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Review

Deep Eutectic Solvent-Based Cell-Wall-Level Functionalization of Lignocellulosic Materials for Fire Safety and Smoke Suppression: Direct Evidence, Mechanistic Analogies, and Valorization

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Abstract

Lignocellulosic materials, represented by natural wood and bamboo, are widely used in construction, interior decoration, and transportation because of their specific strength, renewability, and carbon sequestration, but their organic polysaccharide–lignin skeleton is inherently flammable and releases dense smoke and toxic gases during thermal decomposition. Conventional halogen-, ammonium salt-, and borate-based flame retardants are limited by toxic decomposition products, leaching under humid conditions, acid-catalysed cellulose degradation, and mechanical deterioration. Deep eutectic solvent (DES)-based modification has been proposed as a cell-wall-level route to introduce phosphorus-, nitrogen-, or sulfur-containing functionalities while preserving the lignocellulosic skeleton. However, the evidence that flame-retardant elements are actually localized within the cell wall, rather than in lumen or surface deposits, remains system-specific and is rarely established by spatially resolved spectroscopy or bonding-specific characterization. Studies that provide paired fire–mechanical data report performance gains, but they do not simultaneously establish cell-wall anchoring chemistry, quantify long-term leaching resistance, and confirm mechanical retention under identical conditioning. This review therefore evaluates DES-based cell-wall functionalization for fire safety and smoke suppression by separating direct cell-wall evidence from cross-material analogies, and measured mechanisms from proposed mechanisms. The reviewed literature shows that DESs can swell and plasticize the cell wall and can introduce flame-retardant elements that remain detectable after short-term water exposure, but a validated general mechanism of durable cell-wall fixation with simultaneous mechanical retention has not yet been demonstrated. Remaining challenges, including viscosity, cost, and solvent recycling, can be mitigated by water dilution, component substitution, and membrane filtration, although recycling efficiency still declines. Future directions include multifunctional integration of flame retardancy, smoke suppression, superhydrophobicity, and mechanical reinforcement, as well as synergistic combination with densification and resin impregnation. Accordingly, valorization claims for DES-based flame retardancy should be framed in terms of demonstrated performance endpoints—such as limiting oxygen index, peak heat release rate reduction, and tensile or flexural strength—rather than as evidence of a generalized cell-wall fixation mechanism with established long-term durability. The literature is evaluated using a framework that separates direct cell-wall evidence from cross-

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material analogies, measured mechanisms from proposed mechanisms, and different fixation modes. Key wood- and bamboo-based studies are further evaluated in an evidence matrix that separately records the evidence available for (i) spatial localization, (ii) bonding chemistry, (iii) leaching or washing resistance, (iv) fire performance, (v) smoke response, and (vi) mechanical properties, with direct cell-wall evidence distinguished from cross-material analogies and proposed mechanisms.

Keywords: deep eutectic solvents; lignocellulosic materials; cell-wall functionalization; fire safety; smoke suppression

1. Introduction

1.1. Bottlenecks of Conventional Wood Flame Retardants in the Industry

Natural wood, as the most representative lignocellulosic material, owing to its exceptional specific strength, renewability, anisotropic natural texture, and low-carbon sequestration characteristics, has long been extensively employed in building structures, interior decoration, and rail transportation. However, lignocellulosic materials are primarily composed of organic polysaccharides and aromatic polymers, such as cellulose, hemicellulose, and lignin, and this inherent polymeric carbon skeleton endows them with high flammability. In fire scenarios, the intense combustion of wood not only leads to a rapid loss of structural load-bearing capacity but also releases substantial amounts of dense smoke and toxic gases through thermal decomposition, thereby readily inducing secondary disasters [1].

To mitigate fire risks, industrial practices commonly introduce halogen-, ammonium salt-, or borate-based flame retardants via impregnation. Nevertheless, each of these systems has its own inherent limitations. Halogen-containing flame retardants release hydrogen halides and dioxin-like toxic compounds upon high-temperature decomposition. Borates, although capable of promoting char formation and suppressing smoke, exhibit strong water solubility and lack chemical bonding with the cell wall, resulting in rapid leaching under humid and thermal conditions; moreover, boric acid has been listed as a Substance of Very High Concern by the EU REACH regulation [2,3]. Ammonium- and phosphate-based flame retardants show improved leaching resistance, but their acidic hydrolysis catalyzes cellulose degradation, leading to a pronounced decline in mechanical properties [2]. Furthermore, most of these water-soluble treatments increase the hygroscopicity of wood, exacerbating dimensional instability and long-term durability deterioration.

Many conventional waterborne flame retardants are lumen-dominant and rely largely on physical deposition or adsorption; however, some systems may partially penetrate or interact with cell-wall polymers. The key limitation is therefore not a categorical absence of cell-wall interaction, but the frequent lack of spatially resolved localization and mechanism-specific bonding evidence [4]. This scale mismatch underlies the trade-off among toxicity, leaching resistance, and mechanical retention [5,6], and prevents the simultaneous achievement of fire safety and high-value utilization of lignocellulosic materials. It is therefore evident that existing flame-retardant technologies cannot fully meet the requirements of advanced engineering applications, necessitating an urgent exploration of novel solutions.

1.2. Cell-Wall-Level Supramolecular Reconstruction by Deep Eutectic Solvents

Deep eutectic solvents (DESs) provide a route to overcome the scale mismatch of conventional flame retardants. Unlike lumen-level impregnation, DESs are designed to

act within the cell wall, where they compete with the native hydrogen bonds among cellulose, hemicellulose, and lignin. This competition disrupts the original supramolecular network, induces moderate swelling of the amorphous regions, and enables the subsequent reconstruction of a new hydrogen-bonding network that incorporates the DES components. Depending on DES composition, flame-retardant elements can be retained within the cell wall through hydrogen bonding, metal coordination, and/or in situ covalent grafting, rather than solely by lumen deposition. Not every DES system establishes covalent anchoring, and the dominant fixation mechanism should be verified by spatially resolved spectroscopy and bonding-specific characterization [7,8].

This cell-wall-level action mode effectively addresses the leaching and mechanical retention problems of conventional flame retardants, because the flame-retardant elements are fixed within the cell wall rather than adsorbed on its surface. It also allows the simultaneous introduction of phosphorus-, nitrogen-, or sulfur-containing functionalities through the compositional tunability of DESs, enabling modification and flame-retardant functionalization in a single step. Consequently, this approach offers a promising pathway for converting low-value lignocellulosic materials into high-value flame-retardant engineering materials, thereby achieving valorization in advanced engineering applications [9].

1.3. Review Objectives, Scope, and Methodology

This work is a narrative review. Literature was identified through searches of Web of Science, Scopus, and Google Scholar using combinations of the following terms: deep eutectic solvent, DES, lignocellulose, wood, cell wall, flame retardancy, smoke suppression, and leaching resistance. The search covered publications from 2003, the year in which Abbott et al. [10] first reported deep eutectic mixtures, through 2025. Studies were eligible if they addressed DES-mediated modification of lignocellulosic materials and reported outcomes relevant to cell-wall functionalization, flame retardancy, smoke suppression, or leaching resistance. Studies on non-lignocellulosic substrates were included only when they provided mechanistic insight that was not available from wood-based systems, and such studies are identified accordingly in the text. Selection was topic-driven, prioritizing studies that offered mechanistic evidence or quantitative performance data. As a narrative review, this work does not follow a systematic search protocol, and the selection of literature is therefore subject to potential selection bias. Evidence quality was considered by preferentially citing peer-reviewed studies with well-characterized materials and clearly reported test conditions, and by distinguishing direct experimental evidence from proposed mechanisms and from analogies drawn from related material systems.

Existing reviews have comprehensively addressed DES-based pretreatment, fractionation, and wood modification, but they have not critically evaluated cell-wall-level anchoring of flame-retardant elements in intact wood, nor distinguished direct cell-wall evidence from cross-material analogies or measured mechanisms from proposed mechanisms. This review therefore focuses on intact wood and lignocellulosic cell walls; studies on extracted lignin, regenerated cellulose, fabrics, foams, and composites are included only as supporting or analogous evidence and are identified as such. Accordingly, this review aims to clarify how DESs interact with intact cell walls and through which spatial and chemical modes flame-retardant elements are retained, to evaluate which flame-retardancy and smoke-suppression mechanisms are directly measured rather than proposed, and to assess whether leaching resistance and mechanical retention are supported by appropriate durability and controlled-processing data. The literature is evaluated using a framework that separates direct cell-wall evidence from cross-material analogies, measured mechanisms from proposed mechanisms, and different fixation modes. To make this framework operational and to avoid conflating different types of evidence, a

comprehensive matrix (detailed in the subsequent sections) compiles the key wood- and bamboo-based studies discussed in this review and separately records, for each study, the evidence available for (i) spatial localization within intact wood/bamboo, (ii) bonding chemistry, (iii) leaching or washing resistance, (iv) fire performance, (v) smoke response, and (vi) mechanical properties. Each entry is classified as direct evidence from intact wood/bamboo, indirect/proposed evidence, not reported, or analogous evidence from non-intact wood systems. A flame-retardant performance value is not taken as evidence for cell-wall localization or bonding. Studies on surface coatings, cellulose derivatives, nanofibre laminates, and composites are included only as mechanistic analogies and are labeled accordingly. This matrix is used throughout Sections 2 and 3; where a study does not report a given evidence category, this is stated explicitly rather than inferred from another property.

2. Classifications and Cell Wall Binding Mechanics of DESs

The cell-wall-level action of DESs described above is not a generic property of all DES systems, but depends on their chemical composition and structural characteristics. DESs are classified according to the types of hydrogen bond acceptors and hydrogen bond donors, and this classification directly determines their affinity and reactivity towards lignocellulosic components. Different DES systems exhibit markedly different penetration behaviour within the wood porous network, different degrees of cell-wall swelling, and different modes of supramolecular hydrogen-bond reconstruction and in situ chemical bonding. Understanding how DESs bind to the cell wall therefore requires a systematic consideration of their chemical classification, their penetration and swelling behaviour, and the interfacial bonding mechanisms that govern their interaction with lignocellulosic components. In this review, direct cell-wall evidence is defined as evidence obtained from intact wood or bamboo in which DES treatment is localized within the cell wall and supported by cell-wall penetration/swelling, chemical bonding, or preservation of cellulose crystalline regions; flame-retardant performance alone is not treated as direct cell-wall evidence. Studies on surface coatings, extracted lignin/cellulose, nanocellulose laminates, fabrics, polymer composites, foams, and elastomers are used only as mechanistic analogies or valorization examples and are explicitly identified as such. Accordingly, "direct cell-wall evidence" in this review requires at least one spatially resolved or cell-wall-specific measurement, and is recorded in Table 1 separately from bulk uptake, flame-retardant performance, or mechanical improvement. Bulk mass gain, dye ingress, or LOI/UL-94 data alone are not classified as direct cell-wall evidence.

Chemical Classification of Flame-Retardant DESs and Cell-Wall Swelling/ Penetration Kinetics

DESs used for wood modification can be systematically classified according to the types of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). It is important to distinguish mild cell-wall functionalization from extensive fractionation or dissolution. Mild functionalization involves moderate swelling, limited lignin removal, high absolute cellulose retention, and preservation of crystalline domains and degree of polymerization (DP). In contrast, extensive fractionation/dissolution systems can remove 86%–97% of lignin, dissociate cellulose bundles, and reduce DP; these outcomes should not be generalized as "mild" modification of intact wood. DESs are divided into four categories: Type I, consisting of quaternary ammonium salts as the HBA and metal chlorides as the HBD; Type II, consisting of quaternary ammonium salts as the HBA and metal chloride hydrates as the HBD; Type III, consisting of quaternary ammonium salts as the HBA and non-ionic HBDs such as amides, carboxylic acids, and polyols; and Type IV, consisting of metal chlorides as the HBA and non-ionic HBDs [11]. Among them, the third

category, which employs quaternary ammonium salts as HBAs and organic acids, amides, polyols, or phosphorus-containing compounds as HBDs, represents the most widely applied system in current wood flame-retardant modification research. Choline chloride is the most representative HBA in this category, and its system with urea at a molar ratio of 1:2, known as Reline, is one of the earliest classic DESs to be systematically studied. Abbott et al. [10] first reported the formation phenomenon of deep eutectic mixtures in 2003, which initiated the research boom on DESs as green solvents.

Building upon the ChCl-urea system, researchers have progressively expanded the variety of HBDs. Zhang et al. [12] systematically reviewed the research progress of DESs in lignocellulosic biomass pretreatment, pointing out that DESs have attracted extensive attention due to their low melting points, excellent solubility, environmental friendliness, and recyclability; Figure 1c illustrates the synthesis mechanism of DES formation from choline chloride and urea. Early studies mainly focused on organic acid HBDs such as lactic acid and oxalic acid, as these acidic DESs can effectively disrupt the native hydrogen-bond networks among lignocellulosic components. Zhao et al. [13] investigated the regulatory effects of DESs composed of choline chloride with different HBD combinations on the pretreatment and pyrolysis of pine wood, finding that the choice of HBD significantly influenced the delignification efficiency and cellulose retention, with the lactic acid-containing system exhibiting the highest delignification efficiency. Figures 1a and 1b present the characteristic diffraction peaks of cellulose, hemicellulose, and lignin, as well as the holocellulose model incorporating the lignin–carbohydrate complex (LCC) structure, respectively. Zhu et al. [14] pretreated wood using a $ZnCl_2$-lactic acid DES and found that this system could significantly increase the interlayer spacing of cellulose microfibrils from 3.80 nm to 5.20 nm at 120 °C, while simultaneously enhancing cell-wall porosity and selectively cleaving the ether bonds of lignin, with a maximum dissolution of up to 10 wt%, an energy consumption of only 5.01 kJ/g, and a degree of polymerisation retention exceeding 70%. These results indicate that DESs with metal chlorides as HBAs can achieve controllable expansion of the interlayer spacing of cellulose microfibrils and improvement of cell-wall porosity at the molecular level without severely degrading the cellulose backbone, while also enabling targeted disassembly of the amorphous region of the cell wall through selective cleavage of β-O-4 ether bonds in lignin. In essence, this approach represents a mild yet selective means of cell-wall structural regulation, wherein the Lewis acidity provided by $ZnCl_2$, synergised with the Brønsted acidity from lactic acid, serves as the key driving force for this process. Table 1 classifies this study as direct cell-wall evidence for interlayer-spacing expansion and porosity change; the β-O-4 cleavage and Lewis/Brønsted acid synergy are mechanistic proposals, while leaching, fire, smoke, and mechanical performance were not reported in this system. Ji et al. [15] systematically investigated acidic DES-mediated pretreatment of softwood and found that the TEBAC-lactic acid system achieved 97.41% lignin removal and 97.09% glucose yield under optimised conditions of 150 °C for 90 min. Density functional theory (DFT) calculations, as shown in Figure 2, further revealed at the molecular level the strong interaction between the TEBAC-lactic acid system and the lignin model compound guaiacylglycerol, with a binding energy of −162.37 kcal/mol, providing a theoretical explanation for the molecular origin of the excellent delignification capability of this system. Wang et al. [16] further systematically summarised the recent advances in process-intensification-assisted DES pretreatment for lignocellulosic biomass fractionation, covering the enhancing effects of microwave-assisted, ultrasonic-assisted, and other intensification methods on DES penetration efficiency.

