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Review

Lignin-Based Phenol-Formaldehyde Resins: Activation Strategies and Synergistic Pathways from Physical Pretreatment to Chemical Modification

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Abstract

Traditional phenol-formaldehyde (PF) resin adhesives rely on petroleum-based phenolic monomers, facing dual pressures from resource constraints and environmental concerns. Lignin, an abundant renewable aromatic polymer in wood cell walls with a molecular structure rich in phenolic hydroxyl groups, serves as an ideal bio-based precursor for producing green PF resins. Developing lignin-based phenol-formaldehyde (LPF) resins not only enables the high-value utilization of forest biomass but also aligns with sustainable development strategies. However, the large-scale industrial application of lignin remains challenging due to its inherent drawbacks, such as low reactivity. This review focuses on lignin-modified PF resins, systematically summarizing the main physicochemical modification methods—including phenolation, hydroxymethylation, demethylation, and depolymerization activation—along with their mechanisms of influence on resin properties. It compares and discusses the advantages and disadvantages of different modification routes, analyzes current key technical bottlenecks, and prospects future development directions, aiming to provide a reference for research and application of forest-based green adhesive materials. This review concludes that the combination of physical pretreatment and targeted chemical modification is the most promising approach for enhancing lignin reactivity and resin performance. Future research should prioritize developing green modification technologies, such as those based on deep eutectic solvents (DESs) and aqueous systems, and establish quantitative structure–property relationships for lignin-based resins to accelerate the transition of lignin-based phenolic resins from laboratory research to industrial-scale production.

Keywords: lignin; phenol-formaldehyde resin; physical pretreatment; chemical modification; research progress

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1. Introduction

As the main component of terrestrial ecosystems, forests not only maintain global carbon balance and biodiversity but also provide vast reserves of woody biomass resources [1]. Within the wood cell wall structure, lignin, coexisting with cellulose and hemicellulose as one of the three major components, is the second most abundant renewable aromatic

polymer in nature after cellulose, accounting for approximately 15%–35% of wood dry weight [2,3]. Globally, the pulp and paper industry and forestry biorefineries alone generate over 50 million tons of industrial lignin annually [4]. However, the vast majority of this lignin is used as low-value fuel for direct combustion or discarded, with less than 2% being converted into high-value-added products like water reducers or dispersants [5,6]. This utilization pattern represents not only a tremendous waste of forest biomass resources but also causes significant environmental pollution [7], including the release of greenhouse gases and particulate matter from combustion, and the accumulation of lignin-rich effluents that require costly treatment. Therefore, developing high-value utilization pathways for lignin, transforming it from inefficient fuel into high-performance materials, has become a key strategic direction for achieving the sustainable full-component utilization of forest resources, promoting green material development, and addressing the challenge of dwindling fossil resources [8]. Among these pathways, using lignin to partially substitute fossil-based phenol in PF resin preparation is one of the most industrially promising and actively researched directions.

As one of the earliest synthesized and industrially produced resins, PF resin is widely used in adhesives, wood-based panels, coatings, foam plastics, carbon fiber composites, air filter paper, and other industries due to its low cost, wide raw material availability, good weather resistance, high bonding strength, and excellent thermal and dimensional stability [9,10]. Its applications also extend to high-tech fields such as transportation, national defense, military equipment, and aerospace [11–13]. Traditional PF resins are primarily formed through the polycondensation of phenols and aldehydes, with most of these raw materials derived from fossil resources. This not only presents resource sustainability issues but also leads to drawbacks like high curing temperatures, poor mechanical properties, susceptibility to glue penetration, and formaldehyde emissions, posing potential hazards to the environment and human health [14–16]. Against the backdrop of increasingly scarce global petroleum resources, utilizing renewable biomass resources to replace phenol has become a research hotspot and inevitable trend in the polymer materials field to enhance the "green" attributes and sustainable competitiveness of PF resins [17,18].

