinity.[77] These conditions can cause excessive degradation of biomass components, undesired side reactions, and possible environmental issues, ultimately hindering downstream valorization. Therefore, integrating DES pretreatment with other environmentally friendly technologies offers a promising strategy to improve overall processing efficiency under mild conditions and increase the potential value-added utilization of biomass components. Such synergistic strategies also contribute to a cleaner, more energy-efficient pretreatment process with minimized negative

environmental impacts. In this section, a summary and analysis of various intensified technologies are provided from the perspectives of physical effects- and chemical effects-intensified DES pretreatment.

3.1 Physically intensified DES pretreatment processes

Physical intensification technology refers to the use of various physical fields or mechanical effects to accelerate and optimize DES pretreatment processes. These technologies are implemented using mechanical equipment and, except in specific cases, typically occur simultaneously with DES pretreatment to achieve intensification. Meanwhile, they require no chemical reagent additions, reflecting their environmentally friendly characteristics. These strategies often mitigate the drawbacks of DES to some extent and effectively enhance the efficiency of DES-based biomass pretreatment.

3.1.1 Microwave-assisted DES pretreatment. Microwaves are electromagnetic waves with frequencies ranging from 300 MHz to 300 GHz, characterized by strong directionality and linear propagation.[34] Compared with traditional conductive heating methods, microwaves interact with target materials at the molecular level through dipole polarization and ion conduction, providing rapid and uniform volumetric heating.[78] Dipole polarization aligns the dipoles of polar materials with the oscillating electromagnetic field generated by microwaves to dissipate energy as heat, whereas ion conduction involves charged species oscillating and colliding within the microwave field.[79] When microwave irradiation is combined with DES pretreatment, it facilitates the conversion of more thermal energy due to enhanced ionic characteristics, thus improving overall processing efficiency, shortening reaction time, decreasing reaction temperature, and reducing energy loss (Fig. 4a). This process subsequently promotes the disruption of the biomass structure and the cleavage of chemical bonds by the localized hot-spots, while also reducing the formation of by-products.[5,50] Furthermore, microwave excitation enhances the molecular mobility and effective polarity of the DES, which improves its interaction with biomass. This synergistic effect accelerates the breakdown of the hydrogen-bonding network and the subsequent depolymerization of biomass compositions.[2] As previously reported, the extraction of lignin using DES usually requires several hours or a high temperature to achieve the desired results, which significantly increases energy consumption and reduces efficiency.[80] Wang *et al.* proposed that DES diffusion is the rate-limiting step during the initial stage of biomass dissolution, while surface chemical reactions dominate in subsequent stages.[81] Microwave radiation directly affects the polar components of both the biomass and DES, promoting frequent collisions among these molecules due to dielectric polarization and relaxation phenomena.[82] On one hand, microwaves weaken the hydrogen bond network within a DES, reducing its viscosity and enhancing the mass transfer efficiency. On the other hand, the collisions of polar molecules facilitate biomass swelling and the cleavage of LCC, which in turn increases the accessibility of DES to the internal components of the biomass. Therefore, microwave irradiation can effectively reduce the diffusion energy barrier of DES, thereby enhancing biomass deconstruction and significantly improving the removal rates of lignin and hemicellulose (Fig. 4b). Liu *et al.* also reported that microwave-assisted DES pretreatment (800 W) of wood flour required only 3 min of irradiation at 80 °C to attain a delignification efficiency comparable to that achieved by conventional oil bath heating at 110 °C for nearly 9 h.[49] This demonstrated that this coupled model can rapidly break LCC bonds and achieve effective lignin separation. Kumar *et al.* reported that, for achieving comparable separation performance in the acidic DES pretreatment of rice husk, microwave assistance reduced energy consumption by 67.7% and shortened the reaction time by 75.0% relative to conventional conductive heating.[83]

Although the microwave-assisted DES method has enhanced the pretreatment efficiency and demonstrated advantages such as eco-friendliness, lower energy consumption, and lower costs, it encounters some bottlenecks in practical applications. The limited penetration depth of microwaves (2–10 cm) exacerbates the problem of uneven heating in large reactors and hinders their application in such large systems, which requires innovative reactor designs.[84,85] Moreover, the presence of various hot spots and temperature fluctuations in large reactors makes it challenging to achieve uniform microwave heating throughout the entire volume.[34] This has an adverse effect on the separation of biomass components. Although operating multiple reactors in parallel can broaden the applications, it undoubtedly increases the overall investment cost. However, the reduced energy costs resulting from the microwave-assisted process can partially offset the total cost. Additionally, it is crucial to manage potential microwave leakage to enhance safety, which also imposes requirements on the rational design of the reactor. In addition, in microwave-assisted DES treatment, it is generally agreed that lower temperatures are not conducive to biomass disruption, while higher temperatures tend to cause excessive degradation of components. Therefore, controlling the appropriate reaction temperature and monitoring the reaction process will help ensure the smooth progress of biomass pretreatment. Finally, the diversity in biomass types and morphologies can also interfere with the effect of microwave irradiation, which increases the complexity of microwave-assisted DES pretreatment and warrants more in-depth investigation.

3.1.2 Ultrasound-assisted DES pretreatment. Ultrasound is another potential green auxiliary technology for enhancing biomass pretreatment, as it facilitates biomass deconstruction through mechanical and sonochemical effects during cavitation of bubbles.[86] Mechanical acoustic waves with frequencies of 20–200 kHz are typically used for ultrasonic pretreatment.[87] As illustrated in Fig. 4c, this cavitation phenomenon refers to the process where numerous microbubbles are generated in a liquid medium during ultrasonication, followed by their growth and subsequent violent collapse after absorbing ultrasonic energy.[86,88] This process exerts intense hydrodynamic shear forces on the biomass due to the strong shock waves and

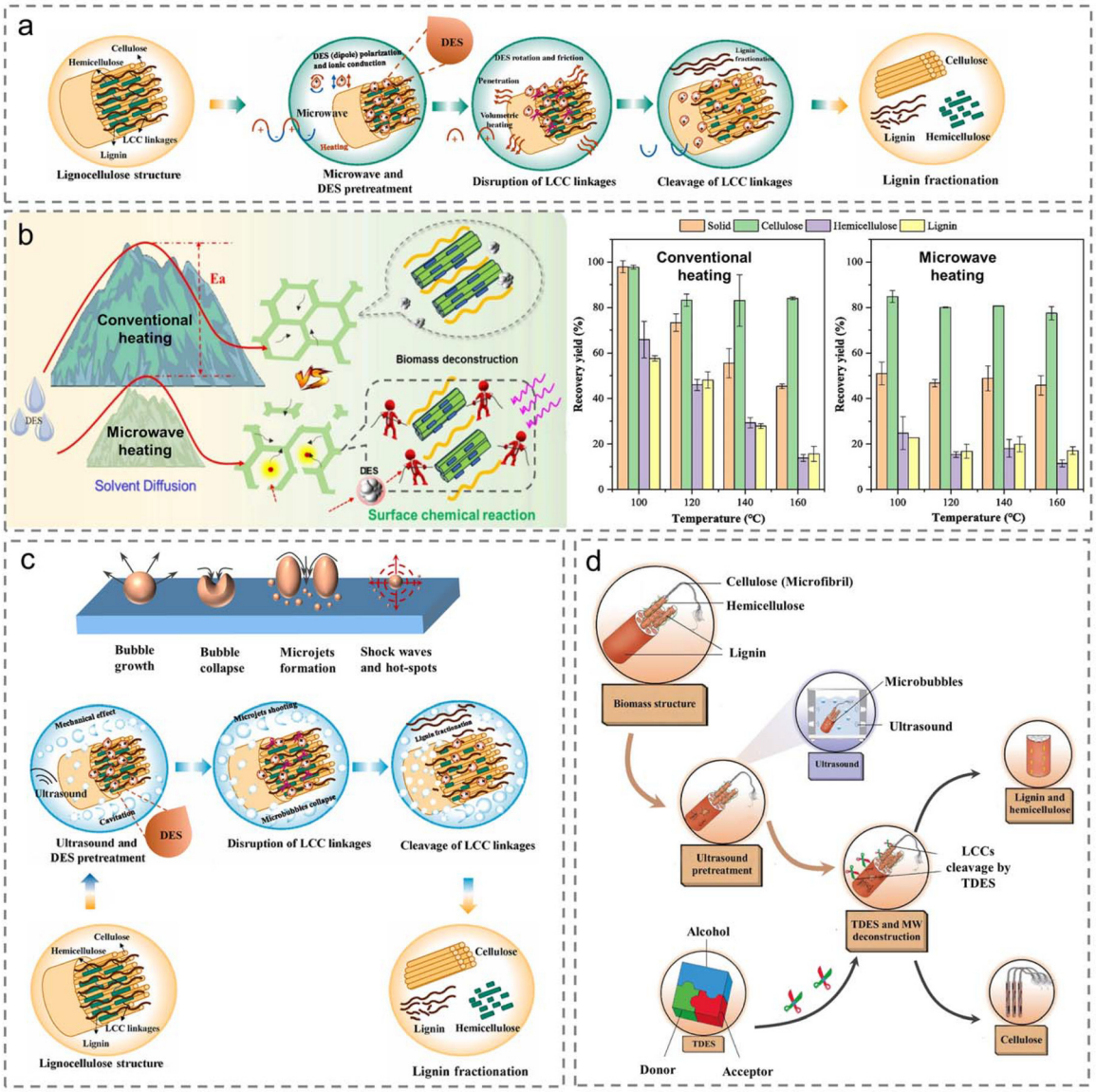

Fig. 4 (a) Microscopic mechanism of microwave-assisted DES pretreatment of biomass.[2] Adapted from ref. 2. Copyright 2022, Elsevier. (b) Comparison of the biomass pretreatment pathways using DES without and with microwave-assisted heating and changes in composition.[81] Adapted from ref. 81. Copyright 2025, Elsevier. (c) Microscopic mechanism of ultrasound-assisted DES pretreatment of biomass.[2,86] Adapted from ref. 2 and 86. Copyright 2022 and 2020, Elsevier. (d) Schematic diagram of corn stalk deconstruction by DES under sequential ultrasound and microwave assistance.[92] Adapted from ref. 92. Copyright 2021, Elsevier.

microjets, and is accompanied by turbulence and agitation, which collectively contribute to the breakdown of the biomass recalcitrant structure.[2,86] Meanwhile, in the DES medium, the vigorous agitation induced by these mechanochemical acoustic effects not only increases the microporosity of the biomass, thereby enlarging its contact surface area with the solvent, but also promotes the transfer of heat and mass.[2,50] In addition, the cavitation-induced cleavage of DES solvent molecules generates hydroxyl radicals, which promote the rupture of linkages within the LCC.[89] Similarly to microwaves, ultrasound-assisted DES treatment also offers an efficient and green approach for biomass deconstruction and component extraction, along with lowered reaction time, temperature, and enzyme requirements. For example, a comparative study by Sharma *et al.* showed that sugarcane bagasse pretreated with ultrasound-assisted glycerol-DES achieved a higher reducing sugar yield (276.8 mg g^{-1} biomass), which was 17.6% and 58.6% higher than the results of DES or ultrasound pretreatment alone, respectively.[32] Ong *et al.* reported that the incorporation of ultrasound with alkaline DES boosted lignin removal by 52% over the non-sonicated method, by facilitating the formation of oil palm frond surface voids and enhancing solvent wettability.[90] Lee *et al.* also demonstrated that ultrasound-assisted DES treatment exhibited a synergistic effect, resulting in a reducing sugar

yield from the products that was twice as high as that from DES pretreatment alone.[91] Furthermore, this yield surpassed that achieved by acid, alkali, and steam explosion pretreatment under comparable conditions.

The positive effects of ultrasound have also spurred research into combining it with other methods for treating biomass. For example, given the respective advantages of efficient heating by microwave radiation and ultrasound-enhanced mixing, Yan *et al.* conducted sequential ultrasound and microwave-intensified natural DES pretreatment of corn straw (Fig. 4d).[92] The results demonstrated that the sequential multimode intensification increased the lignin removal rate to 61%, while the cellulose content in the residue also rose from 34.70% to 76.08%. This dual-physical-field-assisted DES pretreatment achieved a more efficient and energy-saving dissociation of biomass components. Due to different cavitation effects, the rapid collapse of microbubbles at the biomass interface during ultrasonication erodes the biomass surface and damages its structural integrity.[93] Under such conditions, the penetration resistance of the DES is reduced, allowing it to easily penetrate the biomass structure and dissolve the target compounds. Meanwhile, ultrasonication accelerates the mixing of DES with biomass particles and reduces mass transfer barriers for the solvent. Subsequently, microwave radiation directly acts on the solvent molecules, weakening the energy barrier of heat transfer, and thereby achieving rapid heating of DES and greatly increasing the reaction rate.[94] Moreover, microwave irradiation disrupts the hydrogen bonding network of biomass, facilitating the dissociation of biomass components by DES. In addition, Wang *et al.* proposed a new pulsed ultrasound-assisted DES extraction for biomass components, noting that this pulsed mode not only enhances extraction efficiency but also effectively mitigates overheating issues compared to continuous ultrasound.[95]

The scale-up of ultrasound-assisted processes from laboratory to industrial applications requires specialized equipment and precise process control to ensure that large volumes of biomass are uniformly pretreated in a low-energy manner. For example, compared to the uneven distribution of acoustic energy caused by the ultrasonic probe, the sonicator with a cup horn can provide a non-intrusive mechanical treatment and uniformly disperse the acoustic energy intensity to the target.[96] However, this inevitably increases equipment and operational costs, posing a barrier to widespread adoption. Moreover, the efficiency of lignin removal remains relatively low under low-temperature conditions, because the high-viscosity DES prevents the transmission of ultrasonic energy through the medium.[92] However, the high-value conversion of the treated products can partially offset the overall costs. For example, the cellulose from the dissociated products can be converted into ethanol and other products, while lignin can serve as fuel or additives.[97] Therefore, developing energy-efficient ultrasonic systems and optimizing process parameters can help offset energy costs and reduce environmental impact. Furthermore, leveraging the mixing advantages of ultrasound to appropriately increase solid loading can also lower feedstock costs. Beyond these individual strategies, the combined ultrasound-microwave enhancement strategy demonstrates great potential.