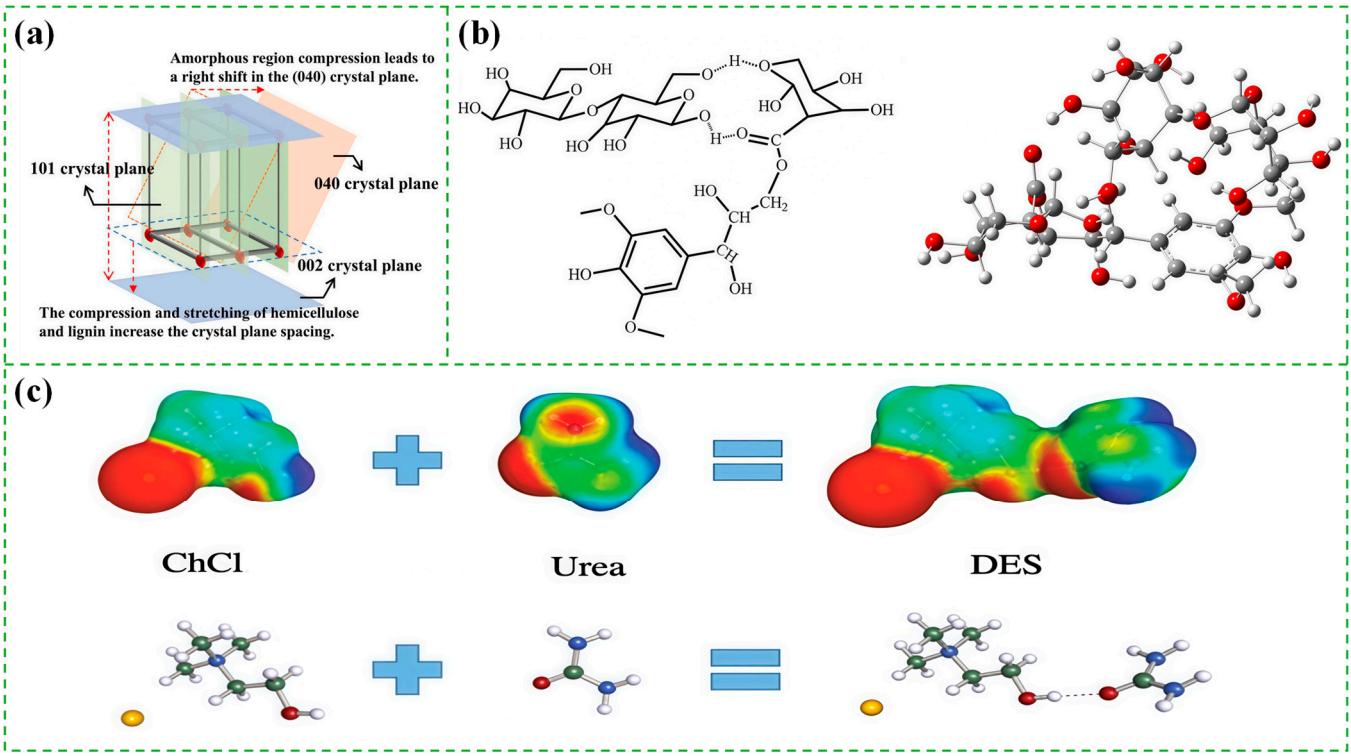

Figure 1. (**a**) Characteristic peaks in cellulose, hemicellulose, and lignin [13]. (**b**) Holocellulose models with an LCC moiety and two hydrogen [13]. Reproduced with permission from Ref. [13]. (**c**) Synthesis mechanism of ChCl with urea to form DESs [17]. Reproduced with permission from Ref. [17].

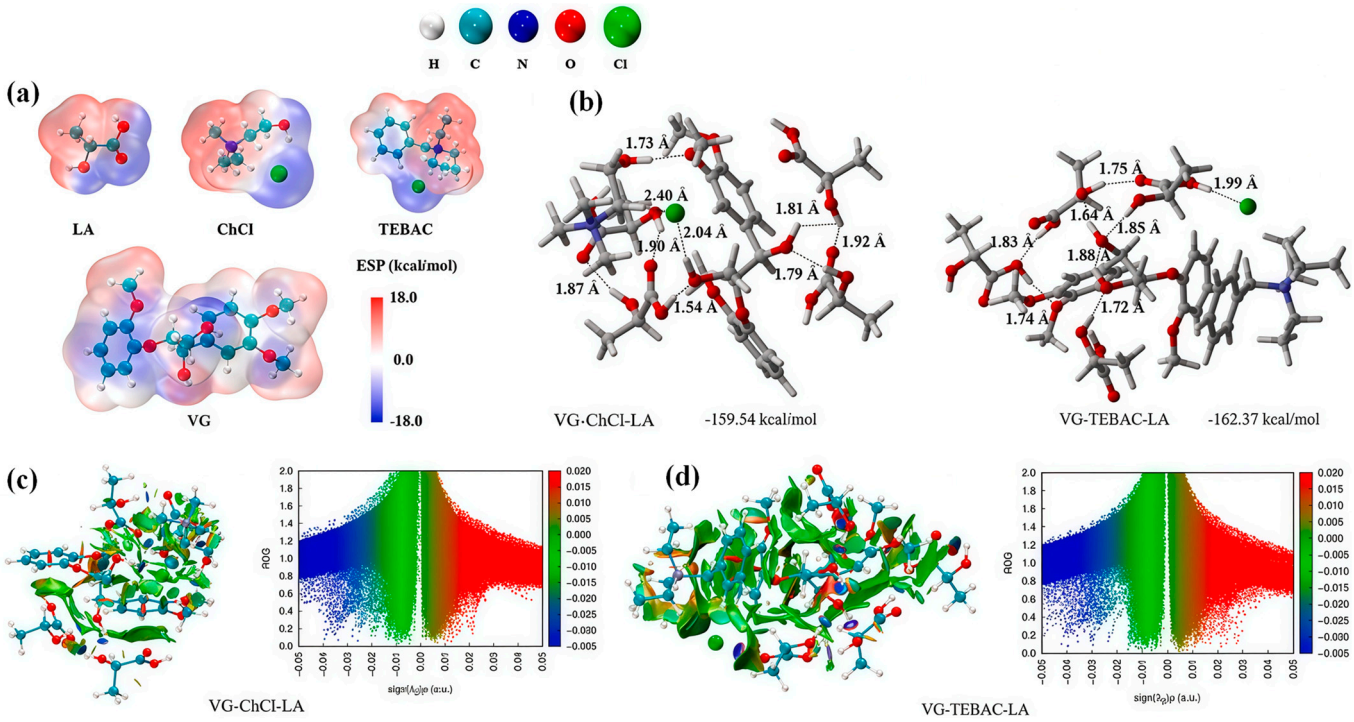

Figure 2. DFT calculations of DES interactions with lignin. (**a**) The geometric configurations and electrostatic potential surfaces of LA, ChCl, TEBAC, and VG. (**b**) Stabilized structures of VG-ChCl-LA and VG-TEBAC-LA with the lowest energy. (**c**) RDG equivalent surface and scatter plot of the VG-ChCl-LA system. (**d**) RDG equivalent surface and scatter plot of the VG-TEBAC-LA system [15]. Reproduced with permission from Ref. [15].

Directly incorporating phosphorus-containing active components into DES formulations to achieve flame-retardant functionalisation represents a current research focus in the field of wood flame-retardant modification. The design strategy of phosphorus-containing DESs involves introducing phosphorus-containing compounds such as phosphorous acid and guanidine phosphate as hydrogen bond donors or third components into the choline chloride-based DES system, thereby anchoring phosphorus elements onto the wood cell-wall skeleton through chemical bonding via the cell-wall penetration capability of DESs, and consequently exerting the typical gas-phase and condensed-phase flame-retardant effects of phosphorus-based flame retardants during combustion. Luo et al. [18] systematically investigated the modification effects of lithium-based DESs prepared from lithium chloride with ligands such as lactic acid, glycerol, and urea on poplar wood, finding that these systems could achieve functional restructuring at the cell-wall level through metal coordination between lithium ions and oxygen-containing functional groups of wood. Chen et al. [19] employed Fe^{3+}-assisted DES for the softening treatment of beech wood and found that Fe^{3+}, serving as an active site providing acidic protons, could significantly enhance the softening efficiency of DES; the treated wood removed 86% of lignin and 48% of hemicellulose, and exhibited enhanced flexibility and qualitatively reported but not quantified. It is thus evident that whether through the chemical bonding of phosphorus-containing DESs, the metal coordination of lithium-based DESs, or the acid-catalysed softening of iron-based DESs, the essence of their functionalisation consistently points to the molecular-level interactions between DES components and wood cell-wall components.

In this review, "penetration" is used in two different senses: macroscopic reagent access into the porous wood structure (bulk uptake) and molecular-scale localization within the cell wall. Complete penetration of wood chips, mass gain, or dye ingress should be described as bulk uptake/macroscopic penetration unless complemented by microscopy or spectroscopy showing cell-wall localization. The key to the penetration process lies in the chemical action of DESs on cell-wall components. The hydrogen bond donors and acceptors in DESs can disrupt the native hydrogen-bond networks among lignocellulosic components, leading to partial dissolution or structural relaxation of lignin and hemicellulose in the matrix regions of the cell wall, thereby inducing moderate swelling of the cell wall [7]. Molecular dynamics simulations and cellulose-model studies provide mechanistic analogies for DES–cellulose interactions, but they do not establish spatial penetration into intact wood cell walls or identify covalent bonding in the native cell wall. Molecular dynamics simulations provide a mechanistic analogy for this process; Figure 3 displays the initial configurations and the structural evolution before and after simulation of cellulose bundles in Reline and Oxaline DES systems, demonstrating that both DES systems can cause significant dissociation and extension of cellulose bundles at room temperature, with the Oxaline system exhibiting a more pronounced swelling effect, indicating that DESs can effectively disrupt the hydrogen-bond networks between cellulose chains and promote the deconstruction of their supramolecular structure [20]. These simulations are not direct cell-wall evidence for intact wood; they support the proposed DES–cellulose interactions at the molecular level. The swelling capacity varies considerably among different DES systems, which is closely related to the acidity/basicity of the DES, the type of hydrogen bond donor, and the treatment temperature. The review by Chen et al. [19] systematically compared the swelling effects of various DES systems on wood cell walls and found that acidic DESs generally exhibit stronger swelling capability, while neutral DESs are relatively milder. A direct consequence of swelling is the enlargement of existing pores and the generation of new pores within the cell wall. Research on DES-based wood softening treatments has shown that DES-treated wood forms a highly porous network structure. Abouzeid et al. [21] employed a combined microwave energy-deep eutectic solvent

pretreatment for linden wood, followed by sequential resin/silica impregnation and high-temperature densification to improve the mechanical properties, structural stability, and dimensional stability of the wood. After MWE-DES pretreatment, the linden wood exhibited a highly porous network structure, with partial removal of lignin and hemicellulose. The flexural strength of linden wood increased from 60.9 MPa of the original wood to 83.2, 87.4, 99.9, and 105.8 MPa, respectively. These mechanical improvements were obtained after combined microwave-assisted DES pretreatment, resin/silica impregnation, and high-temperature densification. The DES-only contribution is not isolated; untreated, DES-only, and densification-only controls under identical conditions are needed to attribute the improvement to DES treatment, together with final density, loading direction, and moisture-conditioning conditions. The significant increase in cell-wall porosity further enhances the penetration capability of DESs into the deep cell wall, forming a positive feedback process of penetration–swelling–re-penetration. It should be noted that moderate swelling and crystalline-region preservation are system- and condition-specific, not universal DES properties. They should be claimed only when supported by combined evidence of absolute cellulose retention, DP, and crystalline-domain preservation; in extensive fractionation systems, cellulose-bundle dissociation and matrix depolymerization may occur [20]. The DES-retention strategy recently reported by Ran et al. [8] confirmed that DES pretreatment induced matrix depolymerisation and cellulose swelling, while the subsequent hot-pressing process promoted the rearrangement of cellulose and the re-condensation of lignin; the retention of DES reduced the softening temperature of wood from 100 °C to 55 °C, and the final densified wood achieved a density of 1.01 g/cm^3, a flexural strength of 197.04 ± 9.88 MPa, and an elastic modulus of 10.17 ± 0.71 GPa; after cyclic soaking, boiling, and drying treatments, the shape recovery rate was only 1.5%. This densified wood was produced by DES retention followed by hot pressing; the mechanical improvement therefore reflects combined DES plasticization and densification rather than DES treatment alone, and the corresponding fire performance was not measured in the same material system. Figure 4 systematically summarises the entire multi-scale mechanism of this process, from DES-induced cell-wall plasticization and lubrication, to hot-pressing-driven densification and locking, and finally to the formation of cross-linked networks, presenting a complete progressive modification pathway from chemical action, physical remodelling, to structural fixation [8]. The cyclic soaking/boiling/drying shape-recovery result is dimensional stability evidence, not leaching resistance; fire and smoke performance were not measured in the same material system. These studies indicate that the penetration and swelling of DESs in the wood cell wall are the synergistic results of physical diffusion and chemical interactions, and it is precisely this synergistic mechanism that endows DESs with the unique capability for functional modification at the cell-wall level.