Among various biomass feedstocks, lignin exhibits natural advantages as a phenol substitute. During the biosynthesis of wood, lignin acts as a natural "binder", filling the spaces between cellulose microfibrils, imparting rigidity and mechanical strength to the plant cell wall [19,20]. Chemically, lignin is a three-dimensional amorphous polymer composed of phenylpropane units linked by carbon–carbon and ether bonds [21]. The monolignol composition varies significantly by plant species: softwood lignins are predominantly guaiacyl (G-type, derived from coniferyl alcohol), hardwood lignins contain both guaiacyl and syringyl (S-type, from sinapyl alcohol) units in varying ratios (typically G/S = 1:1 to 1:3), and grass lignins additionally incorporate p-hydroxyphenyl (H-type, from p-coumaryl alcohol) units [22]. These structural differences have profound implications for LPF resin performance: S-rich lignins, with their lower degree of condensation and higher proportion of reactive C_5 positions, generally exhibit higher reactivity toward formaldehyde and enable higher phenol substitution rates (up to 60%–70%) compared to G-rich softwood lignins (typically 30%–50%) [23]. Moreover, the S/G ratio influences the product distribution during chemical modification—S units are more susceptible to demethylation, whereas G units show higher phenolation efficiency [24]. Its molecular skeleton is rich in structures such as phenolic hydroxyl, guaiacyl, and syringyl groups, which are highly similar to those of phenol, making it an ideal bio-based precursor for PF resin synthesis [25,26]. Using lignin to partially replace phenol can not only reduce dependence on fossil resources but also leverage its abundant phenolic hydroxyl groups

and aromatic structure as reactive sites, thereby lowering the free formaldehyde content in the resin and improving the thermomechanical properties of the cured product [27,28]. The exploration of using lignin to prepare PF resin adhesives dates back to the early 20th century, with significant technological advancements achieved by the 1990s. Despite extensive research worldwide on modifying and applying various types of lignin, the industrial application of LPF resins still faces several key bottlenecks. It has yet to achieve widespread large-scale production outside pioneering efforts in the Nordic region [29].

The fundamental challenges and shortcomings in current research mainly focus on the following aspects: Firstly, the diversity of lignin sources and isolation processes leads to broad molecular weight distribution and strong structural heterogeneity, resulting in significant batch-to-batch variations in reactivity that severely affect product consistency and controllability [30]. Secondly, the aromatic rings in lignin molecules experience steric hindrance and have relatively limited reactive sites. When unmodified lignin is used directly to substitute phenol, the substitution rate typically struggles to exceed 30%–50%; higher rates often drastically deteriorate the resin's bonding performance and water resistance. Thirdly, although various chemical modification strategies such as phenolation, hydroxymethylation, demethylation, and depolymerization activation have been proposed to enhance lignin reactivity, most methods still face issues like high reagent consumption, non-green processes, and difficulty balancing modification efficiency with cost. These shortcomings collectively constitute the key bottlenecks hindering the transition of lignin-modified PF resins from laboratory research to industrial, high-performance applications.

In light of this, systematically reviewing research progress in this field and identifying future development pathways hold significant academic and practical value for promoting the high-value utilization of forest biomass and the development of eco-friendly adhesive materials. The present review distinguishes itself from previous summaries by adopting a comparative and critical approach, systematically evaluating multiple activation strategies through the lens of their mechanism of action, activation efficiency, process practicality, and industrial potential. This paper focuses on lignin-modified phenolic resins. Taking the sustainable utilization of lignin—a core component of forestry—as its starting point, it provides a comprehensive review of the structures and properties of lignin from various sources, the mechanisms by which major chemical modification methods regulate resin performance, including physical pretreatment strategies, demethylation, phenolation, hydroxymethylation, and degradation-based activation, and the current status of their applications in wood adhesives, composite matrix materials, and other fields. The review further identifies key knowledge gaps—particularly in quantitative structure–property relationships, synergistic effects among modification strategies, and industrial-scale implementation—and proposes priority research directions to address these challenges. The aim is to provide a theoretical basis and practical guidance for developing green polymer materials derived from forest biomass.