3.1.3 Pulsed electric field-assisted DES pretreatment. The emerging pulsed electric field (PEF) technology (also known as electroporation or electropermeabilization) has recently exhibited potential in biomass deconstruction, component extraction, and digestion due to its high extraction efficiency, economic benefits, and environmentally benign characteristics.[98,99] The implementation of PEF treatment relies on high-voltage pulses generated by a pulse generator to process the target materials. In this stage, biomass particles are suspended in a suitable solvent and positioned between two electrodes, and then they are exposed to an electric field of 0.1–100 kV cm^{-1} for several microseconds to milliseconds.[100] The generated electrical pulses trigger electrochemical effects within the biomass cells, causing mechanical stress and electro-disruption of the cell wall structure.[99] As shown in Fig. 5, the irreversible pores induced in the biomass cell wall by high-voltage electrical pulses not only facilitate the infiltration of DES but also permanently disrupt the lignocellulosic matrix, effectively breaking the hydrogen bonds between cellulose and lignin/hemicellulose. After solid–liquid separation, the solid is rich in cellulose, while the other components are mainly present in the DES solvent. The cellulose microfiber structure of the biomass was damaged and decomposed into fibers, with the lignin removal rate reaching 66–79%. Therefore, the incorporation of the PEF process can improve mass transfer within biomass under relatively mild conditions, accelerate the overall processing, and shorten the treatment duration.[100] This process reduces energy consumption, minimizes inhibitor formation, and improves product quality. Putranto *et al.* also demonstrated that, at a comparable lignin removal rate, PEF-assisted DES pretreatment reduced energy consumption by 96% compared to conventional DES pretreatment alone, while also yielding higher solid recovery (~77%), cellulose yield (84–89%), and solvent recovery (77.5–90.71%).[101] They concluded that, compared to purely non-thermal PEF treatment, the conventional DES process involving higher temperatures can cause excessive biomass degradation and increased solvent loss. However, when this strategy is applied on a large scale, the uniformity of the electric field distribution and the impact of high-viscosity DES on the electric field penetration need to be further studied. Moreover, under a high voltage, the corrosiveness of chloride ions or the acidic environment in the DES toward the electrode and the stability of the DES itself may be potential challenges. The high initial cost of the PEF system (*e.g.*, power supply, pulsed voltage generator, and cooling system installation) also hinders its widespread application.[102] Thus, the economic feasibility of this intensified process relies heavily on high-value conversion of the products and the recovery of DES.

3.1.4 Mechanical activation-assisted DES pretreatment. Mechanical activation (*e.g.*, crushing, ball milling, and extrusion) is a commonly employed physical biomass pretreatment method. It reduces the particle size and alters the surface

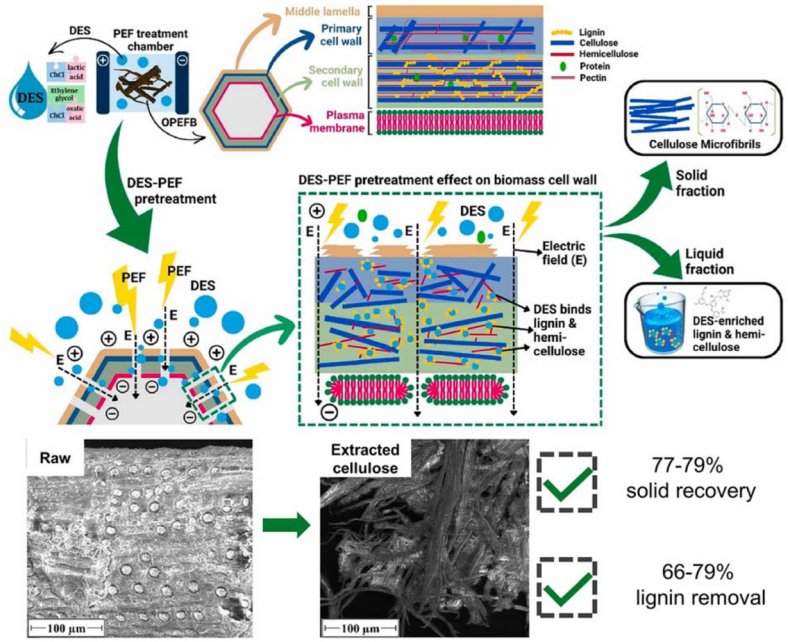

Fig. 5 The mechanism of DES-PEF pretreatment effect on the lignocellulose bonds of oil palm empty fruit bunches.[98] Adapted from ref. 98. Copyright 2025, Elsevier.

structure and crystallinity of the solid, thereby moderating the subsequent reaction conditions and enhancing the reactivity.[103] Our previous study demonstrated that mechanical milling can promote the defibrillation of biomass.[104] When combined with DES pretreatment in a biorefinery, mechanical treatment effectively disrupts the recalcitrant biomass structure and increases the contact area between the substrate and solvents, which significantly enhances the efficiency of DES in extracting lignocellulosic components. The resulting milder processing conditions (*e.g.*, lower temperature and shorter duration) also help preserve the integrity of dissociated component structures.[105] For example, Xiong *et al.* sequentially subjected cassava residues to coarse crushing followed by fine ball milling prior to treatment with a ternary DES (Fig. 6a).[106] Owing to the efficient removal of other components, the cellulose-enrichment capability of the DES was markedly enhanced, resulting in a cellulose content as high as 82.52%. This enhancement is attributed to the fact that ball milling effectively strips starch particles and reduces lignocellulose particle size, which facilitates the dissociation of non-cellulosic constituents by the acidic DES through hydrogen bonding interactions. Considering that mechanochemical effects can enhance the solvent performance, Jiang *et al.* developed a one-pot refining method for treating straw based on ball milling-assisted alkaline DES (Fig. 6b).[107] This approach successfully produced a high-value amphiphilic LCC with high β-O-4 bond content (48.8/100 Ar) and structurally intact xylan with high activity. Concurrently, it achieved nearly 100% cellulose recovery coupled with a high saccharification efficiency (74.2–96.4%).

Besides, extrusion has emerged as a cost-effective biomass pretreatment method, leveraging its efficient mixing, rapid heat transfer, and high shear capabilities.[108] A key advantage of this technology is its unique ability to handle high solid loadings, which significantly enhances process productivity and economic feasibility. The integration of extrusion with DES thus represents a promising strategy for intensified biomass pretreatment (Fig. 6c). For example, Ai *et al.* developed a process combining twin-screw extrusion with neutral DES pretreatment for sugarcane bagasse, which increases the solid loading from 10% to 50% and reduces the treatment time to tens of minutes while still sufficiently disrupting the rigid biomass structure.[109] Under these conditions, the glucose and xylan yields after enzymatic saccharification both exceeded 85%.

Therefore, the mechanical-assisted DES pretreatment process is simple and effective, with the extrusion process in particular demonstrating potential for large-scale continuous production. It also alleviates the harshness of processing conditions and promotes the saccharification yield of cellulose. The improvement in treatment efficiency brought by the optimization of processing conditions, together with the valorization of dissociated products, will enhance the overall benefits of this process. However, it should be noted that mechanical activation usually consumes a large amount of energy and may damage the cellulose structure during high-speed rotation, which could pose a challenge for large-scale applications. Thus, a balanced consideration of pretreatment efficiency, subsequent component utilization, and energy consumption will guide the sustainable application of this technology.

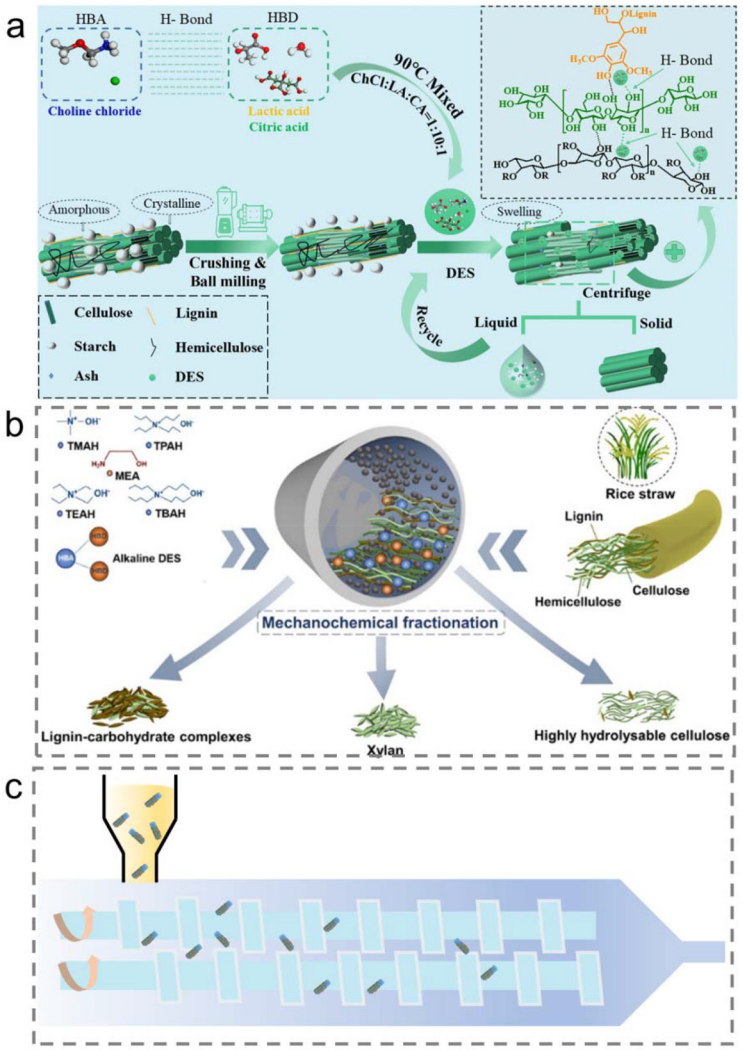

Fig. 6 (a) Mechanistic diagram of treating biomass by sequential mechanical activation-assisted DES.[106] Adapted from ref. 106. Copyright 2024, Elsevier. (b) Schematic diagram of ball milling combined with alkaline DES for synchronous fragmentation of straw biomass.[107] Adapted from ref. 107. Copyright 2024, American Chemical Society. (c) Schematic diagram of twin-screw extrusion-assisted DES pretreatment of biomass.

3.2. Chemically intensified DES pretreatment processes

Efficient deconstruction and component separation of biomass are the keys to achieving high-value utilization of biomass. DES pretreatment alone is difficult to effectively separate and recover higher purity components. Different pretreatment technologies often exhibit selectivity for specific components. Coupling chemical effect-based intensification strategies with DES can promote the separation and recovery of biomass components and reduce the equipment investment involved in the physically intensified process. Depending on the characteristics of different technologies, they can improve processing efficiency through simultaneous enhancement or stepwise coupling processes.

3.2.1 Hydrothermal pretreatment-assisted DES pretreatment. It is well known that hydrothermal (HT) pretreatment is widely used in biomass biorefineries, owing to its eco-friendliness, low cost, and operational simplicity.[110] The HT process is usually carried out at 160–200 °C under appropriate pressure (*i.e.*, a subcritical state). Under these conditions, enhanced autohydrolysis generates abundant hydronium ions that catalyze the hydrolysis of hemicellulosic acetyl groups into acetic acid, which in turn significantly accelerates the cleavage of hemicellulose into oligosaccharides, especially at higher temperatures.[111] In addition to efficient hemicellulose removal, the acidic medium produced in the hydrothermal reaction also partially promotes the dissociation of lignin. Moreover, the removal of hemicellulose also creates space for the subsequent separation of lignin and cellulose.[112] Therefore, after HT pretreatment preferentially removes hemicellulose, the implementation of a DES pretreatment process with efficient delignification will enable efficient fragmentation and recovery of biomass components. For example, Basak *et al.* applied this combined strategy to treat rice straw, achieving nearly 96%

hemicellulose dissolution with negligible formation of inhibitory by-products, and removing 81.3% of the lignin in the subsequent DES treatment (Fig. 7a).[113] Similarly, the research group led by Yuan demonstrated that integrating HT with alkaline DES efficiently fractionated bamboo for valorization (Fig. 7b). This combined approach not only selectively converted hemicellulose into xylooligosaccharides (XOS), accounting for 65.9% of the hydrolyzed xylan, but also enhanced the efficiency of subsequent delignification (93.1%) by the DES.[114] Compared with single DES pretreatment, this combined approach also increased the glucose yield from 67.9% to 90.2%. Chang *et al.* also demonstrated that sequential HT and DES pretreatment effectively fractionated bamboo, achieving high removal rates of hemicellulose (88.6%) and lignin (79.1%).[115] The synergistic pretreatment also enhanced the saccharification yield to nearly twice that of HT alone, highlighting its great potential for biomass component separation. The combination of HT and DES pretreatment forms an environmentally friendly strategy. By leveraging their respective advantages in dissociating hemicellulose and lignin, this approach synergistically enhances biomass fractionation efficiency and reduces overall costs. HT requires only low-cost water, showing the potential for large-scale application. When applied sequentially with DES pretreatment, it can reduce separation costs and obtain relatively high-purity components, thereby increasing the conversion benefits. Moreover, the costs of DES can be partially offset by selecting efficient systems and recycling the solvent.[116] It should be noted, however, that the substantial time consumption associated with HT pretreatment, together with the inherent complexity of the two-step procedure, presents challenges to the deployment of this strategy in industrial applications. Therefore, further optimization of process parameters is necessary to enhance fractionation efficiency and product conversion benefits.