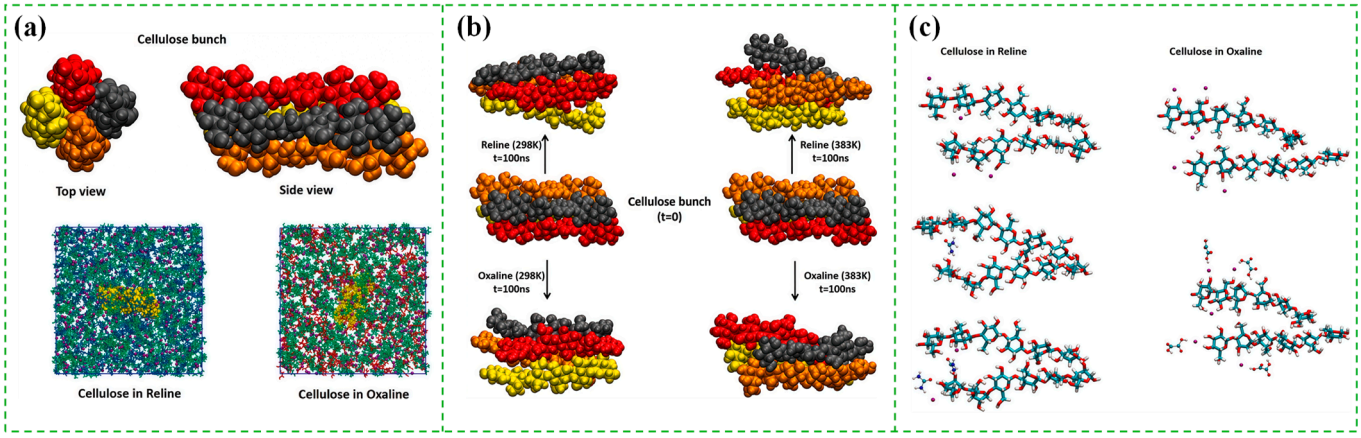

Figure 3. (**a**) Graphical representation of initial structure of cellulose bunch and its solvation with reline and oxaline in the simulation box at the t = 0. (**b**) Graphical representation of cellulose bunch before and after simulations in reline and oxaline at room temperature (298 K) and 383 K. (**c**) Molecular mechanism of cellulose dissolution in reline and oxaline; the related molecular confgurations were extracted from the fnal simulation step at t = 100 ns [20]. Reproduced with permission from Ref. [20].

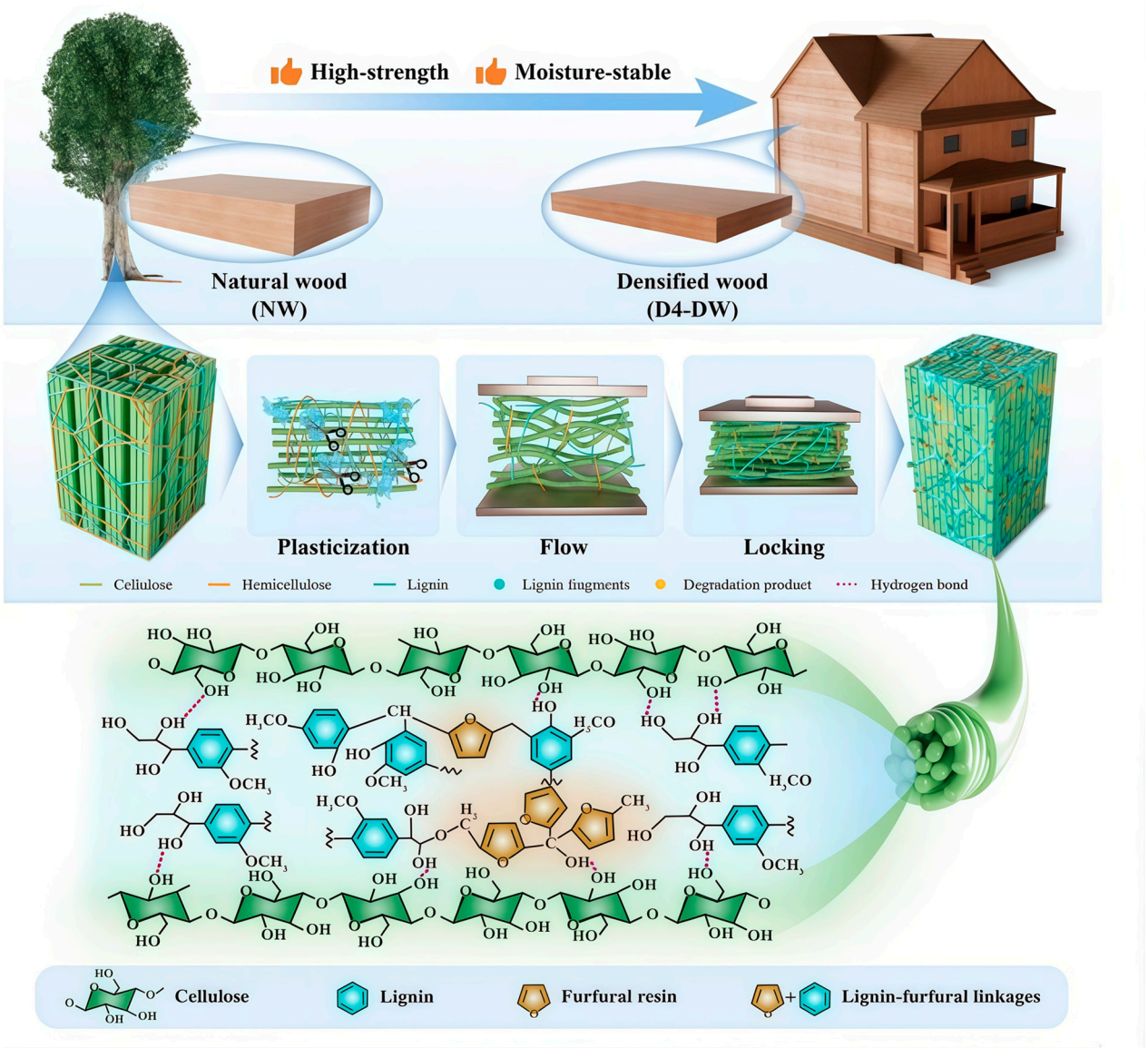

Figure 4. Schematic illustration of the multi-scale mechanism: from DES-induced plasticization/lubrication (middle) to densification-driven locking (right), highlighting the formation of cross-linked networks [8]. Reproduced with permission from Ref. [8].

Table 1. Comparison of penetration, swelling, and mechanical effects of different DES systems on lignocellulosic substrates.

DES System	Substrate	Treatment Conditions	Evidence Type	Key Findings/Outcomes	Ref.
ChCl–lactic acid	Populus tomentosa wood chips	100 °C, 4 h	Experiment	Macroscopic bulk uptake (complete chip penetration observed visually)	[8]

ChCl–ethylene glycol	Populus tomentosa wood chips	100 °C, 4 h	Experiment	Macroscopic bulk uptake (lower efficiency than ChCl–lactic acid)	[8]
ChCl–urea (Reline, 1:2)	Cellulose–xylan/cellulose–lignin hybrid models	Molecular dynamics simulation	Simulation	Removal of 78.3% (cellulose–xylan) and 68.4% (cellulose–lignin) hydrogen bonds	[7]
ChCl–glycerol	Cellulose–xylan/cellulose–lignin hybrid model	Molecular dynamics simulation	Simulation	Disruption of original hydrogen-bond network among lignocellulosic components	[7]
Fe^{3+}-assisted DES	Beech wood	Fe^{3+}-assisted DES, 1–4 h, thickness 1–5 mm; no microwave	Experiment	High porous network; 86% lignin and 48% hemicellulose removal; enhanced flexibility	[19]
MWE-DES + resin/silica + densification	Linden wood	Microwave DES pretreatment + impregnation + hot pressing	Experiment	Flexural strength 60.9 → 83.2/87.4/99.9/105.8 MPa (MWE-DES stage); 246 MPa (resin impregnation); 198 MPa (silica impregnation)	[21]
DES retention + hot pressing	Fast-growing wood	DES retention + hot pressing	Experiment	Softening temperature reduced from 100 °C to 55 °C; density 1.01 g/cm^3; MOR 197.04 MPa; shape recovery 1.5%	[8]

Table note: HBA = hydrogen bond acceptor; HBD = hydrogen bond donor; ChCl = choline chloride; MWE-DES = microwave energy-deep eutectic solvent combined pretreatment; MOR = modulus of rupture. "Bulk uptake" refers to macroscopic reagent access into the porous wood structure and does not imply molecular-scale localization within the cell wall. Molecular dynamics simulation outputs reflect theoretical interaction energies at the molecular level and are separated from experimentally measured macroscopic properties.

Based on the above discussion on the classification of systems and the mechanisms of penetration and swelling, it is evident that the modification of wood cell walls by DESs is not simply a matter of macropore filling, but is instead based on the targeted disassembly and reconstruction of the hydrogen-bond networks among lignocellulosic components. Different categories of DESs, through selective disruption of the native hydrogen bonds in the amorphous regions of the cell wall, achieve a controllable process spanning from macroscopic penetration to molecular-scale swelling, while, in systems where crystalline domains and DP are explicitly shown to be preserved, providing a structural basis for mechanical retention. However, an increased relative crystallinity index after removal of amorphous components should not be interpreted as undamaged cellulose or retained mechanical properties; absolute cellulose retention, DP, and crystalline-domain preservation must be assessed separately. This unique cell-wall-level action mode not only provides a structural prerequisite for the chemical bonding and uniform distribution of flame-retardant active components within the wood interior, but also fundamentally distinguishes itself from the physical impregnation pathway of conventional flame retardants, thereby constituting the physicochemical basis for understanding the enhancement mechanisms of flame retardancy and smoke suppression in DES-modified wood.

DES components may be retained in wood through different mechanisms that should not be conflated: (i) bulk uptake and lumen/surface deposition, indicated by mass gain, dye penetration, or surface imaging; (ii) cell-wall penetration, requiring spatially resolved

localization within the secondary wall; (iii) hydrogen bonding, inferred from FTIR/NMR shifts but not proof of covalent fixation; (iv) metal coordination, supported by XPS/XAS/FTIR but requiring spatial localization; and (v) covalent grafting, which requires bonding-specific evidence such as solid-state NMR, XPS, model reactions, or hydrolytic stability combined with spectroscopy. Reduced leaching or water uptake indicates retention or barrier effects, but does not by itself identify the bonding mechanism. Furthermore, bulk chemical characterization (e.g., bulk FTIR or XPS) and molecular simulations cannot alone establish cell-wall spatial localization or durable fixation; spatially resolved techniques are required. The contrast between conventional lumen-dominant treatment and DES-mediated cell-wall functionalization is therefore mechanistic and evidence-dependent rather than categorical.

3. Flame Retardancy, Smoke Suppression, and Property Retention

Within this subsection, direct evidence from intact wood/bamboo is presented first where available; studies on surface coatings, cellulose derivatives, and composites are then discussed as supporting mechanistic analogies and are explicitly labeled. Wood combustion involves condensed-phase pyrolysis and gas-phase combustion, two tightly coupled processes. In the condensed phase, phosphorus-containing or acidic DESs catalyse the dehydration and charring of polysaccharide components, forming a carbonaceous barrier that insulates heat and shields oxygen. In the gas phase, nitrogen- or sulfur-containing components release non-flammable but inherently toxic gases such as NH_3 and SO_2 and scavenge active radicals such as H^+ and HO^-, thereby interrupting the combustion chain reaction. Beyond flame retardancy, the formation pathways of smoke precursors and their chemical inhibition, together with the leaching resistance and mechanical property retention of modified wood, determine whether DES-modified wood can be translated from laboratory-scale demonstrations to high-value engineering materials. Smoke suppression is not implied by flame retardancy and must be supported by smoke-specific metrics such as TSP, SPR, smoke density, CO/CO_2 yield, or TG-FTIR gas analysis. Likewise, reduced water uptake or shape recovery is not equivalent to leaching resistance; leaching/washing resistance requires quantified retention of flame-retardant elements or performance after standardized washing/leaching. Where such data are unavailable, the corresponding entry is recorded as "not reported" in Table 1 and is not discussed as a demonstrated mechanism.

3.1. Condensed-Phase Catalytic Char Formation

In the condensed phase, phosphorus-containing or acidic DESs exert their flame-retardant efficacy by catalysing the dehydration and charring reactions of wood polysaccharide components [22]. The chemical pathway can be summarised as follows: upon heating of DES-modified wood, the phosphorus-containing components in the system first thermally decompose to form phosphoric acid or polyphosphoric acid species [23]. These acidic species, through the formation of hydrogen-bonded complexes with the hydroxyl groups on the molecular chains of cellulose and hemicellulose, effectively lower the activation energy of the dehydration reaction. Under the synergistic action of phosphorus and nitrogen sources, hemicellulose undergoes dehydration at relatively lower temperatures, while the pyrolysis pathway of cellulose is directionally shifted from the original tar-generating pathway towards char formation [24]. Studies have shown that the introduction of phosphorus- and nitrogen-containing DESs can significantly alter the pyrolysis pathway of wood, and experimental analyses have confirmed that the system catalyses dehydration reactions and promotes char formation during pyrolysis, while simultaneously suppressing the release of combustible gases [22]. Based on this mechanism,

recent studies have verified the charring effects of phosphorus-containing DESs at different scales, including surface coating, cellulose molecular modification, and biomass composite materials.