2. Physical Pretreatment

The source of the plant material and the isolation method significantly influence the physicochemical properties and processing performance of industrial lignin; obtaining lignin with a uniform structure and a rich variety of functional groups is a key prerequisite for the preparation of high-performance lignin-based phenolic (LPF) adhesives. Before pretreatment, lignin source materials typically require basic preparation steps including drying (to reduce moisture content, generally to <10%), grinding (to achieve particle sizes in the range of 20–200 mesh, depending on the downstream processing requirements), and homogenization to minimize batch-to-batch variation [31]. The particle size of lignin feedstocks has been shown to influence both the efficiency of physical pretreatment and

the subsequent chemical reactivity; smaller particle sizes increase surface area and enhance mass transfer during fractionation or chemical modification, but may also increase dusting and handling challenges [32]. Physical activation methods are designed precisely to achieve this goal. During pretreatment, techniques such as solvent fractionation, membrane separation, ultrasonication, microwave treatment, and steam bursting [33] are employed to effectively improve lignin quality through stepwise purification or energy-field-assisted depolymerization. Based on their mechanisms of action, these methods can be broadly classified into two categories: first, fractionation purification technologies based on differences in solubility or molecular weight, aimed at obtaining more active and homogeneous lignin components; second, technologies utilizing energy-field-assisted depolymerization or activation, aimed at directly increasing the content of functional groups and reactivity. These two strategies can be used independently or in a synergistic and complementary manner.

A critical consideration for industrial implementation is the economic feasibility of these pretreatment steps. The drying and grinding steps described above, while beneficial for characterization and handling uniformity, add considerable operational costs. From an industrial perspective, it is theoretically feasible to bypass the drying step by using the aqueous lignin stream from the pulping process directly in the synthesis of aqueous-phase PF resin. However, this approach would require process adjustments to accommodate residual chemicals and water in the pulping liquor. The use of organic solvents in fractionation and purification strategies (e.g., ethyl acetate, methanol, ethanol) presents additional engineering challenges: (i) solvent recovery requires significant capital investment in distillation or membrane systems, typically recovering 80%–95% of solvents at substantial energy cost; (ii) the flammability and toxicity of organic solvents impose stricter safety and environmental compliance requirements; (iii) most existing PF resin manufacturing facilities are not equipped with solvent handling systems, limiting the compatibility of solvent-based lignin modification with current production infrastructure. These considerations strongly motivate the development of aqueous-based modification strategies, such as water-soluble lignin fractionation via ultrafiltration and water-based chemical modifications (e.g., demethylation in NaOH/urea aqueous systems), which represent more industrially viable pathways.

In fractionation and purification, solvent fractionation leverages differences in hydrogen bonding interactions between different organic solvents and lignin molecules to achieve directional fractionation based on solubility. After fractionation, lignin's methoxy content, relative molecular weight distribution, and alkaline nitrobenzene oxidation products show significant differences from the initial material, indicating substantial changes in its chemical structure and subsequent reactivity [34]. Particularly, low-molecular-weight fractions exhibit lower dispersity and are enriched in guaiacol structures with saturated side chains, whose benzene rings have ortho vacancies more favorable for substituting phenol in LPF synthesis. For instance, using water fractionation to isolate water-insoluble lignin fractions from fast pyrolysis bio-oil (FPBO) for phenol substitution showed that resin viscosity increased with substitution rate, but the resulting pyrolytic lignin-based PF resin exhibited good bonding performance under both dry and wet conditions [35]. Conversely, fractionation with ethyl acetate yielded a soluble lignin fraction (LFSol) with low molar mass, high phenolic hydroxyl content, and good solubility; LPF resins prepared from it showed comparable bonding performance and water resistance to pure PF resin [36]. Complementary to this, ultrafiltration technology selectively retains lignin fractions of different molecular weights based on membrane pore size. Studies on preparing LPF resins from lignin extracted via ultrafiltration from black liquor indicated that when using 18.8% ultrafiltration lignin, 22.9% phenol, and 58.3% formaldehyde, the mechanical properties and water resistance of particleboards pressed with the synthesized resin reached levels