Recently, Bu *et al.* developed a one-pot pretreatment strategy by directly introducing water into the DES system (Fig. 7c).[117] Water incorporation reduced solvent viscosity and cost while enhancing biomass component solubility to a certain extent. When further assisted by microwave irradiation, rapid fractionation was achieved with a delignification of 88.9% and hemicellulose removal rate of 90.2%. Nevertheless, the simultaneous dissolution of multiple components in this process still requires additional complex separation operations, which significantly increases the cost in industrial applications.

3.2.2 Steam explosion-assisted DES. Steam explosion pretreatment, characterized by high efficiency, relatively low energy consumption, and minimal environmental impact, has been extensively studied at pilot and industrial scales for various types of lignocellulosic biomass.[118] Steam explosion pretreatment is typically conducted at 160–260 °C and 0.69–4.83 MPa, with steam as the primary reaction medium.[119] This process involves steam penetration into biomass followed by the abrupt release of pressure, generating intense shear forces that disrupt hydrogen bonds and glycosidic linkages (Fig. 8a).[118] This mechanism breaks down the recalcitrant structure, depolymerizing the soluble hemicellulose while largely retaining cellulose and lignin in the solid residues. To enhance the selective extraction of lignin in DES, the prior removal of hemicellulose is an effective strategy. Compared with HT pretreatment and mechanical milling, steam explosion is more efficient and energy-saving. For instance, Tian *et al.* developed an effective two-step pretreatment method, where biomass undergoes steam explosion pretreatment to extract labile hemicellulose components prior to DES

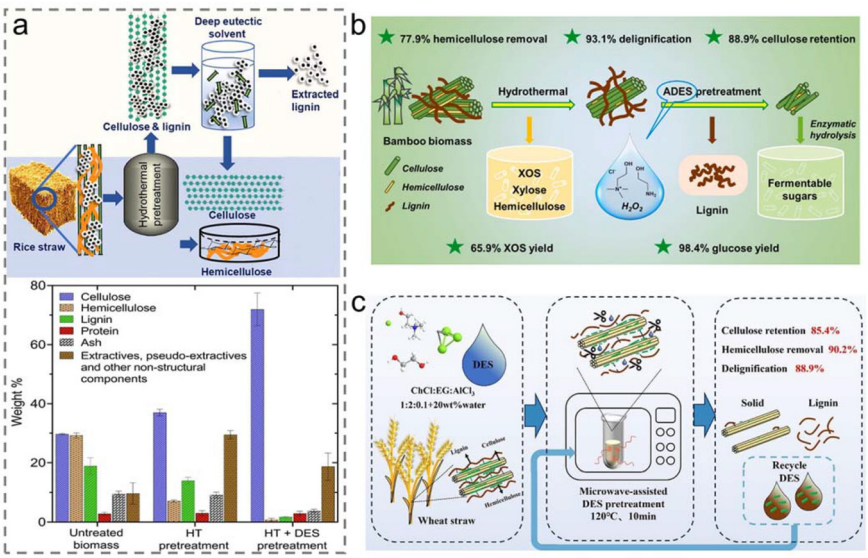

Fig. 7 (a) Process flow diagram for coupling HT with DES pretreatment of rice straw and comparison of different biocomponents in the solid fractions.[113] Adapted from ref. 113. Copyright 2022, Elsevier. (b) Fractionation of bamboo *via* synergistic HT–alkaline DES pretreatment.[114] Adapted from ref. 114. Copyright 2023, Elsevier. (c) Schematic diagram of microwave-assisted hydration DES pretreatment of wheat straw.[117] Adapted from ref. 117. Copyright 2025, Elsevier.

pretreatment (Fig. 8b).[120] This approach not only preserves the structural integrity of the polysaccharide components but also enhances lignin extraction efficiency. Such a combined strategy expands the comprehensive utilization of biomass components.

In this sequential approach, steam explosion rapidly destroys the biomass structure, and the resulting residue can be efficiently permeated by DES for further lignin dissociation. This enhances the performance of DES pretreatment and reduces process costs. In large-scale applications, however, the investment cost of the steam explosion equipment needs to be seriously considered and optimized. Furthermore, the strict conditions of steam explosion facilely induce lignin condensation, while the high temperatures also lead to increased energy consumption.[121] These factors present hurdles for industrial implementation. Therefore, future efforts should focus on regulating steam treatment parameters to disrupt biomass structure while minimizing lignin condensation, followed by the timely dissociation and recovery of lignin through DES pretreatment. A comprehensive consideration of the trade-off between processing costs and product returns throughout the entire process is required to guide the practical application of this approach.

3.2.3 Catalyst-assisted DES pretreatment. Polyol-based DES is a class of environmentally benign solvents frequently used for biomass pretreatment. However, it shows relatively low efficiency in breaking the chemical bonds of biomass and dissociating its components due to insufficient hydrogen-bonding capability to effectively compete with lignin–carbohydrate interactions.[122] The incorporation of catalysts into DES systems has been demonstrated to markedly enhance pretreatment efficiency. Table 2 briefly summarizes the commonly used catalysts and corresponding treatment results reported for DES pretreatment in recent years. For instance, Zhang *et al.* systematically evaluated the pretreatment performance of EG-based DES incorporating various Brønsted acids, such as HCl, H_2SO_4, H_3PO_4, and *p*-toluenesulfonic acid (*p*-TsOH).[123] The acid-catalyzed process achieved a lignin removal rate as high as 90.08% and near complete hemicellulose removal, while maintaining over 70% of the cellulose. However, the utilization of strong acids easily leads to excessive carbohydrate degradation and causes additional challenges in waste liquid disposal and solvent recycling.

In comparison, the Lewis acid catalytic process is gentler and more environmentally friendly, and the resulting dissociation products have higher activity. Yuan's team applied multiple Lewis acids (*e.g.*, $AlCl_3$, $FeCl_3$, and $CuCl_2$) to catalyze glycerol-based DES pretreatment, resulting in a marked increase in delignification efficiency to 85% (Fig. 9a).[124] In particular, the $FeCl_3$-catalyzed DES achieved a high delignification rate (91%) and high lignin purity (only 3.15 wt% polysaccharides in lignin). This is attributed to the enhancement of solvent system acidity and hydrogen bonding interactions by Lewis acid catalysts, which leads to increased cleavage of β-O-4 linkages within the lignin structure, thereby promoting lignin fragmentation (Fig. 9c).[125] Subsequently, the benzyl carbocations generated under acidic conditions facilitate lignin condensation to form new C–C bonds. Additionally, acid-sensitive benzyl ether bonds and phenyl glycosidic bonds readily undergo hydrolysis and cleavage, contributing to hemicellulose dissociation. Bai *et al.* further developed a bifunctional DES system by combining a Brønsted acid and a Lewis acid for the extraction of lignin from poplar, achieving a lignin recovery of 95.2% and a purity of 92.1%.[126] Compared with the homogeneous catalytic process above, solid acid catalysts are

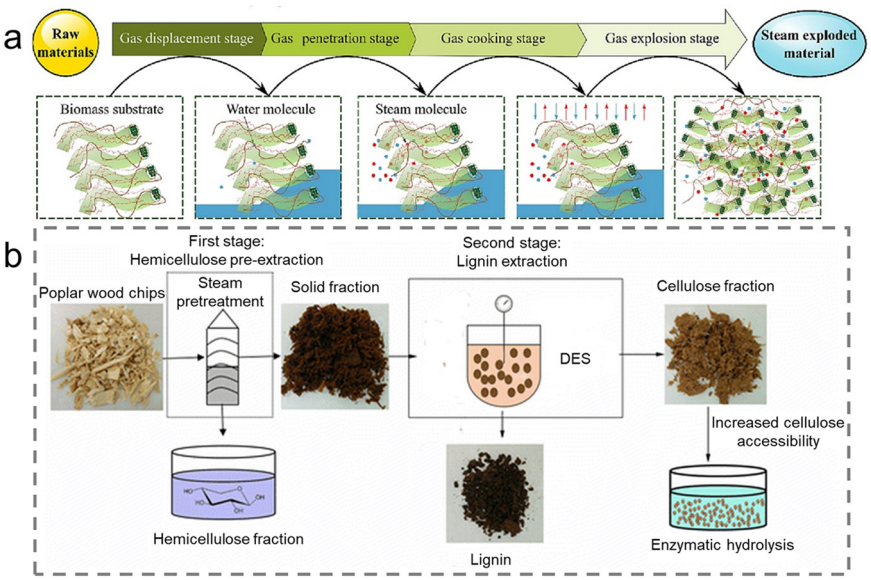

Fig. 8 (a) Illustration of the steam explosion process for biomass pretreatment.[118] Adapted from ref. 118. Copyright 2023, Elsevier. (b) Schematic diagram of steam explosion-coupled DES pretreatment to enhance cellulose enzymatic hydrolysis of poplar wood.[120] Adapted from ref. 120. Copyright 2017, Springer.

Table 2 Summary of various DES catalyst-intensified DES pretreatments

Catalyst type	Catalyst	Compositions and conditions	Lignin removal	Hemicellulose removal	Cellulose retention	Ref.
Brønsted acid	H_2SO_4	ChCl–Gly, 100 °C, 40 min	52.6%	80.5%	65.0%	130
	HCl	ChCl–Gly, 120 °C, 2 h	90.08%	90.13%	76.84%	123
	H_3PO_4	ChCl–Gly, 120 °C, 2 h	65.18%	69.77%	73.86%	123
	OA	ChCl–EG, 110 °C, 2 h	73.5%	80.4%	91.7%	131
	p-TsOH	TEBAC–Gly, 90 °C, 160 min	92.0%	88.2%	96.8%	132
	TBAC	TBAC–LA, 140 °C, 3 h	86.4%	76.72%	87.15%	133
	OA	ChCl–BDO, 110 °C, 4 h	76.25%	79.72%	93.25%	134
Lewis acid	$FeCl_3$	ChCl–Gly, 120 °C, 6 h	91.0%	—	—	124
	$CuCl_2$	ChCl–Gly, 120 °C, 6 h	88.4%	—	—	124
	$AlCl_3$	ChCl–BDO, 110 °C, 1 h	59.5%	88.8%	91.9%	135
	$ZnCl_2$	$ZnCl_2$–LA, 120 °C, 3 h	96.3%	92.0%	93.8%	126
	$FeCl_3$	ChCl–LA, 130 °C, 3 h	56.2%	99.6%	77.2%	122
Solid acid	AT-Sn-MMT catalyst	ChCl–OA, 160 °C, 20 min	59.5%	~100%	55.7%	127
	Magnetic carbon-based solid acid	Gly–DES–GVL, 181.2 °C, 20 min	57.69%	81.25%	62.20%	136
Brønsted base	NaOH	ChCl–EG, 150 °C, 2 h	56.78%	63.20%	89.26%	137
Lewis base	Na_2S	ChCl–EG, 150 °C, 2 h	74.67%	54.3%	93.83%	137
	Na_2CO_3	ChCl–EG, 120 °C, 2 h	88.1%	80.4%	91.8%	128
	CH_3COONa	ChCl–EG, 120 °C, 2 h	69.9%	59.7%	96.6%	128

TEBAC – benzyltriethylammonium chloride; TBAC – tetrabutylammonium chloride; GVL – γ-valerolactone.

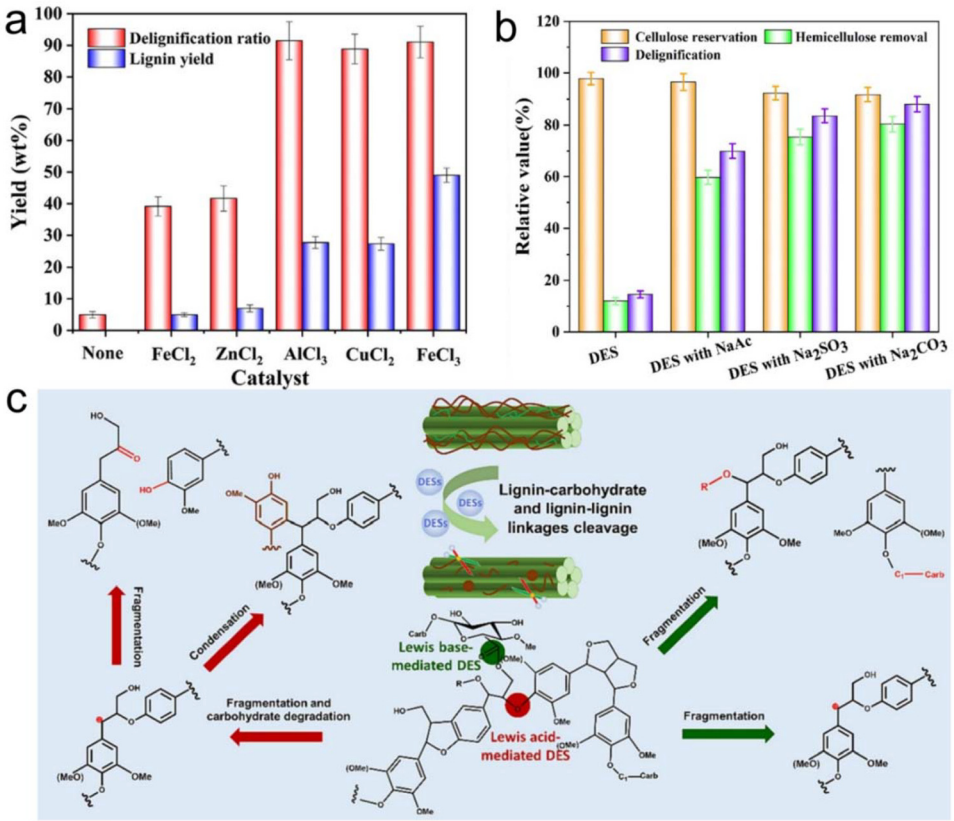

Fig. 9 (a) Comparison of lignin removal rate and yield in biomass after different Lewis acid-catalyzed DES treatments.[124] Adapted from ref. 124. Copyright 2020, American Chemical Society. (b) Comparison of the dissociation results of various components in corn straw after different Lewis base-catalyzed DES pretreatment.[128] Adapted from ref. 128. Copyright 2022, Elsevier. (c) Mechanism of lignin extraction by Lewis acid/base-mediated DES.[125] Adapted from ref. 125. Copyright 2024, Elsevier.

gradually being used in DES pretreatment due to their good separability and reusability. Yang *et al.* combined a Sn-loaded sulfonated montmorillonite solid acid catalyst (AT-Sn-MMT) with a DES/GVL system, which effectively promoted the conversion of xylo-oligosaccharides.[127] Notably, the catalyst retained over 70% of its catalytic activity after five cycles.