For the modification of bulk wood, surface coating represents the most direct technical approach. As a surface-coating analogy rather than direct cell-wall evidence, Zeng et al. [22] constructed a uniform and dense composite flame-retardant film on the surface of Chinese fir using natural chitosan, citric acid, and a ternary DES composed of choline chloride–urea–phosphorous acid. This strategy combined the catalytic char-forming function of DESs with the intrinsic charring ability of chitosan, resulting in an increase in the limiting oxygen index from 23.9% to 41.4%, achieving a UL-94 V-0 rating, a reduction in the average heat release rate by 61.8%, a decrease in total heat release by 11.4%, and an extension of combustion duration by 183%. Figure 5 schematically compares the intense combustion process of untreated Chinese fir with the slow combustion behaviour of the coated wood, and illustrates the chemical pathway of phosphorus–nitrogen–carbon synergistic flame retardancy, visually presenting the dual functions of this coating in condensed-phase catalytic char formation and gas-phase dilution flame retardancy [22]. Moreover, this coating can be rapidly dissolved in citric acid for recycling and reprocessing, and it completely degrades in soil within 10 days. Distinct from the external barrier pathway of surface coatings, molecular-scale modification strategies focus on directly introducing flame-retardant elements at the chemical structural level of cellulose. At the cellulose-fibril/nanocellulose level, Yang et al. [25] designed a synergistic system of ammonium dihydrogen phosphate and binary DES, achieving dual phosphorylation and sulfonation functionalisation of straw fibres through a combined pretreatment scheme. The introduction of sulfonic and phosphate groups promoted the nanofibrillation of straw fibres and enhanced the hydrogen-bond interactions among cellulose nanofibres, resulting in a self-bonded straw cellulose nanofibre laminate with a LOI of 74.9%, a reduction in heat release rate by 74.3%, and more than a three-fold increase in tensile strength. Figure 6 systematically presents the chemical processes of sulfonation and phosphorylation in this system, along with the corresponding flame-retardant mechanism, clearly illustrating the complete pathway from DES treatment to char-layer formation [25]. The advantage of this pathway lies in its fundamental alteration of the thermal degradation behaviour of cellulose at the molecular level; however, its application scenarios are relatively confined to specific material forms such as nanofibre membranes.

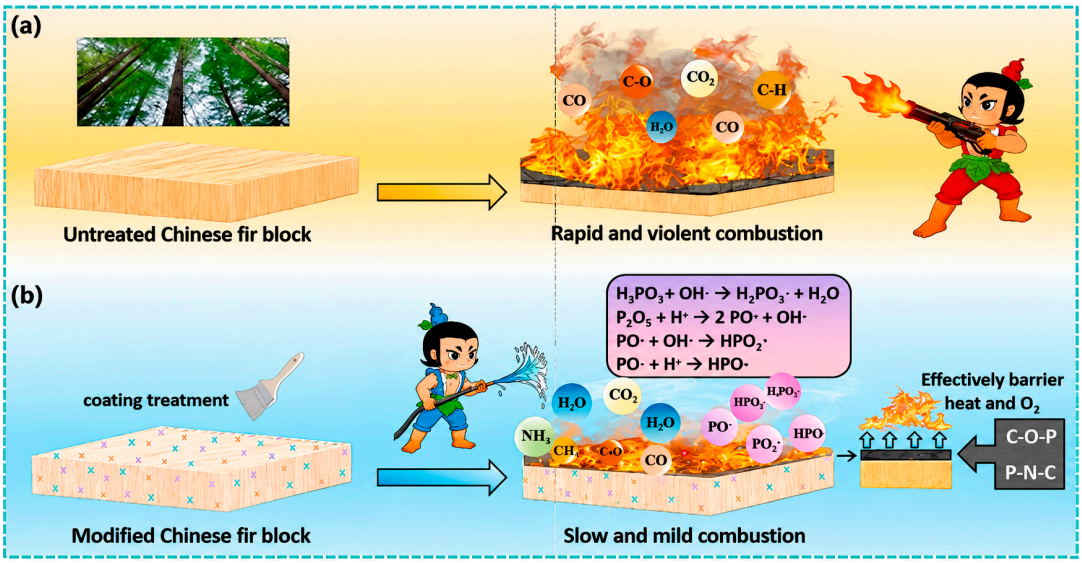

Figure 5. (**a**) Combustion process of NW; (**b**) Flame retardant mechanism of P-N-C synergy in D/C-W [22]. Reproduced with permission from Ref. [22].

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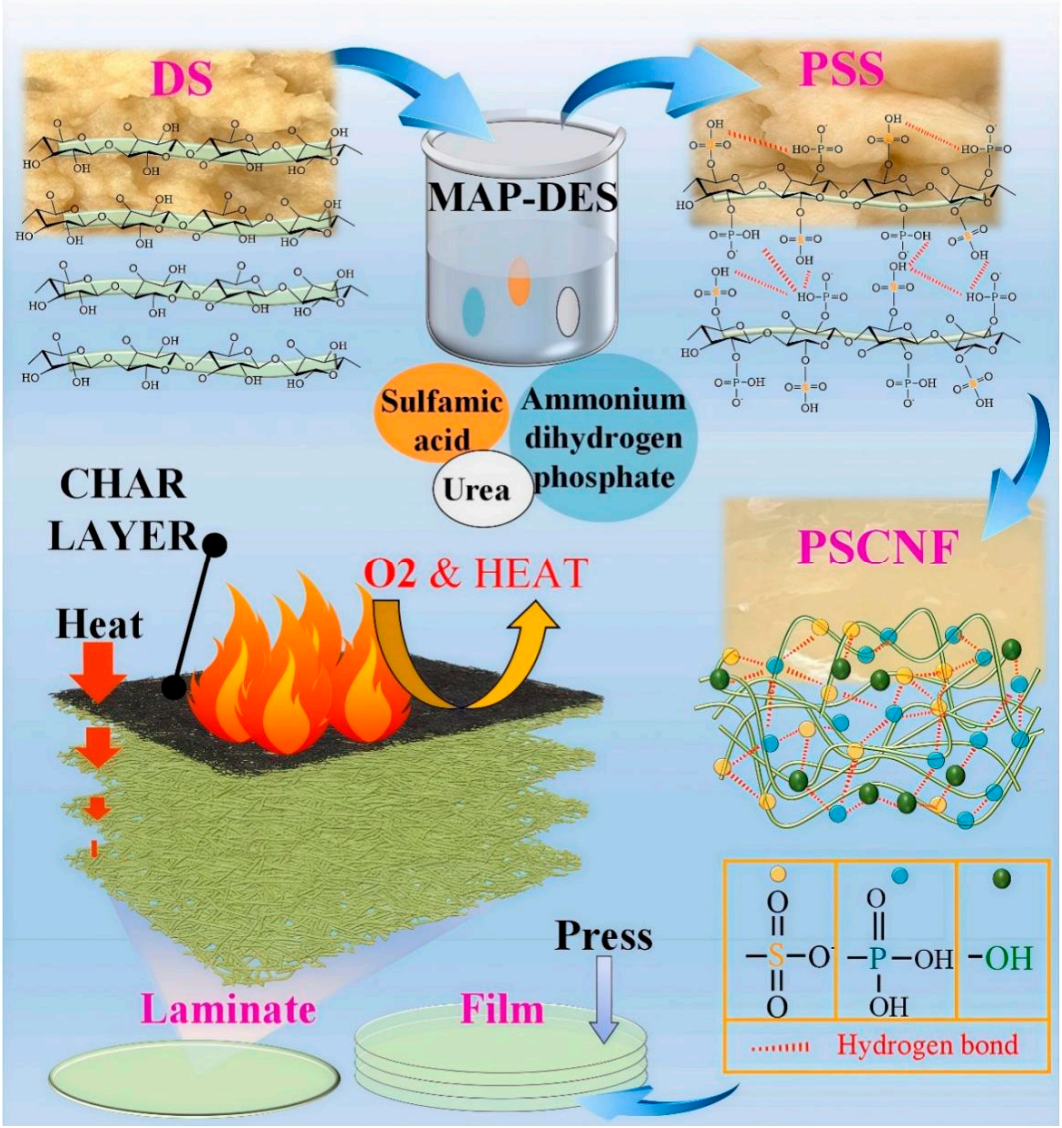

Figure 6. The schematic diagram illustrating the sulfonation and phosphorylation processes along with their flame-retardant mechanisms was presented [25]. Reproduced with permission from Ref. [25].

Further extending the scope of DES-mediated phosphorylation modification, researchers have applied this strategy to reinforcements in engineering composite materials. At the composite-reinforcement level, Zhu et al. [9] employed a ternary reactive DES composed of phytic acid, urea, and sulfamic acid to perform phosphorylation functionalisation of bamboo fibres, which were then used as the reinforcement phase in combination with water-soluble epoxy resin. The limiting oxygen index of the modified bamboo fibre/epoxy composites increased from 22.3% to 44.5%. Similarly, Zabihi et al. [26] phosphorylated macadamia nutshell powder; this supports phosphorus-based char chemistry but does not demonstrate penetration into intact wood cell walls. This phosphorus-containing DES was applied to phosphorylate macadamia nut shell powder under mild conditions, simultaneously achieving partial delignification of the shell powder, which significantly enhanced its crystallinity. The biocomposite containing 20 wt% of the modified powder attained a UL-94 V-1 rating, with a 74% reduction in peak heat release rate and a maximum smoke temperature decrease to 344 °C. A common feature of these two studies is that the char-forming function of DESs does not act directly on the cellulosic material itself, but rather indirectly imparts flame-retardant properties to the composite system

through the modification of cellulose reinforcements or biomass fillers, thereby extending the applicability of phosphorus-containing DESs to the field of polymer matrix composites.

From surface coatings and cellulose molecular modification to the modification of reinforcements and fillers in composites, although the processing scales and modes of action differ among these three approaches, they all converge on the same chemical essence. Phosphorus-containing DESs thermally decompose to generate acidic species, which catalyse the dehydration and crosslinking of biomass polysaccharide components to form a char layer; the introduction of nitrogen components further enhances the compactness and intumescence of the char layer through the phosphorus–nitrogen synergistic effect. This char layer exerts its physical barrier function through a triple mechanism involving low thermal conductivity, dense shielding, and intumescent thermal insulation.

3.2. Gas-Phase Radical Trapping

It is crucial to note that non-flammability does not establish harmlessness. Gases such as NH_3 and SO_2 are inherently toxic and irritating; their release may shift the hazard from flammability to acute inhalation toxicity. The dilution effect reduces the concentration of combustible volatiles, but the safety implications of these evolved gases require specific toxicological assessment. Recent studies have attributed flame-retardant performance to these two gas-phase mechanisms across different material systems; however, direct spectroscopic detection of PO· and HPO_2· under combustion conditions is rare, and most studies infer radical trapping from thermal analysis, char characterization, and literature-based mechanisms.

In this subsection, a distinction is made between direct detection and inferred mechanisms. Direct detection refers to spectroscopic or mass-spectrometric identification of radical species or non-flammable gases under pyrolysis/combustion conditions (e.g., EPR, molecular-beam mass spectrometry, TGA-FTIR/TG-MS for stable gases). Inferred mechanism refers to attribution based on LOI, cone calorimetry, thermogravimetry, char residue, or literature-based schematics. Unless direct detection is explicitly reported, radical trapping is presented as a proposed mechanism rather than an established one. The dilution effect is primarily achieved through the thermal decomposition of nitrogen- or sulfur-containing DES components. As a fabric-surface analogy, Gao et al. [27] synthesised a recyclable ternary DES using choline chloride as the hydrogen bond acceptor and phosphoric acid and sulfamic acid as dual hydrogen bond donors, for the surface ammonium phosphate modification of cellulosic fabrics. Figure 7a schematically illustrates the chemical grafting and cationic dyeing mechanism on the cellulosic fabric surface during this process. In this system, sulfamic acid releases non-flammable but irritating gases such as NH_3 during pyrolysis, reducing the concentration of combustible volatiles through the gas-phase dilution effect; however, the toxicological hazard of this NH_3 emission remains a concern. Figure 7b further demonstrates the synergistic flame-retardant mechanism comprising gas-phase dilution and condensed-phase char formation, wherein phosphate groups on the modified fabric pyrolyse to generate a P_2O_5-based char layer while simultaneously releasing non-flammable gases such as H_2O and CO_2. The limiting oxygen index of the modified cellulosic fabric reached 48%, and it remained at 33.5% after 50 washing cycles. It should be noted that improved LOI and reduced heat release do not by themselves isolate gas dilution from condensed-phase charring or radical trapping; the dilution mechanism here is inferred from the release of non-flammable gases and is not independently quantified. As a foam-coating analogy, Vishvakarma et al. [28] composited a choline chloride–urea DES with graphene oxide to fabricate a flame-retardant coating for expanded polystyrene foam. Figure 8 illustrates the preparation process of this DES-GO composite coating and its application onto the EPS surface. The DES-GO composite coat-

ing releases nitrogen-containing gaseous species during combustion, reducing the combustible gas concentration through the dilution effect, while the lamellar structure of GO forms a physical barrier at the early stage of combustion, synergising with the gas-phase dilution effect of DES. Zhu et al. [9] employed a ternary reactive DES composed of phytic acid, urea, and sulfamic acid to phosphorylate bamboo fibres. In this system, urea and sulfamic acid release non-flammable but potentially toxic gases including NH_3 and SO_2, respectively, during pyrolysis. The LOI of the modified bamboo fibre/water-soluble epoxy composites increased from 22.3% to 44.5%.