typical of commercial PF resins [37]. Furthermore, as a simple and green physical separation method, ultrafiltration membrane fractionation can also improve lignin's color and biocompatibility, enhancing the uniformity of lignin nanoparticle size distribution [38]. Overall, fractionation/purification strategies are effective in obtaining lignin fractions with high reactivity and low dispersity. However, they essentially involve screening and enrichment of existing lignin, and the trade-off between yield/purity and solvent recovery costs remains a factor for industrial consideration.

Nevertheless, even after obtaining relatively uniform fractions through fractionation, the inherent functional group heterogeneity, relatively high molecular weight, and low hydroxyl group content of industrial lignin still constrain its high-value utilization. Energy-field-assisted depolymerization/activation technologies can further break the molecular skeleton and increase active sites. Ultrasound-assisted depolymerization is a mild, efficient, and economical method whose core lies in the acoustic cavitation effect attacking aryl ether bonds in lignin, degrading macromolecules under high acceleration from fluctuation and shear forces (Figure 1a) [39]. Combining piezoelectric materials with photocatalytic materials can leverage the periodic potential generated by ultrasonic stirring to regulate carrier motion, enhancing depolymerization efficiency. For example, MoS_2/ZnO heterostructure photocatalysts perform excellently in sonophotodepolymerization systems (Figure 1b–d) [40]. After ultrasonic depolymerization, the hydroxyl content of depolymerized lignin (DL) increased by 36.9%. This DL could be directly used to prepare depolymerized lignin phenol-formaldehyde (DLPF) resin, resulting in significantly improved bonding strength, a reduced curing temperature of 60 °C, and over 50% reduction in formaldehyde emission [41]. Microwave-assisted conversion achieves lignin activation through the synergistic effects of thermal and non-thermal mechanisms. In a methanol/formic acid solvent system at 140 °C, the conversion rate for microwave-assisted depolymerization of kraft lignin reached 78%. Using mixed metal oxide (MMO) catalysts further increased the conversion to 89%, with the main liquid products being G-type phenolic monomers (~60%) [42]. Microwave irradiation can also be used for phenolation modification of acid-insoluble lignin. After phenolation, molecular weight and glass transition temperature decreased, making it more suitable for PF resin adhesives [43]. Additionally, an HBr-catalyzed activation method utilizing microwave irradiation significantly increased the phenolic hydroxyl content of modified lignin and its reactivity with formaldehyde [44]. Compared to ultrasound, microwave heating is more efficient and rapid, but controlling reaction selectivity and quantifying non-thermal effects remain issues requiring deeper investigation.

Different from the energy injection modes of ultrasound and microwave, steam explosion (SE) pretreatment offers lignin a deconstruction method integrating physical tearing and chemical separation. For coconut husk soda lignin, impregnation with dilute acid (ASEL), water (WSEL), or 2-naphthol (NSEL) followed by SE treatment showed that the impregnation method significantly affected lignin yield and structure. ASEL had the highest solid recovery rate (55.89%), and its weight-average molecular weight (Mw) was as high as 72,725 $g \cdot mol^{-1}$, far exceeding WSEL (13,112 $g \cdot mol^{-1}$) and NSEL (6891 $g \cdot mol^{-1}$). This difference directly influenced its reaction activity and incorporation efficiency in PF resin synthesis. All SE lignins were enriched in non-condensed G- and S-type units, indicating that regulating SE pretreatment conditions and impregnation media can directionally regulate lignin's physicochemical properties [45]. This method combines physical and chemical effects, but equipment investment and the difficulty of precise parameter control limit its large-scale promotion.