In addition, to mitigate the excessive degradation of carbohydrates under acidic conditions, Lewis base catalysts were also applied in DES systems.[68] They not only promote fiber swelling but also release hydroxide ions that facilitate the cleavage of intermolecular ether bonds, thereby leading to effective delignification and hemicellulose degradation. Xie *et al.* conducted EG-based DES pretreatment catalyzed by Lewis bases (*e.g.*, CH_3COONa, Na_2SO_3, and Na_2CO_3) at 120 °C for 3 h, demonstrating that all three catalysts effectively removed the majority of the hemicellulose and lignin from corn straw (Fig. 9b).[128] In particular, Na_2CO_3 achieved the highest lignin removal and glucose yield of 94.5%. Under alkaline conditions, β-O-4 linkages are relatively resistant to cleavage. Lignin is mainly extracted *via* alkali-catalyzed cleavage of lignin–carbohydrate complex linkages, particularly the γ-ester bonds (Fig. 9c). However, because phenyl glycosidic bonds are relatively stable in this environment, the extracted lignin often contains carbohydrate residues, which reduces lignin purity to some extent.[125] Although catalysts significantly improve the efficiency of DES pretreatment, several challenges may arise during its large-scale application. Currently, these catalyst-assisted DES pretreatment systems depend strongly on metal salts, some of which may precipitate during the reaction and compromise the reaction efficiency.[54] Therefore, selecting suitable metal salts and controlling metal ion concentrations are crucial for achieving efficient lignin extraction and catalytic depolymerization. Moreover, the introduction of catalysts increases costs (particularly for expensive metal salts) and causes difficulties in subsequent separation. To address these issues, the development of magnetically separable catalysts in recent years has offered a new approach for their recovery and reuse.[129] Furthermore, some acidic or alkaline catalysts may corrode the reaction vessels. Consequently, the development of suitable catalytic systems represents a future research direction to promote the widespread application of this technology.

In short, in order to improve the applicability of DES in biomass pretreatment, various strategies have been developed by integrating intensification technologies with DES pretreatment systems, as summarized briefly in Table 3. They are coupled with DES processing through either simultaneous synergistic intensification or stepwise sequential intensification processes, facilitating biomass deconstruction *via* physical, chemical, or combined physicochemical effects. These strategies exhibit different characteristics in terms of dissociation efficiency, selectivity, component recovery, and process cost.

4. Recovery of DESs

Because the DES dissolves impurities originating from cellulose and lignin during biomass pretreatment, its effectiveness gradually declines. Therefore, recovery and purification are essential for the recycling of DESs. Moreover, the recovery of DESs is of great significance for reducing overall production costs. Currently, the market prices of biomass-derived com-

Table 3 Summary of different intensifying technologies in DES systems

Intensifying technologies	Mechanism	Advantage	Disadvantage	General direction of application
Microwave-DES	Physics, synchronous process	Short time, rapid heating, low energy costs	High equipment costs, limited heating depth, difficulties in large-scale application	Laboratory or medium-scale applications, efficient delignification, particularly suitable for assisting acidic DES
Ultrasound-DES	Physics, synchronous process	Improve mass transfer, mild reaction conditions	Limited ability to break chemical bonds, reduced treatment efficiency in large-scale application	High-viscosity DES, protection of component structure, integration with microwave technology
Pulsed electric field-DES	Physics, synchronous process	High extraction efficiency, low energy costs, environmental friendliness, protection of carbohydrate structure	Limited ability to break chemical bonds, technology requires further development	Technology requires further development, focus on downstream applications of sugar platform products, reduce lignin condensation
Mechanical activation-DES	Physics, synchronous or sequential process	Simple operation, enhance mass transfer, environmental friendliness, increase solid loading	High energy costs, structural damage to components affecting downstream utilization	Recalcitrant biomass, typically used as a pretreatment step in combination with other approaches
Hydrothermal pretreatment-DES	Chemistry, sequential/ synchronous process	Environmental friendliness, high efficiency, sufficient collection of components, large-scale application	Excessive water consumption, formation of complex by-products (*e.g.*, pseudo-lignin)	Preferential hemicellulose removal, high-moisture biomass, industrial application
Steam explosion-DES	Chemistry, sequential process	Environmental friendliness, short time, low energy costs, improve accessibility of components	High equipment costs, limited removal of hemicellulose, condensation of lignin	Industrial application, relatively low process costs
Catalyst-DES	Chemistry, sequential process	High treatment efficiency, reduced temperature and time, easy integration with other approaches	High costs, potential contamination and corrosiveness, separation issues of catalysts	High demand for lignin removal, high-value utilization of biomass components

ponents such as cellulose and hemicellulose are still relatively low, and research on their high-value conversion is still insufficient, resulting in very limited profit margins for entire biorefinery processes. The synthesis and processing costs of DES remain major bottlenecks hindering their large-scale application.[138] In addition, regarding environmental impacts, Wang *et al.* conducted a prospective life cycle assessment (pLCA) of the DES pretreatment system and identified solvent recovery as a key factor in mitigating environmental impacts on a large scale.[139] Their results indicate that increasing the DES recovery rate from 50% to 90% can reduce the overall environmental impact by approximately 70%. Consequently, the development of effective recovery technologies is a critical prerequisite for the large-scale commercialization of DES pretreatment.

Anti-solvent addition is a simple and rapid approach for DES recovery, which is frequently used in laboratory-scale studies. It typically involves adding large amounts of low-cost anti-solvents (*e.g.*, water, ethanol, and acetone) to the treated solvent, causing the disruption of hydrogen bonds and changes in solvent polarity within the DES.[140] This leads to the precipitation of soluble solids from the mixture. As shown in Fig. 10, the remaining mixed solvent is then subjected to rotary evaporation to remove the anti-solvent, thereby recovering the DES for recycling. Among these anti-solvents, water is the most commonly used; its addition can precipitate lignin. In contrast, ethanol and acetone usually need to be combined with water, and their joint use enables the sequential separation of dissolved hemicellulose and lignin.[8] For example, Cheng *et al.* employed an acetone/water mixture as an anti-solvent to recover the DES, demonstrating a DES recovery rate exceeding 90% for each cycle.[61] Furthermore, although the lignin removal rate gradually decreased, it remained at approximately 70% over 2–4 cycles.

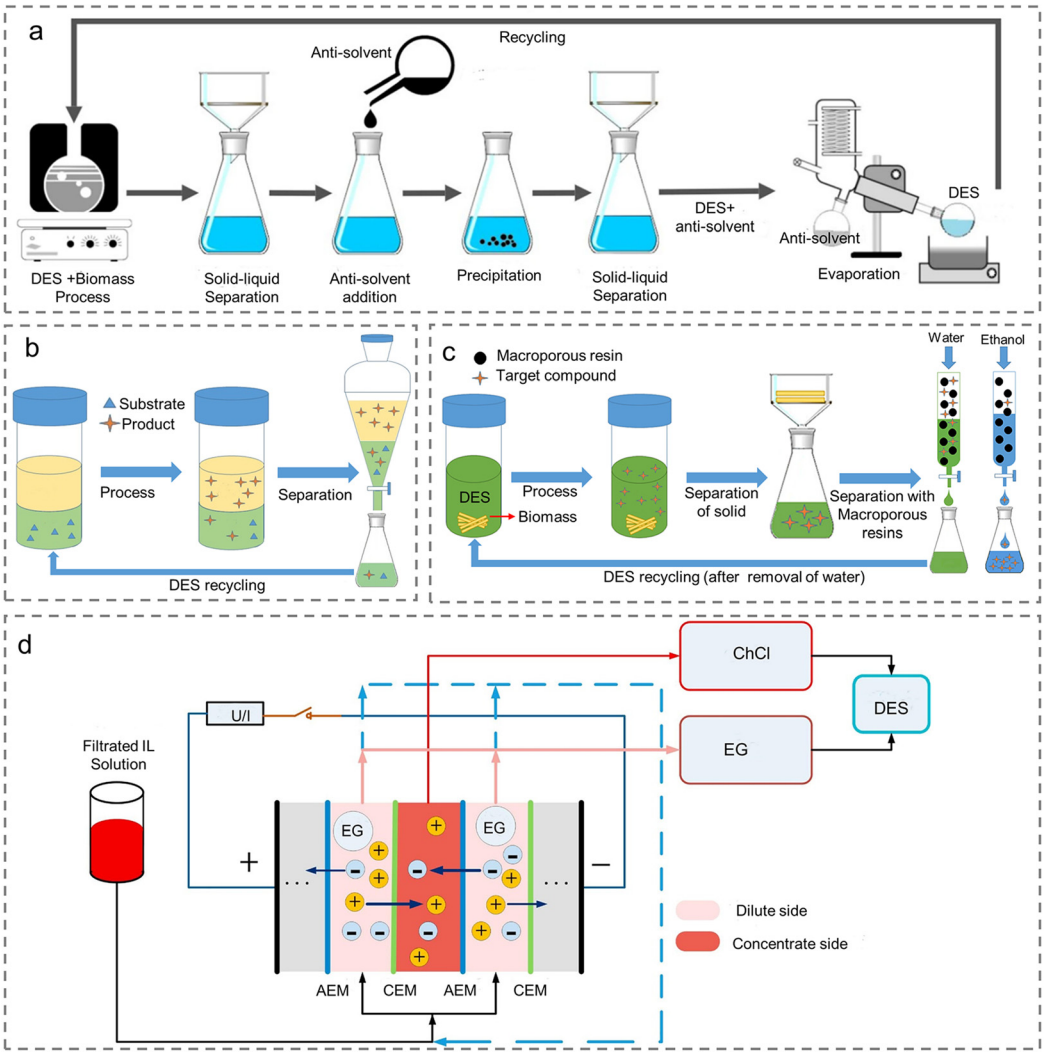

Fig. 10 Separation and recycling of DES using different technologies:[140,143] (a) anti-solvent addition, (b) *in situ* liquid–liquid extraction, (c) solid–liquid macroporous resin extraction, and (d) electrodialysis treatment. Adapted from ref. 140 and 143. Copyright 2022, Springer and Copyright 2019, Elsevier.

Liquid–liquid extraction is an energy-efficient separation technique that relies on the principle of distribution differences between two immiscible solvents to separate the target solutes. In biomass pretreatment, this technology separates dissociated products (*e.g.*, lignin) from the DES phase by adding an extractant immiscible with DES, followed by phase separation and recovery of the denser DES phase. For instance, Smink *et al.* identified a biphasic system formed by 2-methyltetrahydrofuran with choline chloride/lactic acid DES, enabling efficient recovery of dissociated lignin and subsequent DES purification.[141] Although this separation approach is environmentally friendly and efficient, its application remains limited to specific scenarios, particularly when the extractant is immiscible with DES and the target product exhibits different partition coefficients between the two phases. In miscible systems, the emulsions formed easily lead to solvent entrainment and loss. Moreover, this technique shows better potential in low-viscosity systems, as high-viscosity solvents hinder mass transfer across the phase interface and prolong the separation process. Finally, the high capital investment in equipment should also be considered for large-scale industrial application.

Solid–liquid extraction using macroporous resins is a widely adopted eco-friendly separation method in the food industry and the extraction of plant bioactive compounds. It offers advantages such as simple operation, high stability, and excellent selectivity. This process relies on the macroporous structure of solid resins to selectively adsorb target compounds from liquid mixtures *via* van der Waals forces or hydrogen bonding. In recent years, this technology has also been applied to the separation and purification of products derived from DES-based biomass pretreatment. As illustrated in Fig. 10, the DES filtrate obtained after filtering the DES-pretreated product is eluted through a column packed with macroporous resin.[140] During this process, the target compounds adsorb onto the solid structure. Subsequently, water washes away the DES, while low-cost ethanol is used as the desorption solvent to capture the eluted products. After evaporation of water from the DES phase, the DES can be recycled within the system. For instance, after producing anthocyanins from grapes treated with DES, Panić *et al.* used a macroporous resin (Sepabeads 825L) as the stationary phase, achieving recoveries of 96.8% for the DES and 99.5% for anthocyanins, respectively.[142] However, it should be noted that this process requires a large amount of solvent to elute the adsorbed compounds from the resins, and additional purification of the eluent further increases the overall cost.

Electrodialysis is employed in industrial applications for the directed transfer and concentration of electrolyte chemicals. Its operating principle involves the selective migration of anions and cations through periodically arranged ion-exchange membranes upon the application of an electric potential.[143] Given the unique characteristics of ChCl-based DES, researchers have begun employing electrodialysis to recover DES solvents following biomass pretreatment. In this process, the electrolyte components within the DES (such as ChCl) migrate through the ion-exchange membranes, whilst other constituents (such as polyols) remain *in situ* due to their non-electrolyte nature. For example, an electrodialysis approach was employed by Liang *et al.* to recover DES solvents after biomass fractionation, achieving recovery rates of 92% for ChCl and 96% for EG with corresponding purities ranging from 98–99%.[143] However, this approach necessitates ultrafiltration purification of the treated mixture followed by high-volume dilution of the desalted solution in water, adding complexity to large-scale application.