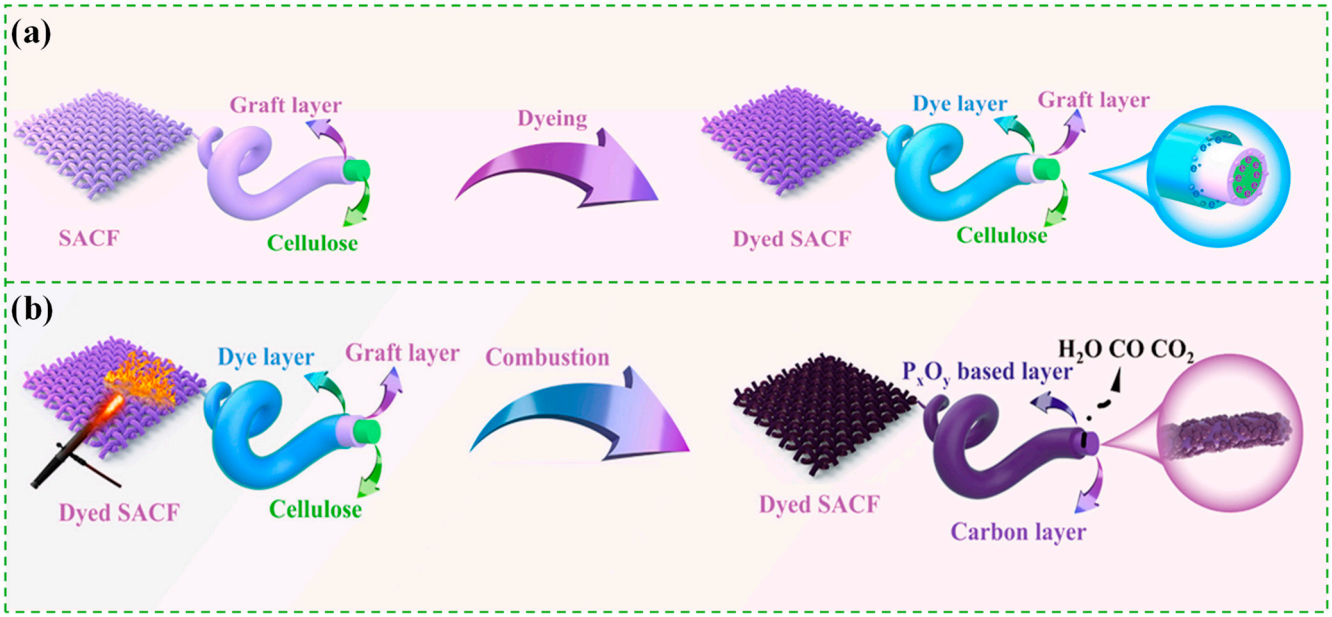

Figure 7. (**a**) Schematic illustration of the preparation mechanism of modified and dyed cellulose fabrics, showing the surface ammonium phosphate modification of pristine cellulose fabrics by ternary DES, followed by electrostatic adsorption of cationic dyes onto the negatively charged ammonium phosphate graft layer, forming a multifunctional fabric structure with combined graft and dye layers. (**b**) Schematic illustration of the combustion mechanism of modified and dyed cellulose fabrics, showing the thermal decomposition of phosphate groups during combustion to form a P_2O_5-based char layer covering the fabric surface, while releasing H_2O and CO_2 as non-flammable diluent gases, achieving flame retardancy through the synergistic effect of condensed-phase charring and gas-phase dilution [27]. Reproduced with permission from Ref. [27].

Radical trapping constitutes the other core mechanism of gas-phase flame retardancy, which is primarily achieved through phosphorus-containing active species generated from the thermal decomposition of phosphorus-containing DESs. Zeng et al. [23] modified bamboo using a ternary DES composed of choline chloride, urea, and phosphorous acid, and attributed the flame-retardant action to phosphorus-containing radicals such as PO· and HPO_2· that are proposed to scavenge H· and HO· radicals, while NH_3 released from urea may exert a dilution effect. However, these radical species were not directly detected in this study; the mechanism was inferred from thermal analysis, char characterization, and literature-based schematics. The modified bamboo exhibited a limiting oxygen index of 37.3%, a 20.6% reduction in peak heat release rate, a 23.0% decrease in total smoke production, and a 204.3% increase in char residue rate. As a cotton-coating analogy, Guidugli et al. [29] synthesised a series of phytic acid-based DESs using phytic acid as the hydrogen bond donor and choline chloride or ethylene glycol as the hydrogen bond acceptor, and applied them as coatings onto cotton fabric surfaces. Although Figure 9a pre-

sents a schematic of the proposed free radical quenching mechanism, the successful deposition of the DES coatings and the uniform distribution of phosphorus and nitrogen on the cotton fabric surfaces were confirmed by SEM and EDX analyses as reported in the original study. Phytic acid releases phosphorus-containing radical species including PO· during pyrolysis, exerting gas-phase radical trapping through scavenging H· and HO· radicals. Figure 9b schematically summarises the synthetic route of the phytic acid-based DESs, the dip-coating process on cotton fabric surfaces, and the condensed-phase/gas-phase dual-mode flame-retardant mechanism [29]. After coating with the DES at a choline chloride-to-phytic acid molar ratio of 1:5, the peak heat release rate of the cotton fabric decreased from 213.4 kW/m² to 50.3 kW/m², with a 78% reduction in total heat release, and no smoke release or afterflame was observed. Thermogravimetric analysis indicated that the char residue rate increased from 11.8% to 33.5%.

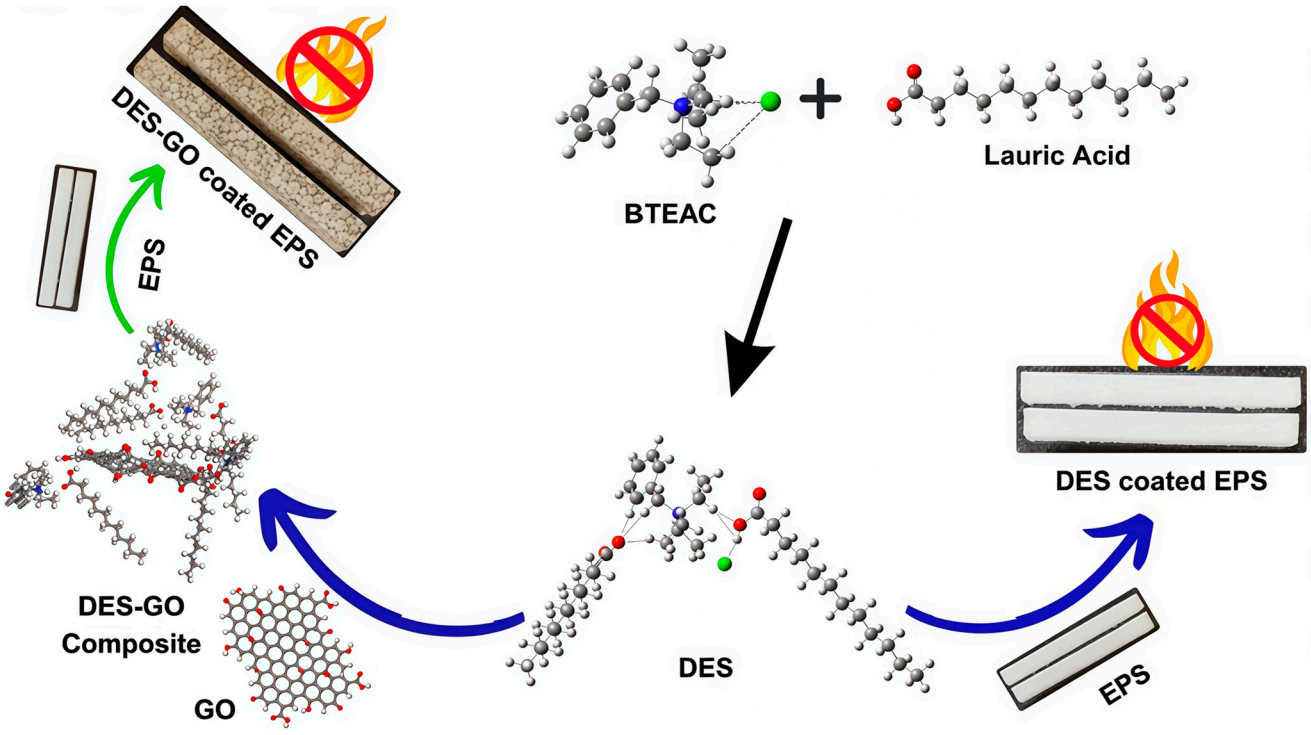

Figure 8. Schematic illustration of the preparation process of DES-GO composite coating and its application on expanded polystyrene (EPS) foam [28]. Reproduced with permission from Ref. [28].

In addition, a phosphorus-based DES-mediated bidirectional modification strategy was employed for carbon fiber reinforced epoxy composites. The researchers designed and synthesised a novel phosphorus-based DES, integrating structural functional units simultaneously into both the epoxy resin and the carbon fiber surfaces. This phosphorus-based DES releases phosphorus-containing radicals including PO· during pyrolysis, exerting gas-phase flame-retardant action through scavenging H· and HO· radicals [30]. The modified epoxy composites achieved a UL-94 V-0 rating, with total heat release and total smoke production reduced by 39.6% and 35.1%, respectively. As an elastomer analogy, Li et al. [31] synthesised a polymerisable DES-based flame-retardant ionic conductive elastomer containing phytic acid and choline chloride via a one-pot UV-initiated radical copolymerisation. Phytic acid releases phosphorus-containing radicals during pyrolysis to scavenge H and HO in the combustion chain reaction, while choline chloride releases nitrogen-containing gaseous species that synergise with phosphorus-containing species to

interrupt the chain-branching combustion. The limiting oxygen index of the elastomer increased from 24.1% to 38.3%. These two mechanisms of condensed-phase char formation and gas-phase radical trapping do not operate in isolation. The dense char layer catalytically formed by the phosphorus–nitrogen system in the condensed phase reduces the release of flammable volatiles into the gas-phase zone, thereby diminishing the fuel supply for gas-phase combustion; concurrently, the trapping of chain-branching radicals by phosphorus- and nitrogen-containing species in the gas phase reduces the heat feedback from the flame to the condensed phase, thereby retarding further pyrolysis of the condensed phase.

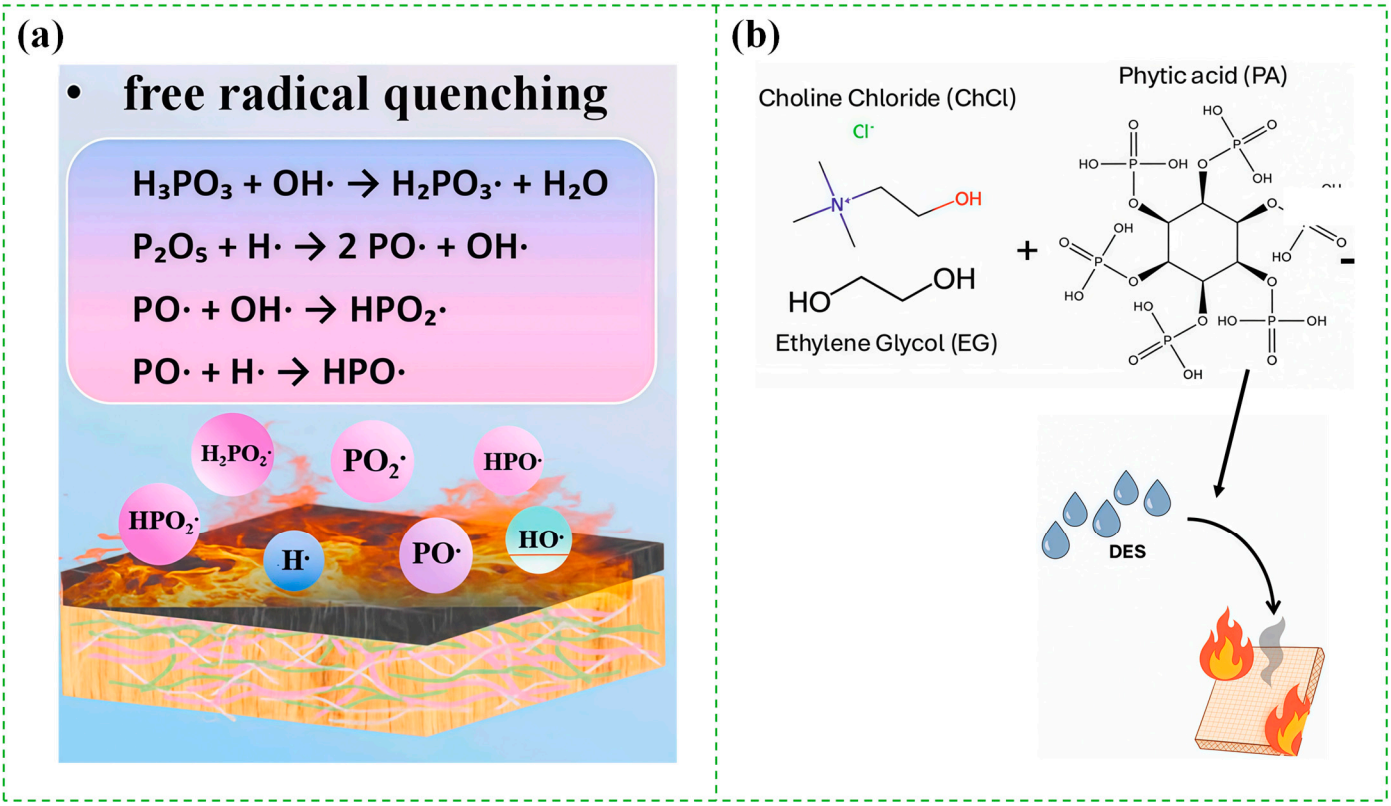

Figure 9. (**a**) Free radical quenching flame retardant mechanism [23]. Reproduced with permission from Ref. [23]. (**b**) Schematic illustration of the synthesis of phytic acid-based deep eutectic solvents (DES), dip-coating application onto cotton fabrics, and the proposed condensed- and gas-phase flame-retardant mechanisms [29]. Reproduced with permission from Ref. [29].

For most DES–lignocellulose systems, gas-phase radical trapping is proposed rather than directly established. LOI, cone calorimetry, and thermogravimetry provide integrated flame-retardant performance but cannot separately quantify radical scavenging and gas dilution; char residue and TGA-FTIR/TG-MS can indicate non-flammable gas release and condensed-phase charring, but they do not detect PO· or HPO_2· directly. Direct evidence would require radical-specific spectroscopy (e.g., EPR) or molecular-beam mass spectrometry under pyrolysis/combustion conditions, preferably coupled with spatially resolved gas-phase analysis. Until such evidence is available, the relative contributions of radical trapping and gas dilution should be described as proposed and system-dependent.

3.3. Chemical Inhibition Pathways of Smoke Precursors

Studies using extracted lignin or cellulose are component-level mechanistic analogies; they clarify how DES-regulated pyrolysis pathways reduce smoke precursors but do not directly demonstrate smoke suppression within intact wood cell walls. The substantial

smoke generated during wood combustion is a major cause of casualties in fires, fundamentally originating from smoke precursors such as tar and polycyclic aromatic hydrocarbons produced during the high-temperature pyrolysis of lignin and cellulose. The smoke-suppression function of DES-modified wood is rooted in the directional regulation of the pyrolysis pathways of lignocellulosic components, and this understanding has progressively deepened through a sequence from pyrolysis product analysis to pyrolysis pathway regulation and ultimately to functional synergistic smoke suppression. Furthermore, it is essential to distinguish between smoke quantity and smoke toxicity. A reduction in total smoke production (or optical density) does not necessarily correlate with a reduction in toxic effluents such as CO, HCN, or NO_x. In most of the reviewed studies, specific toxicity indicators or hazardous gas concentrations were not reported. Therefore, while smoke suppression is indicated, the overall fire safety (including toxicity) of these systems remains incompletely characterized.