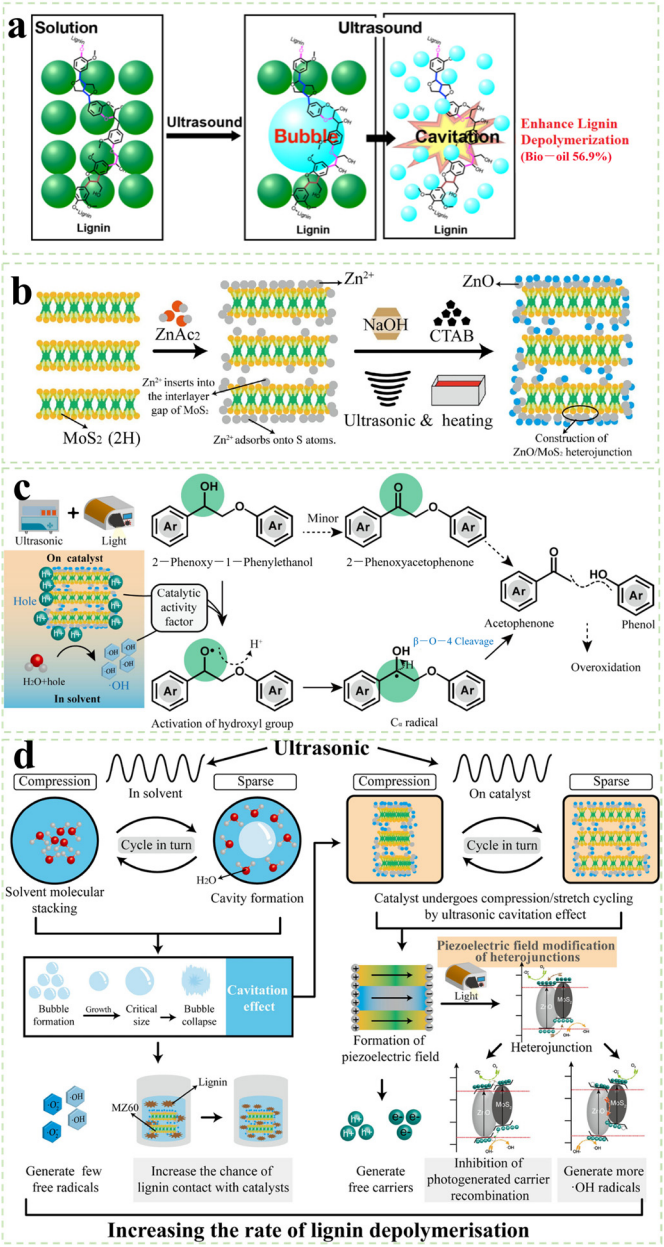


Figure 1. (**a**) Mechanism of ultrasound-assisted lignin depolymerization. Reproduced with permission from reference [39]. Copyright 2020, Elsevier. (**b**) Catalyst synthesis mechanism. (**c**) Conversion pathway of PP-ol under combined ultrasound and light effects. (**d**) Mechanism of ultrasound-enhanced lignin depolymerization efficiency. Reproduced with permission from reference [40]. Copyright 2024, Elsevier.