5. Challenges and future perspectives

As a promising green solvent for biomass pretreatment, DESs have demonstrated markedly enhanced treatment efficiency, particularly when integrated with intensified processing strategies. Ultrasound-assisted DES pretreatment offers broad applicability and is particularly suitable for high-viscosity DES systems with poor mass transfer, as well as for processes involving high solid loadings. It has a significant effect on straw-based lignocellulosic feedstocks. Microwave-assisted DESs enable rapid heating and achieve pretreatment objectives within a relatively short time and at lower temperatures. Mechanical activation effectively reduces biomass particle size and is particularly suitable for high-hardness feedstocks. It is often used as a preliminary pretreatment step. When combined with a DES, it substantially enhances processing efficiency through mechanochemical effects. PEF-assisted DES pretreatment is well suited for the low-temperature treatment of thermosensitive materials. This process consumes less energy but has higher equipment costs. Hydrothermal-assisted DES pretreatment is particularly effective for feedstocks rich in hemicellulose. This process not only recovers high-purity hemicellulose and lignin separately, but also is environmentally friendly and low cost. Steam explosion-assisted DES pretreatment consumes less water and is suitable for dense biomass. This process fully leverages the synergistic effects between physical tearing and the chemical decomposition of DES. Catalyst-assisted DES pretreatment achieves high lignin removal rates and improves the treatability of recalcitrant biomass. However, the presence of catalysts may interfere with the separation and recovery of DES, and may also cause corrosion issues. These intensification techniques are not only applicable to DES pretreatment, but their integration with conventional pretreatment methods also significantly enhances the overall treatment performance. Nevertheless, several challenges remain in the practical application of these technology-intensified DES pretreatments, which will constitute the future development directions of DES-based pretreatment technologies (Fig. 11).

(1) The high viscosity and inadequate selectivity of DES systems often reduce the dissociation efficiency and separation of extracted components. Future research should therefore focus on developing DES formulations to overcome these limit-

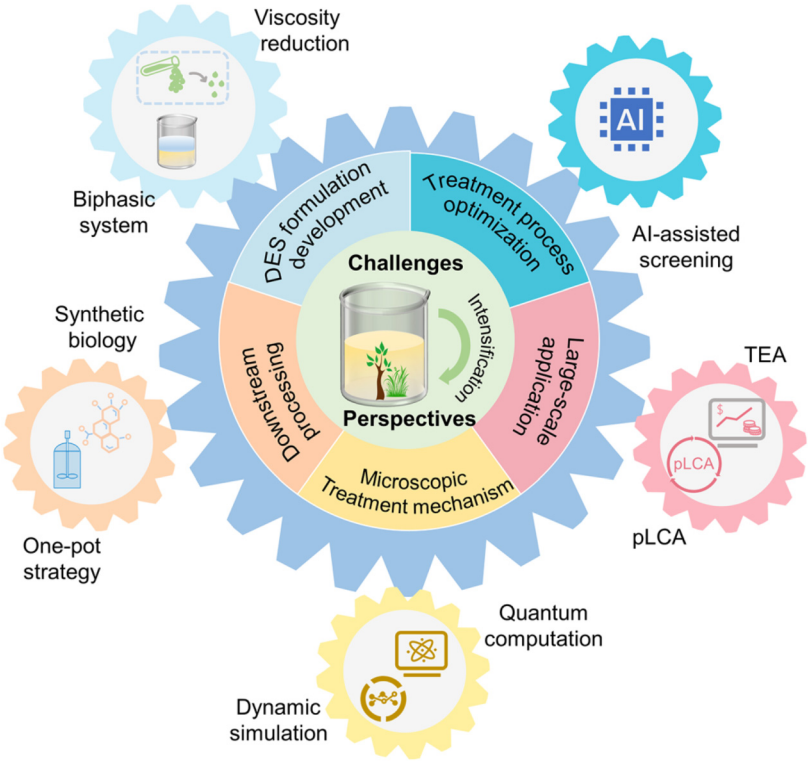

Fig. 11 Challenges and corresponding development perspectives in the process of intensified technology-assisted DES pretreatment of lignocellulosic biomass.

ations. High viscosity hinders mass transfer during pretreatment and complicates solvent recovery. Whilst elevated temperatures can reduce DES viscosity to some extent, they promote side reactions and increase energy consumption. Recent studies indicate that introducing a small amount of water into a DES not only significantly lowers its viscosity and enhances the solubility of components, but also reduces overall processing costs.[144] However, given that excessive water can disrupt the hydrogen-bonding network of DES, strict control of the water content (generally below 30%) becomes a prerequisite for achieving optimal DES pretreatment performance.[22,138] In addition, regarding selectivity, a DES often extracts hemicellulose and lignin simultaneously, which is detrimental to their subsequent respective conversions. Although coupled treatment processes can facilitate the separation of these components, they inevitably increase process complexity. The development of biphasic DES systems with enhanced selectivity is considered a promising strategy for the efficient processing and separation of biomass components.

(2) The DES pretreatment process involves complex multifactorial influences, such as time, temperature, solid–liquid proportion, and the degree of intensification. The optimization of process parameters is crucial for achieving low-cost, high-performance DES treatment, yet its reliance on extensive experimentation constitutes a major bottleneck. The introduction of artificial intelligence (AI), particularly machine learning technologies, can assist in parameter screening, thereby accelerating process optimization and providing a new paradigm for regulating system functionality. For instance, Xu *et al.* employed machine learning algorithms, such as artificial neural networks and random forests, to investigate the effect of DES characteristics and treatment process parameters on pretreatment outcomes.[145] This demonstrated the significant value of AI assistance in optimizing DES pretreatment processes, while reducing experimental time and resource consumption.

(3) Although the intensification technologies enhance DES pretreatment efficiency, the industrial-scale application of DES pretreatment still faces issues related to mixing uniformity, cost-effectiveness and environmental friendliness. For instance, there are issues related to equipment costs involved in ultrasound and PEF intensifications, as well as the non-uniformity of microwave emission. The design of rational and efficient reactors is crucial to improving heat and mass transfer efficiency. Furthermore, a comprehensive techno-economic analysis (TEA) is essential to evaluate the economic viability of different DES systems within the biomass conversion chain. For example , process simulation and TEA for converting lignocellulose into products like bioethanol and lignin *via* DES pretreatment would facilitate solvent system screening and process optimization from a cost perspective.[146]

Besides, it is notable that although DESs are generally greener than traditional solvents, the potential biotoxicity, biocompatibility, and long-term environmental impact of some

DESs remain significant safety concerns, particularly in large-scale industrial applications. For instance, certain alkaline DESs exhibit greater toxicity compared to natural DESs. Therefore, the pLCA approach is vital to establish a reliable scale-up model, systematically evaluating the industrial feasibility and holistic environmental impact of DES pretreatment across different systems. Such integrated assessments will guide the rational design of environmentally friendly DESs and promote their sustainable application in biorefinery processes. Simultaneously, in-depth investigation of these DES properties is crucial for ensuring their safety in biomedical applications.

(4) At present, studies on intensification technology-assisted DES pretreatment mainly focus on component removal rates and product yields, while lacking in-depth investigation into the treatment mechanisms of different strategies. Elucidation of microscopic treatment mechanisms can efficiently guide the optimization of pretreatment processes. Various intensification technologies are coupled with DES through either synchronous or asynchronous approaches, accompanied by diverse effects such as physical and/or chemical interactions. This complexity poses challenges to clarifying the mechanisms of the pretreatment processes. In the future, integrating molecular dynamic simulation and quantum chemical calculations with advanced molecular-level characterization of products is expected to become an important strategy for revealing the mechanisms of different treatment processes.

(5) Following DES pretreatment, the resulting substrates can be further converted into downstream products through enzymatic hydrolysis. Nevertheless, residual DES may remain in the solid fractions after solvent separation, which can impair enzymatic activity and hinder the conversion of biomass components.[147] Advances in synthetic biology offer opportunities to enhance the tolerance and activity of enzymes and microorganisms in DES-containing environments, enabling continuous bioconversion processes with minimized inhibition and improved productivity. In addition, the extensive washing required to remove DES inevitably generates large volumes of waste liquid and increases energy costs. To address these challenges, several studies have explored one-pot strategies that integrate biomass pretreatment and saccharification into a continuous process, thereby avoiding intermediate separation steps. By optimizing the DES system, researchers have achieved a total sugar yield of 75.7%, with a high recovery of xylose, significantly reducing overall processing costs.[148] Finally, dissociated biomass components may remain in the recovered DES, which can impair solvent recyclability and reduce reuse efficiency. Therefore, improving the recovery performance and recyclability of DES is also a critical future direction for expanding its application in biomass pretreatment.

6. Conclusions

As a novel class of environmentally benign solvents, DESs demonstrate great potential in biorefinery and biomass fractionation. However, biomass pretreatment using DESs alone often delivers an unsatisfactory performance, which has stimulated the development of various intensified DES-based pretreatment strategies. This review systematically analyzes recently reported intensification technologies for DES pretreatment from the perspectives of physical and chemical effects. Physical intensification of DES pretreatment involves microwaves, ultrasound, mechanical activation, and pulsed electric fields. By improving mass transfer, enhancing energy input, and shortening reaction times, these technologies effectively intensify DES pretreatment processes in a green way and generate synchronous enhancement effects. Chemical intensification of DES pretreatment primarily involves the coupling of hydrothermal or steam explosion processes with DES treatment, as well as catalyst-assisted strategies. The former typically enables a stepwise dissociation of biomass components, thereby enhancing the ability of DES to disrupt the biomass structure and improving component separation. The latter, in contrast, enhances the efficiency and selectivity of DES-mediated biomass deconstruction by regulating the acidity or alkalinity of the reaction system. This work focuses on detailing the pretreatment processes, underlying mechanisms, and challenges associated with each technology, while also analyzing the recovery process and future development prospects of DES. In short, these intensification strategies improve DES pretreatment and promote the fractionation of lignocellulosic components, laying a solid foundation for expanding the application of DES pretreated biomass.

Author contributions

Qianli Wang: investigation, writing original draft, writing – review & editing, methodology. Jiaqi Chen: investigation, visualization, writing – review & editing. Xiaoyan Jiang: investigation, writing – review & editing. Chen Huang: investigation, conceptualization, writing – review & editing. Jun-ichiro Hayashi: writing – review & editing. Xianzhi Meng: conceptualization, supervision, writing – review & editing. Yefeng Zhou: funding acquisition, project administration, conceptualization, writing – review & editing.

Conflicts of interest

All authors are aware of the submission and agree to its publication. There are no conflicts of interest to declare.

Abbreviations

DES	Deep eutectic solvent
ILs	Ionic liquids
HBA	Hydrogen bond acceptor
HBD	Hydrogen bond donor
EG	Ethylene glycol
LCC	Lignin–carbohydrate complex

LA	Lactic acid
OA	Oxalic acid
CA	Citric acid
FA	Formic acid
AA	Acetic acid
MA	Malic acid
Gly	Glycerol
BDO	1,4-Butanediol
MEA	Monoethanolamine
PEF	Pulsed electric field
HT	Hydrothermal
XOS	Xylooligosaccharides
p-TsOH	*p*-Toluenesulfonic acid
AT-Sn-MMT	Montmorillonite-supported Sn-based catalyst
GVL	γ-Valerolactone
TEBAC	Benzyltriethylammonium chloride
TBAC	Tetrabutylammonium chloride
pLCA	Prospective life cycle assessment
TEA	Techno-economic analysis

Data availability

No primary research results, software or code have been included and no new data were generated or analyzed as part of this review.