Early studies primarily focused on the effects of DESs on the fractionation efficiency of lignocellulosic components, but had not yet systematically addressed the relationship between pyrolysis pathways and smoke generation. Zhao et al. [13] employed choline chloride as the hydrogen bond acceptor and systematically investigated the regulatory effects of different hydrogen bond donors—including lactic acid, oxalic acid, formic acid, and urea—on the pretreatment and pyrolysis product distribution of pine wood. The results demonstrated that different hydrogen bond donors exerted significantly distinct effects on the fractionation efficiency and crystallinity of holocellulose, thereby directly regulating the yields of key pyrolysis products such as levoglucosan and hydroxyacetaldehyde. Wu et al. [32] pretreated bamboo with a choline chloride/formic acid DES and found that the pretreated bamboo, upon fast pyrolysis, achieved a levoglucosan yield of 198.6 mg/g, which was approximately 43 times higher than that of the original bamboo, while the relative contents of smoke precursors such as phenolics and acids were significantly reduced. Jia et al. [33] prepared a ternary DES using glycolic acid and ethylene glycol as dual hydrogen bond donors and benzyltrimethylammonium chloride as the hydrogen bond acceptor for the pretreatment of corn stover, achieving a lignin removal rate of 90.60%, and the levoglucosan yield in the bio-oil from the pyrolysis of the solid residue reached 36.38%. However, this study is primarily aimed at biomass fractionation and bio-oil valorization, not at evaluating fire safety or smoke suppression. Collectively, these studies demonstrate that DES pretreatment can alter pyrolysis product distributions through lignin removal and changes in cellulose crystallinity. They provide indirect evidence for altered smoke-precursor chemistry, but they did not measure smoke production during oxidative combustion and therefore should not be presented as direct demonstrations of smoke suppression.

On this basis, researchers have simultaneously turned their attention to lignin, another major source of smoke precursors. Li et al. [34] systematically investigated the pyrolysis characteristics and product distribution of DES-fractionated lignins extracted from eucalyptus, pine, and rice straw. The study found that DESs could efficiently isolate lignin with purity ranging from 88.5% to 92.7%, while preserving the cellulose fraction intact. The experiments further confirmed that, with increasing pyrolysis temperature, monomeric aromatic hydrocarbons, p-hydroxyphenyl-type phenolics, and catechol-type phenolics were progressively released during lignin pyrolysis, whereas guaiacyl-type and syringyl-type phenolics correspondingly decreased. More importantly, DES-fractionated lignins from different sources exhibited significant differences in pyrolysis product distribution; pine-derived DES lignin produced more bio-oil upon pyrolysis, while eucalyptus-derived lignin predominantly yielded gaseous products. Li et al. [35] treated Eucalyptus urophylla × E. grandis, larch, and sugarcane bagasse with a choline chloride/lactic acid DES, and the extracted DES lignins achieved yields of 83.46%–88.05% with purities as high

as 86.13%–93.73%, and the yield of phenolic compounds after pyrolysis increased by up to 126%. Subsequently, their team [36] treated lignin with two acidic DESs, choline chloride/formic acid and choline chloride/lactic acid, and found that DES treatment altered the elemental composition of lignin and elevated its theoretical calorific value; the pyrolysis oil yield increased up to 40.3%, wherein the proportion of catechol-type phenolics in the pyrolysis oil increased from 15.1% to 18.9%. Wang et al. [37]. treated softwood kraft lignin with two DES systems, choline chloride/ethylene glycol and zinc chloride/ethylene glycol, and found that DES treatment effectively reduced the molecular weight and β-O-4 linkage content of lignin, while significantly enhancing the yields of H-type and C-type phenolics in the pyrolysis oil.

At the molecular mechanism level of pyrolysis pathways, Wang et al. [38] pretreated sugarcane bagasse lignin with a choline chloride/lactic acid DES, obtaining a lignin yield of 86.63% with characteristics of high purity, high homogeneity, moderate β-O-4 linkage content, and fewer condensed structures. The total yield of monophenols from catalytic fast pyrolysis reached 14.68 wt%, among which 4-ethylphenol exhibited the highest yield of 9.27 wt%, followed by 4-ethylguaiacol at 1.57 wt% and 4-propylguaiacol at 1.69 wt% as the major products. Quantum chemical calculations and reactive molecular dynamics simulations further revealed that strong hydrogen bonds formed between chloride ions and the hydroxyl groups of lignin, and the α-acylated lignin structures generated during the pretreatment inhibited condensation reactions to a certain extent. On this basis, Lu et al. [39] fractionated corncob lignin using two DES systems, lactic acid–choline chloride and K_2CO_3–glycerol, and found that alkaline DES extraction yielded p-coumaric acid and ferulic acid at 15.47 mg/g and 7.44 mg/g, respectively, whereas lignin extracted by acidic DES produced higher yields of monophenols upon subsequent pyrolysis, with a particularly notable increase in low-methoxy phenolic monomers. Figure 10a presents a comparison of the acidic and alkaline DES fractionation processes described above, from which it can be clearly observed that the acidity/basicity of DESs exerts a pronounced influence on both lignin extraction efficiency and pyrolysis product distribution. Building upon the understanding of the acidity/basicity effects of DESs, Wang et al. [40] modified industrial alkali lignin with a choline chloride/ethylene glycol DES. Multi-scale simulations revealed that this system possessed the lowest HOMO–LUMO energy gap of 161.80 kcal/mol and the highest interaction energy of −56.56 kcal/mol. The resulting adduct and acetal structures were identified as the chemical origin of the enhanced monophenol yield; under optimal conditions, the total yield of 4-vinylsyringol and 4-propenylsyringol increased to 12.09 wt% with a selectivity of 40.60%. Meanwhile, the same team further developed a technology combining DES pretreatment with fast pyrolysis for the production of 4-vinylphenol [41]; under optimal conditions, the 4-vinylphenol yield reached 14.19 wt% with a selectivity as high as 69.44%. Multi-scale computational modelling revealed that the hydrogen-bond interactions between chloride ions of DESs and the hydroxyl groups of lignin exist independently of the DES type and can compete with the lignin–carbohydrate complex bonds. He et al. [42] fractionated moso bamboo using a ternary tunable DES of guanidine hydrochloride–lactic acid–ethylene glycol, achieving a delignification rate of 74.3% by adjusting the ethylene glycol content, while retaining 61.3% of β-O-4 linkages; the retained structural integrity resulted in a pyrolysis bio-oil yield of 39.7 wt%. Figure 10b illustrates the relationship between lignin structural preservation and subsequent pyrolysis product distribution during this ternary DES fractionation process; Py-GC/MS identified 4-vinylphenol as the dominant product, and a strong positive correlation was observed between β-O-4 linkage content and bio-oil yield, quantitatively confirming the importance of preserving lignin structural integrity during DES fractionation for directional pyrolysis conversion. Collectively, the above studies confirm that DESs can alter the pyrolysis chemistry of lignin through pathways including reduction of molecular weight, diminishment of

condensed structures, regulation of functional group distribution, and preservation of moderate β-O-4 linkage content. This pathway shift alters the distribution of aromatic pyrolysis products toward monophenolic compounds. However, monophenols themselves contain aromatic rings and may contribute to soot or smoke depending on combustion conditions; increased monophenol yield therefore cannot be equated with reduced smoke. Whether such pathway changes lower smoke production requires direct smoke measurement under oxidative conditions.

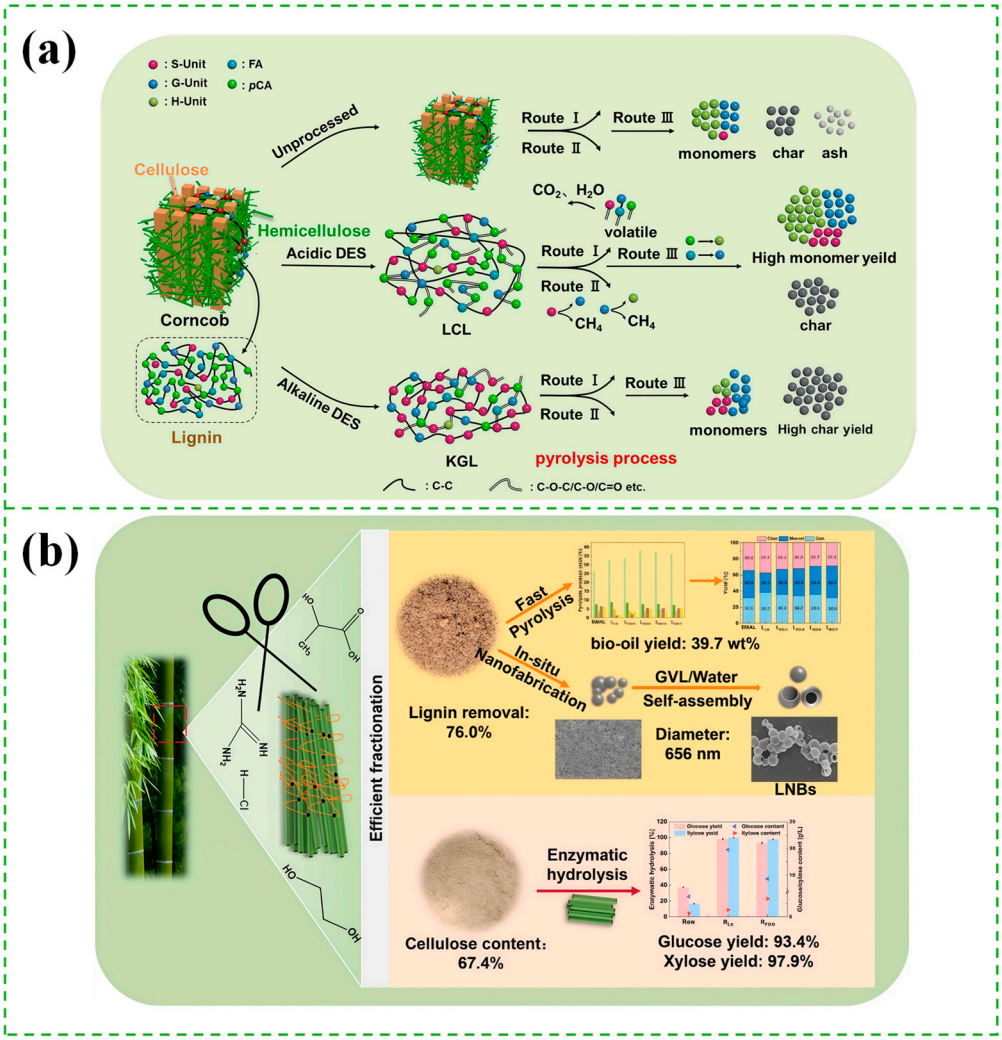

Figure 10. (**a**) Schematic illustrating lignin pyrolysis behavior [39]. Reproduced with permission from Ref. [39]. (**b**) Ethylene glycol-tuned ternary deep eutectic solvent fractionation of moso bamboo [42]. Reproduced with permission from Ref. [42].

Direct smoke-related evidence in this subsection is limited. Zeng et al. [23] reported a 23.0% reduction in total smoke production for DES-modified bamboo under the reported combustion-test conditions; Zhang et al. [43] described smokeless behavior of nanocellulose porous materials, but this was qualitative. Studies reporting only LOI, char residue, heat release, or mechanical properties [44–46] do not provide direct smoke evidence. For non-cell-wall systems, Zhang et al. [30] reported reduced total smoke production in CF/epoxy composites, but this is a composite-level analogy rather than intact wood evidence. As the mechanisms governing pyrolysis pathway regulation have become progressively clarified, researchers have begun to explore synergistic smoke-suppression strategies combining DESs with functional materials, advancing the smoke-suppression efficacy from laboratory-scale mechanistic validation towards performance metrics with

practical application value. Zhang et al. [43] employed microwave-assisted ternary DES combined with bidirectional freeze-casting technology to fabricate nanocellulose porous materials with a hierarchical brick-and-mortar structure; Figure 11a presents the digital photograph, composition, and molecular structure schematic of this ternary DES. The material exhibited thermal conductivities of 36.51 mW/(m·K) and 40.43 mW/(m·K) in the x- and z-directions, respectively, with compressive stresses of 2.00 MPa and 1.75 MPa, and a peak heat release rate of only 90 $W \cdot g^{-1}$, characterised by smokeless and rapid carbonising flame retardancy. As a novel green thermal insulation material, this effectively addresses the industrial challenge of conventional petroleum-based insulation materials releasing large quantities of toxic smoke during combustion, offering a sustainable solution for building energy conservation and fire safety. Xiang et al. [44] pretreated balsa wood with a phosphorus-containing DES prepared from phosphoric acid and choline chloride, and subsequently encapsulated polyethylene glycol via vacuum-assisted impregnation to fabricate flame-retardant wood-based composite phase change materials. The P-DES pretreatment introduced phosphorus elements while preserving the natural porous skeleton of wood; the melting enthalpy reached 122.03 J/g and remained at 122.01 J/g after 100 heating–cooling cycles. Vertical burning tests and char residue analyses indicated that P-DES pretreatment promoted the formation of a continuous and stable phosphorus-containing char layer in the wood skeleton. This material integrates phase-change energy storage functionality with flame retardancy, effectively resolving the critical bottleneck of flammability in phase change materials used in building envelope structures. Kang et al. [45] graft-modified wood fibres using a reactive ternary DES, achieving an increase in char residue rate from 24.2% to 49.23% at 800 °C, an increase in limiting oxygen index from 20.7% to 46.3%, and reductions in peak heat release rate and total heat release from 126.8 W/g and 9.0 kJ/g to 22.7 W/g and 0.4 kJ/g, respectively. As a key reinforcement in wood-based panels, paper-based materials, and automotive interior components, the intrinsic enhancement in flame retardancy of wood fibres implies that high fire-resistance ratings can be met without relying on external flame-retardant additives. Shen et al. [46] employed a multi-scale DES treatment strategy to reconstruct the bamboo cellulose network, producing bamboo-based cellulosic bioplastics with an LOI of 62.17%, along with a tensile strength of 82.32 MPa and a toughness of 20.05 MJ/m^3. Figure 11b illustrates the complete fabrication process of this multi-scale flame-retardant film, from phosphorylated cellulose microfibrils and nanowhiskers to the final film. This material provides a viable solution for replacing plastic products such as biodegradable packaging materials and disposable tableware, combining mechanical performance with fire safety. Collectively, the above studies, spanning diverse application scenarios including nanocellulose insulation materials, phase-change energy storage components, wood fibre reinforcements, and bioplastic packaging, have jointly propelled DES-modified cellulosic materials towards a critical transition from laboratory-scale characterisation to engineering applications.