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References

1 X. Wu, N. Luo, S. Xie, H. Zhang, Q. Zhang, F. Wang and Y. Wang, Photocatalytic transformations of lignocellulosic biomass into chemicals, *Chem. Soc. Rev.*, 2020, **49**, 6198–6223.
2 M. Zhou, O. A. Fakayode, A. E. G. A. Yagoub, Q. Ji and C. Zhou, Lignin fractionation from lignocellulosic biomass using deep eutectic solvents and its valorization, *Renewable Sustainable Energy Rev.*, 2022, **156**, 111986.
3 V. Ashokkumar, R. Venkatkarthick, S. Jayashree, S. Chuetor, S. Dharmaraj, G. Kumar, W. H. Chen and C. Ngamcharussrivichai, Recent advances in lignocellulosic biomass for biofuels and value-added bioproducts - A critical review, *Bioresour. Technol.*, 2022, **344**, 126195.
4 S. Zafar, A. Cherakkara, I. I. Misnon, C. C. Yang and R. Jose, Graphene-like materials from biomass using deep eutectic solvents: a review, *ACS Sustainable Resour. Manage.*, 2024, **1**, 2047–2073.
5 T. Xiao, M. Hou, X. Guo, X. Cao, C. Li, Q. Zhang, W. Jia, Y. Sun, Y. Guo and H. Shi, Recent progress in deep eutectic solvent (DES) fractionation of lignocellulosic components: A review, *Renewable Sustainable Energy Rev.*, 2024, **192**, 114243.
6 Z. Li, E. Sutandar, T. Goihl, X. Zhang and X. Pan, Cleavage of ethers and demethylation of lignin in acidic concentrated lithium bromide (ACLB) solution, *Green Chem.*, 2020, **22**, 7989–8001.
7 M. Wang, X. Fu, Y. Chang, J. Wei and H. Cui, Recent advancements in deep eutectic solvent (DES) pretreatment: applications, mechanisms, and integration with emerging technologies for biorefinery, *Ind. Crops Prod.*, 2025, **229**, 121028.
8 F. Baraka, M. M. Langari, I. Beitia, I. Dávila, J. Labidi, A. Morales and L. Sillero, Enhancing lignocellulosic biomass pretreatment with choline chloride-based deep eutectic solvents, *J. Environ. Chem. Eng.*, 2025, **13**, 117087.
9 Z. H. Chen, L. Chen, K. S. Khoo, V. K. Gupta, M. Sharma, P. L. Show and P. S. Yap, Exploitation of lignocellulosic-based biomass biorefinery: A critical review of renewable bioresource, sustainability and economic views, *Biotechnol. Adv.*, 2023, **69**, 108265.
10 E. Amini, C. Valls and M. B. Roncero, Ionic liquid-assisted bioconversion of lignocellulosic biomass for the development of value-added products, *J. Cleaner Prod.*, 2021, **326**, 129275.
11 S. F. Ahmed, M. Mofijur, S. N. Chowdhury, M. Nahrin, N. Rafa, A. T. Chowdhury, S. Nuzhat and H. C. Ong, Pathways of lignocellulosic biomass deconstruction for biofuel and value-added products production, *Fuel*, 2022, **318**, 123618.
12 S. B. Jamaldheen, M. B. Kurade, B. Basak, C. G. Yoo, K. K. Oh, B. H. Jeon and T. H. Kim, A review on physicochemical delignification as a pretreatment of lignocellulosic biomass for enhanced bioconversion, *Bioresour. Technol.*, 2022, **346**, 126591.
13 W. Wang and D. J. Lee, Lignocellulosic biomass pretreatment by deep eutectic solvents on lignin extraction and saccharification enhancement: A review, *Bioresour. Technol.*, 2021, **339**, 125587.
14 J. B. Ocreto, W. H. Chen, A. P. Rollon, H. C. Ong, A. Pétrissans, M. Pétrissans and M. D. G. De Luna, Ionic liquid dissolution utilized for biomass conversion into biofuels, value-added chemicals and advanced materials: a comprehensive review, *Chem. Eng. J.*, 2022, **445**, 136733.
15 Z. Y. Zhang, M. D. Harrison, D. W. Rackemann, W. O. S. Doherty and I. M. O'Hara, Organosolv pretreatment of plant biomass for enhanced enzymatic saccharification, *Green Chem.*, 2016, **18**, 360–381.
16 S. Rahmati, W. Doherty, D. Dubal, L. Atanda, L. Moghaddam, P. Sonar, V. Hessel and K. Ostrikov,

Pretreatment and fermentation of lignocellulosic biomass: reaction mechanisms and process engineering, *React. Chem. Eng.*, 2020, **5**, 2017–2047.

17 M. Mohan, K. Huang, V. R. Pidatala, B. A. Simmons, S. Singh, K. L. Sale and J. M. Gladden, Prediction of solubility parameters of lignin and ionic liquids using multi-resolution simulation approaches, *Green Chem.*, 2022, **24**, 1165–1176.

18 L. Szabó, R. Milotskyi, G. Sharma and K. Takahashi, Cellulose processing in ionic liquids from a materials science perspective: turning a versatile biopolymer into the cornerstone of our sustainable future, *Green Chem.*, 2023, **25**, 5338–5389.

19 S. Li, Y. Wang, Q. Dong, Z. Yuan, T. Mu, Z. Xue and L. Cao, Polyol-assisted ternary deep eutectic solvent protective lignocellulose pretreatment for high-efficiency xylan utilization and ethanol production, *Carbohydr. Polym.*, 2024, **346**, 122628.

20 B. B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell and J. R. Sangoro, Deep eutectic solvents: a review of fundamentals and applications, *Chem. Rev.*, 2021, **121**, 1232–1285.

21 M. A. Alam, G. Muhammad, M. N. Khan, M. Mofijur, Y. Lv, W. Xiong and J. Xu, Choline chloride-based deep eutectic solvents as green extractants for the isolation of phenolic compounds from biomass, *J. Cleaner Prod.*, 2021, **309**, 127445.

22 J. Cheng, C. Huang, Y. Zhan, X. Liu, J. Wang, X. Meng, C. G. Yoo, G. Fang and A. J. Ragauskas, A high-solid DES pretreatment using never-dried biomass as the starting material: towards high-quality lignin fractionation, *Green Chem.*, 2023, **25**, 1571–1581.

23 A. A. N. Gunny, D. Arbain, E. M. Nashef and P. Jamal, Applicability evaluation of deep eutectic solvents–cellulase system for lignocellulose hydrolysis, *Bioresour. Technol.*, 2015, **181**, 297–302.

24 P. Li, C. Yang, Z. Jiang, Y. Jin and W. Wu, Lignocellulose pretreatment by deep eutectic solvents and related technologies: a review, *J. Bioresour. Bioprod.*, 2023, **8**, 33–44.

25 A. Procentese, F. Raganati, G. Olivieri, M. E. Russo, L. Rehmann and A. Marzocchella, Low-energy biomass pretreatment with deep eutectic solvents for bio-butanol production, *Bioresour. Technol.*, 2017, **243**, 464–473.

26 M. Rojas, R. Manrique, U. Hornung, A. Funke, C. A. Mullen, F. Chejne and J. C. Maya, Advances and challenges on hydrothermal processes for biomass conversion: Feedstock flexibility, products, and modeling approaches, *Biomass Bioenergy*, 2025, **194**, 107621.

27 H. Xu, J. Peng, Y. Kong, Y. Liu, Z. Su, B. Li, X. Song, S. Liu and W. Tian, Key process parameters for deep eutectic solvents pretreatment of lignocellulosic biomass materials: a review, *Bioresour. Technol.*, 2020, **310**, 123416.

28 Y. Shen, H. Zhou, X. He, F. Shen, Z. Xu, B. Yang, L. Kong and L. Dai, Emerging applications of deep eutectic solvents in the preparation and functionalization of biomass-derived carbonaceous materials: challenges and prospects, *Green Chem.*, 2024, **26**, 8123–8144.

29 Y. T. Tan, A. S. M. Chua and G. C. Ngoh, Deep eutectic solvent for lignocellulosic biomass fractionation and the subsequent conversion to bio-based products - a review, *Bioresour. Technol.*, 2020, **297**, 122522.

30 C. Dong, X. Meng, S.-Y. Leu, L. Xu, Z. Wu, G. Cravotto and Z. Fang, Enhancing α-etherification of lignin in Eucalyptus diol pretreatment to improve lignin monomer production, *Ind. Crops Prod.*, 2022, **185**, 115130.

31 Q. Xia, L. Zhang, P. Zhan, Z. Tong, Y. Qing, J. He, Z. Wu, H. Wang, L. Shao and N. Liu, Combination of microwave with acid deep eutectic solvent pretreatment for reed (Phragmites australis) fractionation, *Renewable Energy*, 2024, **225**, 120286.

32 V. Sharma, P. Nargotra, S. Sharma and B. K. Bajaj, Efficacy and functional mechanisms of a novel combinatorial pretreatment approach based on deep eutectic solvent and ultrasonic waves for bioconversion of sugarcane bagasse, *Renewable Energy*, 2021, **163**, 1910–1922.

33 C. E. Okonkwo, S. Z. Hussain, S. Manzoor, B. Naseer, A. E. Taiwo, M. Ayyash, A. H. Al-Marzouqi and A. Kamal-Eldin, A comprehensive review on the use of deep eutectic solvents for biomass processing, and the synergistic coupling with physical technology and biological method, *Bioresour. Technol. Rep.*, 2023, **23**, 101577.

34 R. Zou, X. Zhou, M. Qian, C. Wang, D. Boldor, H. Lei and X. Zhang, Advancements and applications of microwave-assisted deep eutectic solvent (MW-DES) lignin extraction: a comprehensive review, *Green Chem.*, 2024, **26**, 1153–1169.

35 C. Álvarez, A. Duque, A. Sánchez-Monedero, E. J. González, M. González-Miquel and R. Cañadas, Exploring recent advances in lignocellulosic biomass waste delignification through the combined use of eutectic solvents and intensification techniques, *Processes*, 2024, **12**, 2514.

36 A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed and V. Tambyrajah, Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains, *Chem. Commun.*, 2001, **19**, 2010–2011.

37 Y. Gao, M. Fan, X. Cheng, X. Liu, H. Yang, W. Ma, M. Guo and L. Li, Deep eutectic solvent: synthesis, classification, properties and application in macromolecular substances, *Int. J. Biol. Macromol.*, 2024, **278**, 134593.

38 H. Wang, X. Kang and B. Han, Electrocatalysis in deep eutectic solvents: from fundamental properties to applications, *Chem. Sci.*, 2024, **15**, 9949–9976.

39 A. Kovács, E. C. Neyts, I. Cornet, M. Wijnants and P. Billen, Modeling the physicochemical properties of natural deep eutectic solvents, *ChemSusChem*, 2020, **13**, 3789–3804.

40 W. Wang, Y. Xu, B. Zhu, H. Ge, S. Wang, B. Li and H. Xu, Exploration of the interaction mechanism of lignocellulosic hybrid systems based on deep eutectic solvents, *Bioresour. Technol.*, 2023, **385**, 129401.
41 N. Mqoni, I. Bahadur, S. Singh, X. Meng and A. Ragauskas, Deep eutectic solvents for pretreatment of lignocellulose biomass: physical properties, solubility mechanisms, and their interactions, *Chem. Rev.*, 2026, **126**, 1206–1257.
42 L. He, L. Chen, B. Zheng, H. Zhou, H. Wang, H. Li, H. Zhang, C. C. Xu and S. Yang, Deep eutectic solvents for catalytic biodiesel production from liquid biomass and upgrading of solid biomass into 5-hydroxymethylfurfural, *Green Chem.*, 2023, **25**, 7410–7440.
43 M. Marchel, H. Cieśliński and G. Boczkaj, Thermal instability of choline chloride-based deep eutectic solvents and its influence on their toxicity–important limitations of dess as sustainable materials, *Ind. Eng. Chem. Res.*, 2022, **61**, 11288–11300.
44 Z. Chen, A. Ragauskas and C. Wan, Lignin extraction and upgrading using deep eutectic solvents, *Ind. Crops Prod.*, 2020, **147**, 112241.
45 Z. Guo, D. Li, T. You, X. Zhang, F. Xu, X. Zhang and Y. Yang, New lignin streams derived from heteropoly acids enhanced neutral deep eutectic solvent fractionation: toward structural elucidation and antioxidant performance, *ACS Sustainable Chem. Eng.*, 2020, **8**, 12110–12119.
46 Z. Chen, X. Bai, A. Lusi, H. Zhang and C. Wan, Insights into structural changes of lignin toward tailored properties during deep eutectic solvent pretreatment, *ACS Sustainable Chem. Eng.*, 2020, **8**, 9783–9793.
47 M. Francisco, A. van den Bruinhorst and M. C. Kroon, New natural and renewable low transition temperature mixtures (LTTMs): screening as solvents for lignocellulosic biomass processing, *Green Chem.*, 2012, **14**, 2153–2157.
48 X. Zhang, A. Liu, X. Li, W. Xu, X. Duan, J. Shi and X. Li, Research progress of deep eutectic solvents in lignocellulosic biomass pretreatment, *Cellulose*, 2025, **32**, 4637–4650.
49 Y. Liu, W. Chen, Q. Xia, B. Guo, Q. Wang, S. Liu, Y. Liu, J. Li and H. Yu, Efficient cleavage of lignin–carbohydrate complexes and ultrafast extraction of lignin oligomers from wood biomass by microwave-assisted treatment with deep eutectic solvent, *ChemSusChem*, 2017, **10**, 1692–1700.
50 A. Ullah, Y. Zhang, C. Liu, Q. Qiao, Q. Shao and J. Shi, Process intensification strategies for green solvent mediated biomass pretreatment, *Bioresour. Technol.*, 2023, **369**, 128394.
51 R. Lou and X. Zhang, Evaluation of pretreatment effect on lignin extraction from wheat straw by deep eutectic solvent, *Bioresour. Technol.*, 2022, **344**, 126174.
52 Y. Su, C. Huang, C. Lai and Q. Yong, Green solvent pretreatment for enhanced production of sugars and antioxidative lignin from poplar, *Bioresour. Technol.*, 2021, **321**, 124471.
53 X. J. Shen, J. L. Wen, Q. Q. Mei, X. Chen, D. Sun, T. Q. Yuan and R. C. Sun, Facile fractionation of lignocelluloses by biomass-derived deep eutectic solvent (DES) pretreatment for cellulose enzymatic hydrolysis and lignin valorization, *Green Chem.*, 2019, **21**, 275–283.
54 P. Li, W. Qian, S. Wu and Y. Liu, Acidic Deep Eutectic solvents for lignocellulose pretreatment: insights into lignin extraction efficiency and structural transformation, *ACS Sustainable Chem. Eng.*, 2025, **13**, 9987–10018.
55 M. Lu, S. Sun, X. Li, Q. Liu, W. Zhang and X. Qiu, Fractionation of lignin from corncob with high–yield p–-coumaric acid production in deep eutectic solvents followed by pyrolysis to produce monophenols, *Int. J. Biol. Macromol.*, 2025, **285**, 138331.
56 G. Wan, Q. Zhang, M. Li, Z. Jia, C. Guo, B. Luo, S. Wang and D. Min, How pseudo-lignin is generated during dilute sulfuric acid pretreatment, *J. Agric. Food Chem.*, 2019, **67**, 10116–10125.
57 A. Satlewal, R. Agrawal, S. Bhagia, J. Sangoro and A. J. Ragauskas, Natural deep eutectic solvents for lignocellulosic biomass pretreatment: recent developments, challenges and novel opportunities, *Biotechnol. Adv.*, 2018, **36**, 2032–2050.
58 A. T. Hoang, S. Nizetic, H. C. Ong, C. T. Chong, A. E. Atabani and V. V. Pham, Acid-based lignocellulosic biomass biorefinery for bioenergy production: advantages, application constraints, and perspectives, *J. Environ. Manage.*, 2021, **296**, 113194.
59 M. A. Hossain, M. S. Rahaman, D. Yelle, H. Shang, Z. Sun, S. Renneckar, J. Dong, S. Tulaphol and N. Sathitsuksanoh, Effects of polyol-based deep eutectic solvents on the efficiency of rice straw enzymatic hydrolysis, *Ind. Crops Prod.*, 2021, **167**, 113480.
60 L. Sun, J. Han, C. Tang, J. Wu, S. Fang, Y. Li, Y. Mao, L. Wang and Y. Wang, Choline chloride-based deep eutectic solvent system as a pretreatment for microcrystalline cellulose, *Cellulose*, 2022, **29**, 8133–8150.
61 J. Cheng, C. Huang, Y. Zhan, S. Han, J. Wang, X. Meng, C. G. Yoo, G. Fang and A. J. Ragauskas, Effective biomass fractionation and lignin stabilization using a diol DES system, *Chem. Eng. J.*, 2022, **443**, 136395.
62 S. Phromphithak, N. Tippayawong, T. Onsree and J. Lauterbach, Pretreatment of corncob with green deep eutectic solvent to enhance cellulose accessibility for energy and fuel applications, *Energy Rep.*, 2022, **8**, 579–585.
63 Y. Zhu, T.-X. Yang, B.-K. Qi, H. Li, Q.-S. Zhao and B. Zhao, Acidic and alkaline deep eutectic solvents (DESs) pretreatment of grapevine: component analysis, characterization, lignin structural analysis, and antioxidant properties, *Int. J. Biol. Macromol.*, 2023, **236**, 123977.
64 J. L. K. Mamilla, U. Novak, M. Grilc and B. Likozar, Natural deep eutectic solvents (DES) for fractionation of waste lignocellulosic biomass and its cascade conversion to value-added bio-based chemicals, *Biomass Bioenergy*, 2019, **120**, 417–425.

65 K. A. Mani, L. Kumar, N. Barrios, S. Agate, A. Mittal, J. Yarbrough, H. Jameel, L. Lucia and L. Pal, Emergence of deep eutectic solvents (DES): chemistry, preparation, properties, and applications in biorefineries and critical materials, *Prog. Mater. Sci.*, 2026, **157**, 101586.
66 Z. Zhao, X. Chen, M. F. Ali, A. A. Abdeltawab, S. M. Yakout and G. Yu, Pretreatment of wheat straw using basic ethanolamine-based deep eutectic solvents for improving enzymatic hydrolysis, *Bioresour. Technol.*, 2018, **263**, 325–333.
67 S. Hong, X. J. Shen, Z. Xue, Z. Sun and T. Q. Yuan, Structure-function relationships of deep eutectic solvents for lignin extraction and chemical transformation, *Green Chem.*, 2020, **22**, 7219–7232.
68 H. Zhang, Q. Sun, Y. B. Liu, C. Y. Ma, J. L. Wen, Z. Li and T. Q. Yuan, Green and efficient alkaline DES pretreatment for full-component fractionation of reed biomass: hemicelluloses, uncondensed lignin and easily digestible cellulose, *Chem. Eng. J.*, 2026, **527**, 171659.
69 T. Chen, H. Wang, G. Guo, H. Wang, M. Li and Y. Tang, Acidic deep eutectic solvent pretreatment for enhancing enzymatic hydrolysis of moso bamboo (Phyllostachys pubescens), *Biomass Convers. Biorefin.*, 2024, **14**, 22717–22727.
70 X. Li, W. Tang and Y. C. He, Integrated understanding of acidic deep eutectic solvent choline chloride: Oxalic acid pretreatment to enhance the enzymatic hydrolysis of rape straw, *Ind. Crops Prod.*, 2023, **206**, 117691.
71 W. Li, S. Ma, L. Luo, Z. Li, A. He, C. Wang, L. Lin and X. Zeng, Pretreatment of biomass with ethanol/deep eutectic solvent towards higher component recovery and obtaining lignin with high β-O-4 content, *Int. J. Biol. Macromol.*, 2024, **276**, 133751.
72 P. D. Maibam and A. Goyal, Approach to an efficient pretreatment method for rice straw by deep eutectic solvent for high saccharification efficiency, *Bioresour. Technol.*, 2022, **351**, 127057.
73 Z. Chen, X. Bai, A. Lusi and C. Wan, High-solid lignocellulose processing enabled by natural deep eutectic solvent for lignin extraction and industrially relevant production of renewable chemicals, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12205–12216.
74 H. Li, X. Li, T. You, D. Li, H. Nawaz, X. Zhang and F. Xu, Insights into alkaline choline chloride-based deep eutectic solvents pretreatment for populus deltoides: lignin structural features and modification mechanism, *Int. J. Biol. Macromol.*, 2021, **193**, 319–327.
75 X.-D. Hou, A. L. Li, K.-P. Lin, Y. Y. Wang, Z. Y. Kuang and S. L. Cao, Insight into the structure-function relationships of deep eutectic solvents during rice straw pretreatment, *Bioresour. Technol.*, 2018, **249**, 261–267.
76 Y. T. Tan, G. C. Ngoh and A. S. M. Chua, Evaluation of fractionation and delignification efficiencies of deep eutectic solvents on oil palm empty fruit bunch, *Ind. Crops Prod.*, 2018, **123**, 271–277.
77 Y. Liu, N. Deak, Z. Wang, H. Yu, L. Hameleers, E. Jurak, P. J. Deuss and K. Barta, Tunable and functional deep eutectic solvents for lignocellulose valorization, *Nat. Commun.*, 2021, **12**, 5424.
78 Z. Zhao, H. Li and X. Gao, Microwave encounters ionic liquid: synergistic mechanism, synthesis and emerging applications, *Chem. Rev.*, 2024, **124**, 2651–2698.
79 D. Schieppati, N. A. Patience, F. Galli, P. Dal, I. Seck, G. S. Patience, D. Fuoco, X. Banquy and D. C. Boffito, Chemical and biological delignification of biomass: a review, *Ind. Eng. Chem. Res.*, 2023, **62**, 12757–12794.
80 Z. Chen and C. Wan, Ultrafast fractionation of lignocellulosic biomass by microwave-assisted deep eutectic solvent pretreatment, *Bioresour. Technol.*, 2018, **250**, 532–537.
81 N. Wang, K. Liu, Z. Hou, Z. Zhao, H. Li and X. Gao, Microwave-assisted deep eutectic solvents pretreatment for lignocellulose: Kinetics, intensified mechanism and process optimization, *Chem. Eng. Sci.*, 2025, **302**, 120881.
82 J. Gabhane, S. P. M. P. William, A. N. Vaidya, K. Mahapatra and T. Chakrabarti, Influence of heating source on the efficacy of lignocellulosic pretreatment – a cellulosic ethanol perspective, *Biomass Bioenergy*, 2011, **35**, 96–102.
83 N. Kumar, P. D. Muley, D. Boldor, G. G. Coty and J. G. Lynam, Pretreatment of waste biomass in deep eutectic solvents: conductive heating versus microwave heating, *Ind. Crops Prod.*, 2019, **142**, 111865.
84 N. Wang, K. Liu, Z. Hou, Z. Zhao, H. Li and X. Gao, The comparative techno-economic and life cycle assessment for multi-product biorefinery based on microwave and conventional hydrothermal biomass pretreatment, *J. Cleaner Prod.*, 2024, **474**, 143562.
85 J. Zhou, B. Chen, L. Tong, G. Chong, L. C. Abdullah and H. Guo, Recent advances of microwave-assisted deep eutectic solvent for lignocellulosic biorefining, *Cellulose*, 2025, **32**, 8669–8702.
86 V. Z. Ong and T. Y. Wu, An application of ultrasonication in lignocellulosic biomass valorisation into bio-energy and bio-based products, *Renewable Sustainable Energy Rev.*, 2020, **132**, 109924.
87 C. Devos, A. Bampouli, E. Brozzi, G. D. Stefanidis, M. Dusselier, T. Van Gerven and S. Kuhn, Ultrasound mechanisms and their effect on solid synthesis and processing: a review, *Chem. Soc. Rev.*, 2025, **54**, 85–115.
88 L. Men, S. Feng, J. Zhang, X. Luo and Y. Zhou, A systematic review of efficient recycling for the cathode materials of spent lithium-ion batteries: process intensification technologies beyond traditional methods, *Green Chem.*, 2024, **26**, 1170–1193.
89 V. Sharma, M. L. Tsai, C. W. Chen, P. P. Sun, A. K. Patel, R. R. Singhania, P. Nargotra and C. D. Dong, Deep eutectic solvents as promising pretreatment agents for sustainable lignocellulosic biorefineries: a review, *Bioresour. Technol.*, 2022, **360**, 127631.
90 V. Z. Ong, T. Y. Wu, K. K. L. Chu, W. Y. Sun and K. P. Y. Shak, A combined pretreatment with ultrasound-assisted alkaline solution and aqueous deep eutectic

solvent for enhancing delignification and enzymatic hydrolysis from oil palm fronds, *Ind. Crops Prod.*, 2021, **160**, 112974.

91 K. M. Lee, J. D. Quek, W. Y. Tey, S. Lim, H.-S. Kang, L. K. Quen, W. A. W. Mahmood, S. I. S. Jamaludin, K. H. Teng and K. S. Khoo, Biomass valorization by integrating ultrasonication and deep eutectic solvents: delignification, cellulose digestibility and solvent reuse, *Biochem. Eng. J.*, 2022, **187**, 108587.

92 D. Yan, Q. Ji, X. Yu, M. Li, O. A. Fakayode, A. E. G. A. Yagoub, L. Chen and C. Zhou, Multimode-ultrasound and microwave assisted natural ternary deep eutectic solvent sequential pretreatments for corn straw biomass deconstruction under mild conditions, *Ultrason. Sonochem.*, 2021, **72**, 105414.

93 Q. Zhang, Z. He, C. Ding, Q. Lu and Z. Zhang, Green and efficient extraction of Artemisia integrifolia leaves essential oil via ultrasound coupled with microwave-assisted deep eutectic solvent, *Sustainable Chem. Pharm.*, 2026, **49**, 102272.

94 N. Wang, A. Xu, K. Liu, Z. Zhao, H. Li and X. Gao, Performance of green solvents in microwave-assisted pretreatment of lignocellulose, *Chem. Eng. J.*, 2024, **482**, 148786.

95 N. Wang, Y. Tian, X. Wu, H. Liu, H. Lu and Y. Zhu, Natural hydrophobic deep eutectic solvent for highly efficient extraction of curcuminoids assisted by pulsed ultrasound: experimental and mechanistic insights, *ACS Sustainable Chem. Eng.*, 2025, **13**, 9087–9097.

96 V. Z. Ong, T. Y. Wu, C. B. T. L. Lee, N. W. R. Cheong and K. P. Y. Shak, Sequential ultrasonication and deep eutectic solvent pretreatment to remove lignin and recover xylose from oil palm fronds, *Ultrason. Sonochem.*, 2019, **58**, 104598.

97 V. Sharma, J. X. Wang, M. L. Tsai, A. Yadav, C. D. Dong, P. Nargotra and P. P. Sun, Bioprocessing of pineapple leaf waste biomass using an integrated ultrasound-deep eutectic solvent pretreatment approach for improved bioethanol production, *J. Biotechnol.*, 2025, **404**, 83–93.

98 A. W. Putranto, S. Dutta, C. W. Priananda, H. A. Illias, Q. Syafiqoh, N. Masruchin, Y. Wibisono, S. Suhartini, A. S. M. Chua and G. C. Ngoh, Enhancement of cellulose nanocrystal yield from oil palm empty fruit bunches: a comparative study of binary and ternary deep eutectic solvents with pulsed electric field pretreatment, *Biomass Bioenergy*, 2025, **196**, 107672.

99 Đ. Kovačić, S. Rupčić, D. Kralik, D. Jovičić, R. Spajić and M. Tišma, Pulsed electric field: An emerging pretreatment technology in a biogas production, *Waste Manage.*, 2021, **120**, 467–483.

100 A. Sidana and S. K. Yadav, Recent developments in lignocellulosic biomass pretreatment with a focus on eco-friendly, non-conventional methods, *J. Cleaner Prod.*, 2022, **335**, 130286.

101 A. W. Putranto, A. S. M. Chua, S. Suhartini and G. C. Ngoh, Augmentation of cellulose extraction from oil palm empty fruit bunch via rapid and energy-saving deep eutectic solvent-pulsed electric field pretreatment, *Biomass Convers. Biorefin.*, 2025, **15**, 15867–15883.

102 M. Velusamy, A. Rajan and M. Radhakrishnan, Valorisation of food processing wastes using PEF and its economic advances – recent update, *Int. J. Food Sci. Technol.*, 2023, **58**, 2021–2041.

103 Y. Zhang, Q. Li, J. Su, Y. Lin, Z. Huang, Y. Lu, G. Sun, M. Yang, A. Huang, H. Hu and Y. Zhu, A green and efficient technology for the degradation of cellulosic materials: Structure changes and enhanced enzymatic hydrolysis of natural cellulose pretreated by synergistic interaction of mechanical activation and metal salt, *Bioresour. Technol.*, 2015, **177**, 176–181.

104 Q. Wang, H. Komatsu, S. Kudo, S. Asano and J.-I. Hayashi, Green synthesis of binder-free plate from waste bamboo based on hydrothermal treatment, *Biomass Convers. Biorefin.*, 2025, **15**, 6365–6376.