The above studies, spanning four distinct application scenarios—nanocellulose thermal insulation materials, phase-change energy storage components, wood fibre reinforcements, and bioplastic packaging—have demonstrated the differentiated fire-retardant performance of DES-based modification strategies. Although all four strategies achieve significant improvements in flame retardancy through phosphorus/nitrogen/sulfur functionalisation, their action pathways and application orientations differ in emphasis. The nanocellulose porous materials focus on the synergistic optimisation of thermal conductivity and compressive stress; the phase-change composites balance thermal energy storage density with flame-retardant safety; the graft-modified wood fibres emphasise intrinsic flame retardancy and durability; and the bamboo-based bioplastics concentrate on the trade-off between mechanical properties and fire safety. Collectively, these strategies demonstrate that DES-based modification can simultaneously improve flame retardancy,

smoke suppression, and mechanical/thermal properties, although the emphasis differs depending on the action pathway and application orientation. For most DES–lignocellulose systems discussed here, smoke suppression has not been directly demonstrated under oxidative combustion. Pyrolysis-product analyses and proposed monophenol pathways indicate altered thermal decomposition chemistry, but they do not quantify smoke production, soot yield, or smoke optical density. Direct smoke evidence is limited and sometimes qualitative or obtained under different combustion conditions. Future studies should report total smoke production, smoke production rate, and smoke density under specified heat flux, ventilation, and flaming/non-flaming conditions, and should distinguish oxidative combustion from inert pyrolysis.

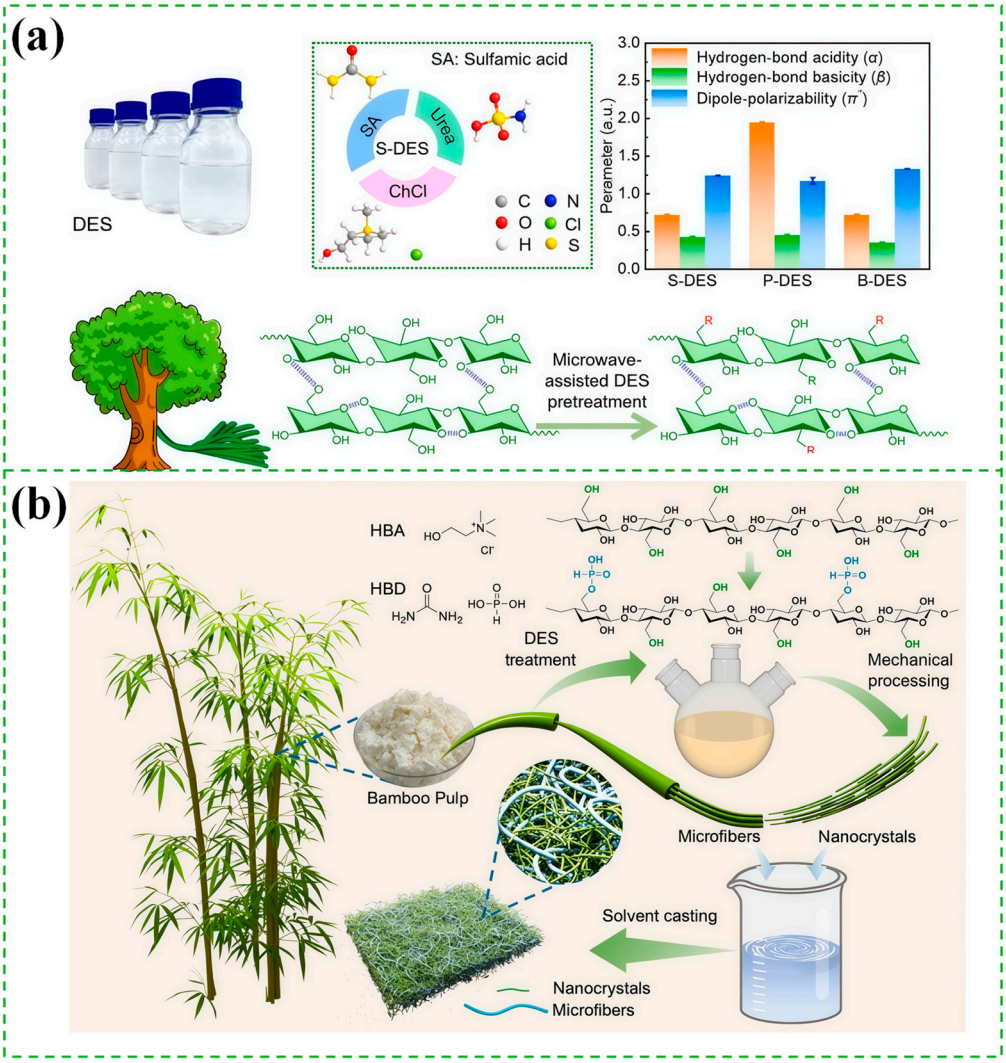

Figure 11. (**a**) Digital photographs and composition of S-DES, and key characteristics of different types of DES and schematic diagram of molecular structure [43]. Reproduced with permission from Ref. [43]. (**b**) Construction of multiscale flame-retardant films [46]. Reproduced with permission from Ref. [46].

3.4. Leaching Resistance and Mechanical Property Retention

In this subsection, leaching-resistance and mechanical-retention claims are based on intact wood/bamboo studies where available; particle-, gel-, and composite-level studies are labeled as indirect or valorization evidence. Conventional flame retardants are prone to leaching in humid and thermal environments, resulting in poor durability of flame re-

tardancy; meanwhile, strongly acidic or alkaline flame retardants can cause chemical degradation of the lignocellulosic skeleton, severely compromising the mechanical strength of wood. DES-modified wood has demonstrated significant advantages in both of these core metrics, thereby laying a performance foundation for its high-value application in advanced engineering materials.

In terms of leaching resistance, minimal specimen mass loss, reduced water absorption, and chemical modification of a biomass filler are not interchangeable measures of durable flame-retardant retention in wood. A durability claim requires the leaching/washing protocol, exposure duration, retained active-element content, and fire performance before and after exposure. Textile washing tests and wood leaching tests are not equivalent, and short-term water uptake should not be equated with long-term durability. Where such data are unavailable, retention is described as limited or short-term rather than durable. Can et al. [47] reported that the weight percentage gain (WPG) of ChCl–urea-treated spruce decreased from 97.63% to 1.82% after a 14-day leaching test. This corresponds to a loss of approximately 98% of the original weight gain (a decrease of 95.81 percentage points), indicating substantial leaching of the treatment rather than substantial leaching or not being durably retained. The result shows that, under the tested conditions, the ChCl–urea components were largely not retained in the wood; it does not provide evidence for cell-wall anchoring or long-term leaching resistance. Because the study did not spatially resolve whether the residual 1.82% WPG was localized within the cell wall, the leaching behavior is best interpreted as a limiting case for neutral DES systems, consistent with a large fraction of the treatment being weakly retained or physically deposited rather than covalently/coordinatively fixed. Zabihi et al. [26] reported phosphorus retention in macadamia nutshell powder under mild conditions; this supports chemical interaction with the biomass matrix, but it is indirect particle-level evidence and does not establish cell-wall localization or a specific covalent bond. Zhang et al. [48] treated Taiwan fir with a metal-salt-based DES and reported reduced water absorption by approximately 58%; this is a short-term water-uptake measurement, not a long-term leaching or durability test, and it does not by itself identify a covalent crosslinking mechanism. These studies report different durability-related endpoints—mass loss, water uptake, or filler-level chemical modification—and do not provide comparable evidence for long-term flame-retardant retention in intact wood. Where the leaching protocol, exposure duration, retained active-element content, and fire performance before and after exposure are not all reported, leaching resistance should be described as limited or short-term rather than a general advantage of DES systems.

Many mechanical improvements summarized below were obtained in combined processes involving hot pressing, resin/silica impregnation, polymerization, or aligned wood reinforcement. These results do not isolate the DES contribution; untreated, DES-only, and subsequent-processing controls should be reported where available, together with final density, loading direction, and moisture-conditioning conditions. Missing controls are identified as limitations, and fire performance and mechanical retention should be measured in the same material system before concluding that both improved simultaneously.

In systems with direct evidence of crystalline-domain preservation, modification may preferentially target amorphous regions; however, this should not be generalized to all DES treatments. Crystallinity index, absolute cellulose retention, DP, and preservation of crystalline domains are distinct metrics: an increased relative crystallinity index can simply reflect removal of amorphous components and does not by itself demonstrate undamaged cellulose or retained mechanical properties.

Ran et al. [8] proposed a DES-retention strategy, in which DES was retained within the cell wall for in situ plasticisation and modification, reducing the softening temperature of wood from 100 °C to 55 °C and significantly improving the viscoelastic deformability of cell-wall polymers during hot pressing. The resulting densified wood achieved a density of 1.01 g/cm^3, a flexural strength of 197.04 MPa, and an elastic modulus of 10.17 GPa, with a shape recovery rate of only 1.5% after soaking–boiling–drying cycles. This strategy successfully addressed the dimensional instability problem of conventional densified wood caused by moisture-induced spring-back, offering a viable pathway for converting fast-growing wood into high-performance structural materials. The wood-based eutectogels reported by You et al. [49,50] are discussed here as multifunctional valorization examples; they do not quantify cell-wall-level leaching resistance or flame retardancy of intact wood. In the field of wood–gel composites, You et al. [49] impregnated a wood skeleton with a polymerisable DES and fabricated multifunctional wood-based eutectogels via initiator-free solar polymerization. Figure 12 illustrates the complete fabrication process of this eutectogel, using choline chloride, acrylic acid, and acrylamide as raw materials through green solvent and solar-driven, initiator- and crosslinker-free polymerization, along with its diverse application scenarios in human motion detection, material adhesion, recyclable reshaping, and smart home systems. The tensile strength reached 52.8 MPa, while environmental tolerance was maintained over a wide temperature range from −80 °C to 200 °C. Concurrently, You et al. [50] prepared wood-based composite gels using the same polymerisable DES system via rapid UV-initiated polymerization; Figure 13 depicts the fabrication process from wood-skeleton impregnation to UV polymerization, as well as a schematic of the oriented cellulose fibres within the wood serving as the reinforcing skeleton. Utilising the aligned cellulose fibres in the wood as the reinforcing framework, the composite gels exhibited a tensile strength of 62.51 MPa, a toughness of 7.77 MJ/m^3, and an elongation at break of 19.91%. These tensile-strength values demonstrate the mechanical performance of the eutectogels but do not establish flame retardancy; fire performance and mechanical retention were not measured in the same material system, and the DES contribution is combined with polymerization and wood-skeleton reinforcement. Such materials combine excellent mechanical properties, sensing performance, and thermal insulation, showing clear application prospects in frontier fields including wearable electronics and intelligent building systems. In the area of wood composites, Abouzeid et al. [21] employed microwave-assisted DES pretreatment combined with resin/silica impregnation and high-temperature densification, resulting in an increase in flexural strength from 60.9 MPa to 105.8 MPa. In this combined process, DES pretreatment primarily creates a porous network, the subsequent resin/silica impregnation fills these voids, and high-temperature densification further compacts the structure. The mechanical enhancement therefore arises from the synergistic interplay of all three steps, rather than DES modification alone. Collectively, while DES treatment can assist in modifying the wood structure, the resulting mechanical retention cannot be generalized merely from the preservation of cellulose crystallinity. It is highly dependent on the entire processing history, the degree of chemical anchoring, and the final composite structure.

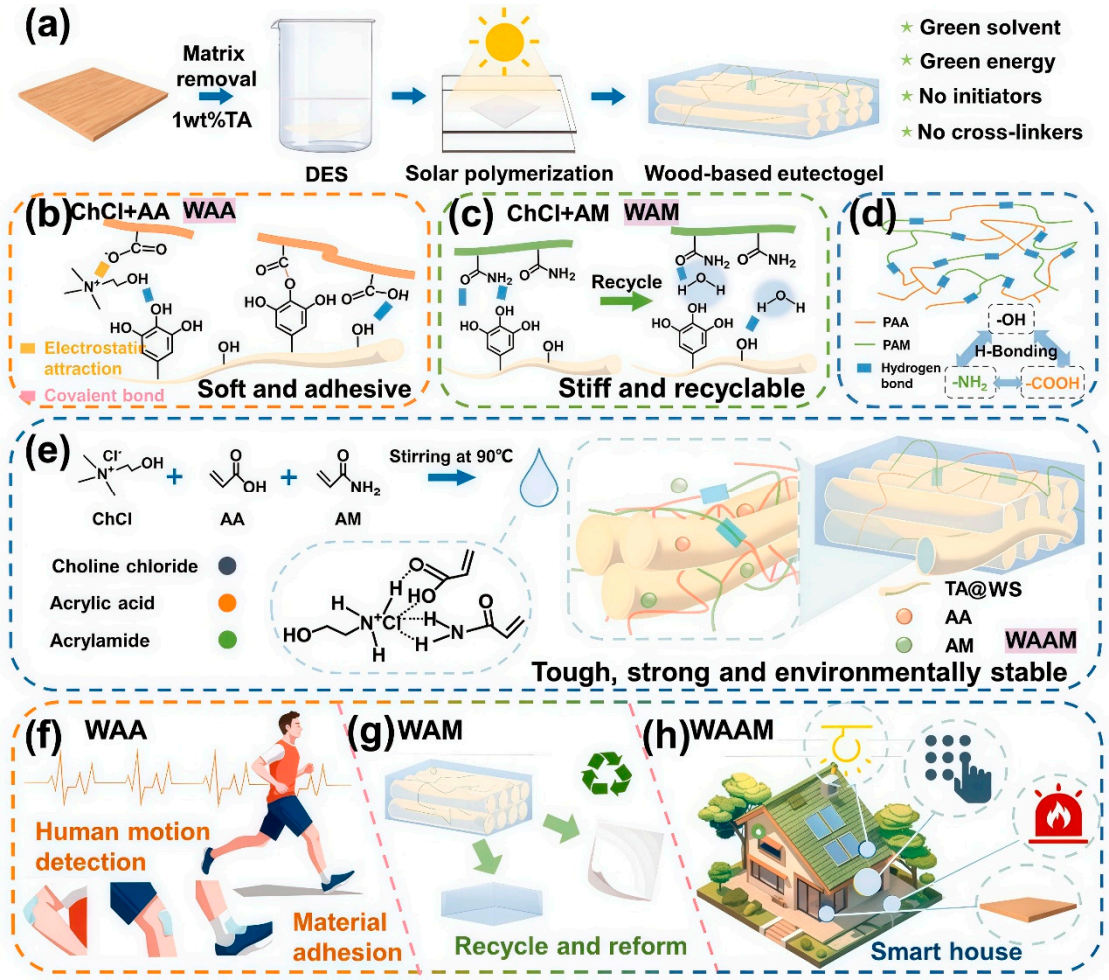

Figure 12. Schematic illustration of synthesis, properties, and applications of the wood-based eutectogels. (**a**) Schematic depicts the fabrication process and advantages of wood-based eutectogels. The molecular structures and interactions of WAA (**b**), WAM (**c**), (ChCl/AA/AM) PDES (**d**), and WAAM (**e**). The applications of WAA (**f**), WAM (**g**), and WAAM (**h**) [49]. Reproduced with permission from Ref. [49].

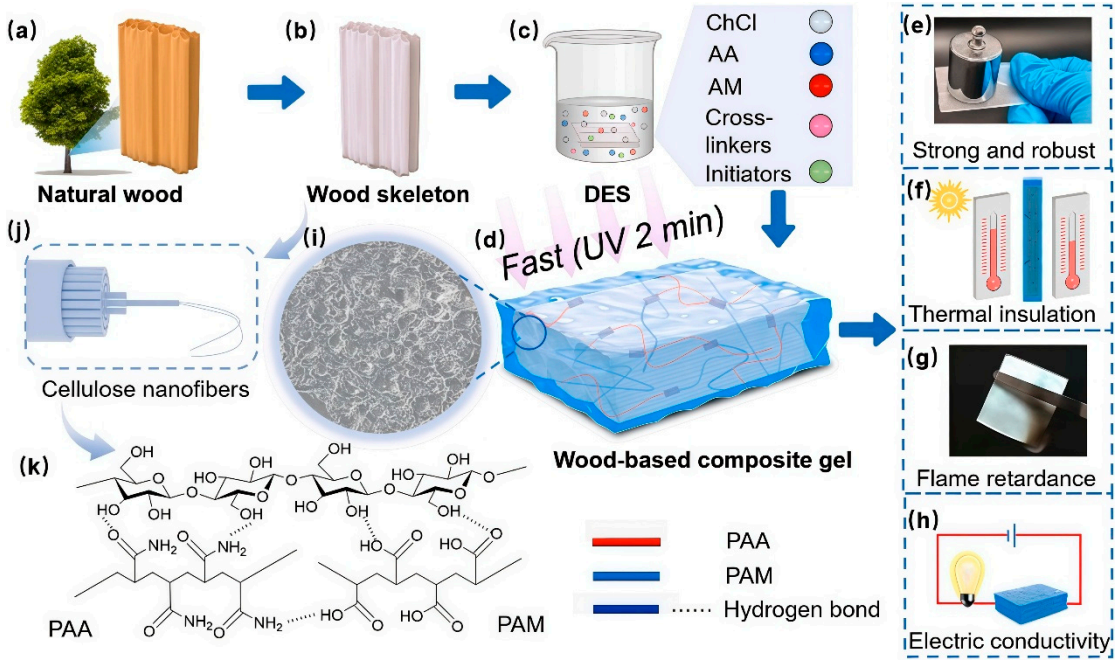

Figure 13. (**a**–**d**) Preparation process of wood-based composite gel (WCG); (**e**–**h**) Advantages of WCG; (**i**) Optical micrographs of AAMG (×1500) in cross section; (**j**) Schematic diagram of cellulose nanofibers in wood skeleton; (**k**) Schematic illustration of multiple hydrogen bond structures in AAMG [50]. Reproduced with permission from Ref. [50].

The metrics in Table 2 are not directly interchangeable. Mass-normalized heat release rates measured by micro-scale calorimetry (W/g) cannot be directly compared with area-normalized cone-calorimeter results (kW/m²), and peak values (PHRR) should not be conflated with average values. TGA-derived char yields depend on the purge gas and final temperature (e.g., N_2, 800 °C), which are often under-reported. Furthermore, small-scale flammability tests (LOI, UL-94) do not constitute structural fire-resistance ratings. Cross-system performance rankings should therefore be interpreted cautiously.

Table 2. Comparative evidence of representative DES-modified systems: test metrics, units, and conditions.

Substrate	DES Formulation	Test Method & Key Metrics	Main Outcomes	Durability/Mechanical	Ref.
Chinese fir (coating)	ChCl–Urea–Phosphorous acid + chitosan	LOI; UL-94; Cone cal. (kW/m²)	LOI 23.9→41.4%; V-0; Average HRR reduction: 61.8% (not peak HRR)	Recyclable in citric acid	[22]
Straw CNF laminate	Ammonium dihydrogen phosphate + binary DES	LOI; Cone cal. (kW/m²)	LOI 74.9%; PHRR −74.3%; Tensile ×3	Self-bonded	[25]
Bamboo fiber/epoxy	Phytic acid–Urea–Sulfamic acid	LOI	LOI 22.3→44.5%	N.A.	[9]
Bamboo (bulk)	ChCl–Urea–Phosphorous acid	LOI; Cone cal.; TGA	LOI 37.3%; PHRR −20.6%; TSR −23.0%	Char +204.3%	[23]
Cellulose fabric	ChCl–Phosphoric acid–Sulfamic acid	LOI; Washing	LOI 48%; 33.5% after 50 washes	50 washing cycles	[27]
Cotton fabric	Phytic acid + ChCl	Cone cal. (kW/m²); TGA	PHRR 213.4→50.3 kW/m²; THR −78%; Char 11.8→33.5%	N.A.	[29]
Wood fiber	Reactive ternary DES	LOI; Micro-scale cal. (W/g); TGA (N_2, 800 °C)	LOI 20.7→46.3%; PHRR 126.8→22.7 W/g; Char 24.2→49.23%	N.A.	[45]
Bamboo bioplastic	Multi-scale DES	LOI	LOI 62.17%; Tensile 82.32 MPa	N.A.	[46]

Table note: Unless otherwise stated, percentage reductions in HRR, THR, and smoke metrics are relative to the untreated or uncoated counterpart of the same wood/bamboo species. Fire tests were conducted by cone calorimetry at the heat flux reported in each source; mechanical data refer to the testing standard and moisture condition reported in the original study. "Average HRR" and "peak HRR" are distinguished and are not used interchangeably.

4. Conclusions and Future Perspectives

Although DESs have demonstrated significant advantages in cell-wall-level flame-retardant modification of wood, current research remains largely confined to laboratory-scale mechanistic validation and performance, and there is still a considerable gap before industrial application can be realized. The viscosity issue of DESs constitutes the primary obstacle to scaling up impregnation efficiency, as most DESs exhibit significantly higher viscosity at room temperature than conventional waterborne flame retardants. Studies have shown that the addition of an appropriate amount of water can effectively reduce

the viscosity of DES systems, with the highest lignin removal efficiency achieved at a water content of 10 wt% in a choline chloride-based DES [51]. However, excessive water can disrupt the hydrogen-bonding network of DES, and strict control of water content below 30% is generally required to maintain optimal pretreatment performance [16]. However, this specific water-content threshold is highly formulation-dependent and may vary across different DES systems. Moreover, substituting low-viscosity components such as ethylene glycol for some high-viscosity counterparts is also an effective strategy to reduce the viscosity of DES systems [52]. However, such substitutions must be evaluated for potential toxicity; the "green" label of DESs is highly composition-dependent. Although continuous heating during large-scale production can improve fluidity, the associated increase in energy consumption and process complexity cannot be overlooked. Concurrently, raw material costs and economic feasibility are equally unavoidable considerations; although raw materials such as choline chloride and organic acids have already achieved industrial-scale production, their costs remain higher than those of conventional inorganic flame retardants. The cost and availability of certain specialized hydrogen bond donors or acceptors may further limit the large-scale application of DESs [53]. Furthermore, a closed-loop recycling system specifically for DES-based flame-retardant functionalization has not yet been established. It is critical to distinguish the recovery of unused processing solvents from the DES components that are irreversibly retained or consumed within the final wood product. Membrane filtration and antisolvent precipitation are currently the two primary technical routes for DES recovery. However, the delignification capacity of DESs gradually decreases during the recycling process due to the accumulation of lignin degradation products and hemicellulose fragments, and the lignin extraction efficiency of DES recovered via ultrafiltration decreases by approximately 15% in the third cycle compared with fresh DES [54]. Supplementation of acid components and additional antisolvent treatment can partially restore the efficiency of recovered DES to 78%, compared with 82% for fresh DES [54]. A recently developed integrated process coupling ultrafiltration with continuous adsorption and nanofiltration has been shown to remove approximately 50% of lignin degradation products, enabling the purified recycled DES to achieve a lignin extraction yield of approximately 90%, close to that of fresh DES [55]. Achieving efficient recovery and recycling of DESs while ensuring the modification effectiveness is critical to the economic viability and environmental friendliness of this technology. However, most of these recovery metrics are based on lignin extraction (fractionation), rather than the retention of flame-retardant components. For functionalization, repeated treatment will be affected by component consumption, water addition, solvent composition changes, and impurity accumulation. Therefore, delignification performance should not be assumed to represent retained functionalization performance; specific recovery studies focused on flame-retardant DES systems are still required.

On the basis of continued advances in fundamental research, the functionalization direction of DES-modified wood is expanding from single-function flame retardancy and smoke suppression towards the integrated multifunctionality of flame retardancy, smoke suppression, anti-decay, and superhydrophobicity. The high designability of DESs provides a unique technological advantage for this integrated approach; by incorporating fluorine- or silicon-containing components, metal ions, or antimicrobial active ingredients into DES formulations, simultaneous in situ construction of multiple functionalities at the cell-wall level can be achieved [56]. Nevertheless, the use of fluorine-containing components raises significant concerns regarding environmental persistence and bioaccumulation. Recent studies have demonstrated that alcohol-amine-based DESs can be used for partial delignification, followed by N/P-functionalization of the dissolved lignin and reincorporation into the wood matrix, yielding tough flame-retardant wood

with a tensile strength of 425.2 MPa [57]. In addition, the synergistic integration of DES modification with other wood modification technologies—such as thermal treatment, compressive densification, and resin impregnation—can further enhance the comprehensive performance and market competitiveness of modified wood [52]. For instance, microwave-assisted DES pretreatment combined with resin/silica impregnation and high-temperature densification has been shown to increase the flexural strength of basswood (linden wood) from 60.9 MPa to 105.8 MPa, while simultaneously improving dimensional stability and termite resistance [21].

In summary, DESs, as a class of green, designable cell-wall-level modification media, offer a novel technological pathway for functionalizing wood with flame retardancy and smoke suppression that is fundamentally distinct from conventional physical impregnation. Although often described as "green," their environmental profile depends heavily on specific composition, treatment conditions, residual chemicals, and recovery requirements. Where direct evidence is available, their potential advantages include durable fixation of flame-retardant components through hydrogen bonding, metal coordination, or covalent grafting, and reduced mechanical degradation through cell-wall-level modification; however, durable fixation and mechanical retention have not been demonstrated simultaneously in all systems. Smoke suppression is described as directly demonstrated only where measured smoke outcomes are reported; for other systems, it remains a proposed mechanism based on pyrolysis-product distribution and char-formation evidence. Although this technology still faces engineering challenges such as viscosity control, cost optimization, and solvent recovery in large-scale applications, as green chemistry principles are further developed and engineering technologies advance, the prospects for high-value utilization of DES-modified wood in high-rise buildings, premium rail transit, and other high-performance engineering fields are promising. These applications are framed as prospective; their realization will depend on the availability of long-term durability, full-scale fire testing, and manufacturing evidence. Collectively, direct evidence for simultaneous cell-wall chemical anchoring, leaching resistance, mechanical retention, and flame/smoke suppression in the same intact lignocellulosic substrate remains limited. Most current support comes from intact-substrate performance tests and component-level mechanistic analogies. Future work should integrate spatially resolved cell-wall characterization, chemical-bonding analysis, leaching tests, and cone-calorimetry/smoke tests on identical intact wood/bamboo samples.

In conclusion, this review demonstrates that DES-based cell-wall-level functionalization offers a promising pathway for enhancing the fire safety of lignocellulosic materials, but the current evidence base remains heterogeneous and requires careful qualification. The evidence matrix (Table 1) shows that direct cell-wall localization, bonding chemistry, leaching/washing resistance, fire performance, smoke response, and mechanical properties are not consistently reported across key wood- and bamboo-based studies. Where supported by spatially resolved and bonding-specific evidence, specific DES systems can penetrate intact wood, induce moderate swelling, and retain flame-retardant elements through hydrogen bonding, metal coordination, or covalent grafting, thereby imparting flame retardancy while largely preserving mechanical integrity in the systems where these properties were measured. However, these advantages are strictly formulation-dependent. The dominant fixation mechanism, the degree of crystalline-region preservation, and the relative contributions of radical trapping versus gas dilution vary significantly with DES composition and treatment conditions, meaning that broad claims regarding "universal" mildness or inherent smoke suppression cannot be generalized. To reliably translate these materials into practical engineering products, critical evidence gaps must be bridged. Future research must prioritize spatially resolved chemical-bonding characterization within intact wood, direct

measurements of smoke toxicity (e.g., CO, HCN) and long-term leaching under realistic conditions, synchronized evaluation of fire and mechanical performance within identical material systems, and recycling strategies tailored to retained functionalization rather than mere delignification. Until such comprehensive data are available, claims of broad environmental friendliness and structural reliability for DES-modified wood remain prospective.

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