105 F. Shen, X. Xiong, J. Fu, J. Yang, M. Qiu, X. Qi and D. C. W. Tsang, Recent advances in mechanochemical production of chemicals and carbon materials from sustainable biomass resources, *Renewable Sustainable Energy Rev.*, 2020, **130**, 109944.

106 Y. Xiong, W. Li, Z. Qin, T. Su, X. Xie and H. Ji, A green extraction technology of lignocellulose from cassava residue by mechanical activation-assisted ternary deep eutectic solvent, *Int. J. Biol. Macromol.*, 2024, **281**, 136339.

107 B. Jiang, Q. Tang, H. Yu, Q. Su, F. Shen, L. Zhao, J. Hu, D. Tian and F. Shen, Mechanochemical fractionation of straw biomass to maximize biorefinery value using alkaline deep eutectic solvents at room temperature, *ACS Sustainable Chem. Eng.*, 2024, **12**, 13960–13971.

108 K. S. Guiao, A. Gupta, C. Tzoganakis and T. H. Mekonnen, Reactive extrusion as a sustainable alternative for the processing and valorization of biomass components, *J. Cleaner Prod.*, 2022, **355**, 131840.

109 B. Ai, W. Li, J. Woomer, M. Li, Y. Pu, Z. Sheng, L. Zheng, A. Adedeji, A. J. Ragauskas and J. Shi, Natural deep eutectic solvent mediated extrusion for continuous high-solid pretreatment of lignocellulosic biomass, *Green Chem.*, 2020, **22**, 6372–6383.

110 T. Scapini, M. S. N. dos Santos, C. Bonatto, J. H. C. Wancura, J. Mulinari, A. F. Camargo, N. Klanovicz, G. L. Zabot, M. V. Tres, G. Fongaro and H. Treichel, Hydrothermal pretreatment of lignocellulosic biomass for hemicellulose recovery, *Bioresour. Technol.*, 2021, **342**, 126033.

111 Q. Wang, J. Chen, Y. Lian, Q. Xiong, J.-i. Hayashi, C. Huang, A. J. Ragauskas, X. Meng and Y. Zhou, Insights into environmentally friendly solvent pretreatment of lignocellulosic biomass: Strategies, mechanisms, and future perspectives, *Carbohydr. Polym.*, 2025, **367**, 124027.

112 S. Tian, S. Fu and C. Li, A biomass refining strategy combining liquid hot water and deep eutectic solvent (DES) treatment: acetylation fractionation of uncondensed

lignin by acetic anhydride DES, *Ind. Crops Prod.*, 2025, **234**, 121614.

113 B. Basak, S. Patil, R. Kumar, G. S. Ha, Y. K. Park, M. A. Khan, K. K. Yadav, A. M. Fallatah and B. H. Jeon, Integrated hydrothermal and deep eutectic solvent-mediated fractionation of lignocellulosic biocomponents for enhanced accessibility and efficient conversion in anaerobic digestion, *Bioresour. Technol.*, 2022, **351**, 127034.

114 S. C. Sun, Y. Xu, C. Y. Ma, C. Zhang, C. Zuo, D. Sun, J. L. Wen and T. Q. Yuan, Green and efficient fractionation of bamboo biomass via synergistic hydrothermal-alkaline deep eutectic solvents pretreatment: valorization of carbohydrates, *Renewable Energy*, 2023, **217**, 119175.

115 L. Chang, R. Ye, J. Song, Y. Xie, Q. Chen, S. Yan, K. Sun and L. Gan, Efficient fractionation of green bamboo using an integrated hydrothermal–deep eutectic solvent pretreatment for its valorization, *Appl. Sci.*, 2023, **13**, 2429.

116 H. Zhu, X. He, Z. Xu and L. Dai, Deep eutectic solvent-mediated hydrothermal treatment for biomass conversion: a review, *Green Chem.*, 2025, **27**, 1278–1299.

117 Q. Bu, Y. Yue, B. Wang, J. Bai, L. Jiao, M. Wang and J. Xu, A synergistic microwave-assisted hydrated deep eutectic solvent (DES) pretreatment for efficient fractionation of wheat straw, *Waste Manage.*, 2025, **208**, 115161.

118 A. T. Hoang, X. P. Nguyen, X. Q. Duong, Ü. Ağbulut, C. Len, P. Q. P. Nguyen, M. Kchaou and W. H. Chen, Steam explosion as sustainable biomass pretreatment technique for biofuel production: Characteristics and challenges, *Bioresour. Technol.*, 2023, **385**, 129398.

119 S. Shamsudin, E. K. Bahrin, M. A. Hassan and Y. Shirai, Chemical-free saturated steam pretreatment of oil palm empty fruit bunch for improved enzymatic saccharification, *J. Wood Chem. Technol.*, 2024, **44**, 44–63.

120 D. Tian, R. P. Chandra, J.-S. Lee, C. Lu and J. N. Saddler, A comparison of various lignin-extraction methods to enhance the accessibility and ease of enzymatic hydrolysis of the cellulosic component of steam-pretreated poplar, *Biotechnol. Biofuels*, 2017, **10**, 157.

121 E. Chevé-Kools, Y. H. Choi, C. Roullier, G. Ruprich-Robert, R. Grougnet, F. Chapeland-Leclerc and F. Hollmann, Natural deep eutectic solvents (NaDES): green solvents for pharmaceutical applications and beyond, *Green Chem.*, 2025, **27**, 8360–8385.

122 F. Shen, S. Wu, M. Huang, L. Zhao, J. He, Y. Zhang, S. Deng, J. Hu, D. Tian and F. Shen, Integration of lignin microcapsulated pesticide production into lignocellulose biorefineries through $FeCl_3$-mediated deep eutectic solvent pretreatment, *Green Chem.*, 2022, **24**, 5242–5254.

123 Y. Zhang, W. Xie, W. Li, Y. Tang, J. Wu, L. Gan, L. P. Xiao, X. Zhang, L. Lin and X. Tang, Acid-assisted pretreatment for sweet elephant grass in choline chloride/glycerol DEs: experimental and mechanism study, *Chem. Eng. J.*, 2024, **500**, 157056.

124 Z. K. Wang, S. Hong, J. L. Wen, C. Y. Ma, L. Tang, H. Jiang, J. J. Chen, S. Li, X. J. Shen and T. Q. Yuan, Lewis acid-facilitated deep eutectic solvent (DES) pretreatment for producing high-purity and antioxidative lignin, *ACS Sustainable Chem. Eng.*, 2020, **8**, 1050–1057.

125 C. He, F. Shen, D. Tian, M. Huang, L. Zhao, Q. Yu and F. Shen, Lewis acid/base mediated deep eutectic solvents intensify lignocellulose fractionation to facilitate enzymatic hydrolysis and lignin nanosphere preparation, *Int. J. Biol. Macromol.*, 2024, **254**, 127853.

126 Y. Bai, X. F. Zhang, Z. Wang, T. Zheng and J. Yao, Deep eutectic solvent with bifunctional Brønsted-Lewis acids for highly efficient lignocellulose fractionation, *Bioresour. Technol.*, 2022, **347**, 126723.

127 Q. Yang, B. Fan and Y. C. He, Combination of solid acid and solvent pretreatment for co-production of furfural, xylooligosaccharide and reducing sugars from *Phyllostachys edulis*, *Bioresour. Technol.*, 2024, **395**, 130398.

128 J. Xie, Z. Cheng, S. Zhu and J. Xu, Lewis base enhanced neutral deep eutectic solvent pretreatment for enzymatic hydrolysis of corn straw and lignin characterization, *Renewable Energy*, 2022, **188**, 320–328.

129 X. Zhao, G. Lyu, C. G. Yoo, Z. Wang and J. Chen, Magnetically recyclable vanadium-substituted phosphotungstic acid in a deep eutectic solvent for effective wheat straw fractionation, *Green Chem.*, 2025, **27**, 10889–10903.

130 Z. Tang, D. Yang, W. Tang, C. Ma and Y. C. He, Combined sulfuric acid and choline chloride/glycerol pretreatment for efficiently enhancing enzymatic saccharification of reed stalk, *Bioresour. Technol.*, 2023, **387**, 129554.

131 C. Zhou, Y. Liu, B. Ouyang, S. Lin and Y. Wang, Systematic evaluation of polyol-assisted acidic deep eutectic solvent pretreatment for improving enzymatic hydrolysis of wheat straw, *Ind. Crops Prod.*, 2024, **212**, 118219.

132 W. Wu, P. Zhu, L. Luo, H. Lin, Y. Tao, L. Ruan, L. Wang and Q. Qing, *p*-Toluenesulfonic acid enhanced neutral deep eutectic solvent pretreatment of soybean straw for efficient lignin removal and enzymatic hydrolysis, *Bioresour. Technol.*, 2024, **395**, 130338.

133 M. Zhang, X. Wang, Z. Guo, C. Yuan, J. Li, F. Xu and F. Zhang, A Staged Biorefinery of Moso Bamboo to Produce Fermentable Sugar, Furfural, and High-Quality Lignin by Integrating a Solvent and a Catalyst Deep Eutectic Solvent, *ACS Sustainable Chem. Eng.*, 2025, **13**, 13709–13717.

134 J. Cheng, T. Chen, X. Liu, X. Zhou, Y. Zhan, C. Huang, G. Fang and C. Huang, A lignin-first biorefinery by integrated deep eutectic solvents towards formaldehyde-free plywood adhesive and monomeric sugars, *Chem. Eng. J.*, 2024, **499**, 155980.

135 T. Wang, C. Huang, X. Zhou, Y. Zhan, J. Cheng, J. Ren, S. Zhang, Y. Fei and Q. Yong, A novel type IV deep eutectic solvent for pretreating wheat straw to co-produce fermentable sugars and hydrophobic micro-nano lignin particle, *Bioresour. Technol.*, 2026, **442**, 133739.

136 X. Zhao, B. Fan and Y. C. He, Co-manufacturing reducing sugars, furfural and xylo-oligosaccharides from *Sorghum*

straw via pretreatment with biochar-based magnetic bifunctional chemocatalyst in deep eutectic solvent Benzyltrimethylammonium chloride:Glycerol/γ-valerolactone, *Fuel*, 2026, **407**, 137265.

137 X. Liu, J. Cheng, C. Huang, J. Wang, G. Fang, K. Shen, X. Meng and A. J. Ragauskas, Alkali-facilitated deep eutectic solvent for effective bamboo saccharification, *Bioresour. Technol.*, 2023, **367**, 128297.

138 C. L. Yiin, Z. Y. Lai, B. L. F. Chin, S. S. M. Lock, K. W. Cheah, M. J. Taylor, A. Al-Gailani, B. W. Kolosz and Y. H. Chan, Green pathways for biomass transformation: A holistic evaluation of deep eutectic solvents (DESs) through life cycle and techno-economic assessment, *J. Cleaner Prod.*, 2024, **470**, 143248.

139 Y. Wang, H. Gao, J. Xiao, Y. Yu, Y. Yi, J. Wu, A. Manzardo, J. Zhang, Z. Wang and Q. Luo, Sustainable valorization of lignocellulose: a prospective life cycle assessment of deep eutectic solvent-based processes and economic viability, *Environ. Sci. Technol.*, 2025, **59**, 24368–24379.

140 A. Isci and M. Kaltschmitt, Recovery and recycling of deep eutectic solvents in biomass conversions: a review, *Biomass Convers. Biorefin.*, 2022, **12**, 197–226.

141 D. Smink, S. R. A. Kersten and B. Schuur, Recovery of lignin from deep eutectic solvents by liquid-liquid extraction, *Sep. Purif. Technol.*, 2020, **235**, 116127.

142 M. Panić, V. Gunjević, G. Cravotto and I. R. Redovniković, Enabling technologies for the extraction of grape-pomace anthocyanins using natural deep eutectic solvents in up-to-half-litre batches extraction of grape-pomace anthocyanins using NADES, *Food Chem.*, 2019, **300**, 125185.

143 X. Liang, Y. Fu and J. Chang, Effective separation, recovery and recycling of deep eutectic solvent after biomass fractionation with membrane-based methodology, *Sep. Purif. Technol.*, 2019, **210**, 409–416.

144 Y. Xu, C. Y. Ma, S. C. Sun, C. Zhang, J. L. Wen and T. Q. Yuan, Fractionation and evaluation of light-colored lignin extracted from bamboo shoot shells using hydrated deep eutectic solvents, *Bioresour. Technol.*, 2023, **387**, 129679.

145 H. Xu, C. Dong, W. Wang, Y. Liu, B. Li and F. Liu, Machine learning prediction of deep eutectic solvents pretreatment of lignocellulosic biomass, *Ind. Crops Prod.*, 2023, **196**, 116431.

146 J. Peng, H. Xu, W. Wang, Y. Kong, Z. Su and B. Li, Techno-economic analysis of bioethanol preparation process via deep eutectic solvent pretreatment, *Ind. Crops Prod.*, 2021, **172**, 114036.

147 A. A. N. Gunny, D. Arbain, M. Javed, N. Baghaei-Yazdi, S. C. B. Gopinath and P. Jamal, Deep eutectic solvents-halophilic cellulase system: an efficient route for in situ saccharification of lignocellulose, *Process Biochem.*, 2019, **81**, 99–103.

148 Z. J. Huang, G. J. Feng, K. P. Lin, F. L. Pu, Y. M. Tan, W. C. Tu, Y. L. Han, X. D. Hou, H. M. Zhang and Y. Zhang, Significant boost in xylose yield and enhanced economic value with one-pot process using deep eutectic solvent for the pretreatment and saccharification of rice straw, *Ind. Crops Prod.*, 2020, **152**, 112515.