A key insight derived from comparisons of various fractionation and depolymerization techniques is that low-molecular-weight lignin fractions (Mw < 3000 Da) exhibit excellent reactivity and compatibility with PF resin matrices. This is attributed to (i) lower polydispersity (PDI < 2.5), which ensures uniform reaction behavior; (ii) a guaiacol-based structure rich in ortho-vacancies, which facilitates electrophilic substitution reactions with formaldehyde; and (iii) a high density of phenolic hydroxyl groups per unit mass (typically >2.5 mmol/g), which provides more cross-linking sites during the polycondensation reaction. However, excessive degradation, resulting in a molecular weight below approximately 2000 Da, compromises the cohesive strength of the resin. In contrast, although high-molecular-weight fractions (Mw > 10,000 Da) may contain a higher total number of phenolic hydroxyl groups per molecule compared to their lower-Mw counterparts, their

macromolecular conformation significantly reduces the spatial accessibility of active sites. Therefore, for phenol substitution, "ideal lignin" should have a medium molecular weight (Mw~2000–5000 Da), a narrow distribution (PDI < 3), a high phenolic hydroxyl content (>2.0 mmol/g), and an abundance of ortho-vacancies. This structure–property relationship warrants systematic investigation in future research.

To facilitate a systematic comparison of the four major physical pretreatment strategies, Table 1 summarizes the goals, mechanisms, advantages, and limitations of each method.

Table 1. Comparison of physical pretreatment strategies for lignin activation.

Method	Goal	Mechanism	Mw Reduction	Hydroxyl Increase	Advantages	Limitations
Solvent Fractionation	Isolate active lignin fractions	Solubility-based separation	40%–70% (low-Mw fraction)	+20%–35% (in enriched fraction)	Simple equipment; effective enrichment of low Mw fractions	Solvent recovery cost; limited yield
Ultrafiltration	Molecular weight-based separation	Membrane pore size exclusion	30%–60%	+15%–25%	Green process; scalable; preserves lignin structure	Membrane fouling; throughput limitations
Ultrasound-Assisted	Depolymerization/activation	Acoustic cavitation cleaves ether bonds	50%–65%	+36.9%	Mild conditions; increased OH content by up to 36.9%	Scalability challenges; energy efficiency
Microwave-Assisted	Rapid depolymerization/activation	Thermal + non-thermal effects	60%–78%	+30%–50%	Fast reaction; high efficiency; conversion up to 89%	Equipment cost; non-thermal effect quantification
Steam Explosion	Physical tearing + chemical separation	Combined physical and chemical deconstruction	45%–70%	+25%–40%	Effective for recalcitrant lignins; enriched G- and S-units	High equipment investment; parameter control

In summary, physical activation strategies—through complementary pathways of fractionation/purification and energy-field-assisted depolymerization/activation—significantly enhance the substitution potential and adhesive performance of lignin in phenolic resins. Among these strategies, ultrafiltration membrane fractionation stands out for its compatibility with aqueous systems, as it can be directly integrated with the aqueous lignin stream from pulping or biorefinery processes, thereby avoiding the energy-intensive drying step. Solvent fractionation, while effective for obtaining highly reactive low-molecular-weight fractions, requires careful consideration of solvent recovery economics and its compatibility with existing PF resin manufacturing facilities. For energy-field-assisted methods, the high energy input and the complexity of industrial-scale equipment must be weighed against the activation benefits they provide. Fractionation and purification provide a more uniform molecular foundation for subsequent modification, while energy-field activation directly disrupts structural constraints and increases the number of reactive sites. Together, they construct a more favorable platform for chemical modification. However, current research predominantly focuses on optimizing individual methods and improving their standalone performance. Systematic investigations into the synergistic effects among different physical pretreatment techniques, as well as the

interfacing mechanisms between physical activation and subsequent chemical modification, remain scarce. This represents a critical direction for future research.

3. Chemical Modification

The core challenge in LPF research lies in how to simultaneously increase lignin reactivity and efficiently incorporate it into the phenolic resin crosslinking network. Unactivated lignin, due to its limited number of active sites, often acts merely as an inert filler when used directly, slowing curing rates and prolonging production cycles, and impairing the resin's crosslinking density and final performance [46]. To address this, researchers have developed various chemical modification strategies aimed at introducing highly reactive functional groups into the lignin macromolecular skeleton or improving its interfacial compatibility with the resin matrix. These mainly include direct substitution, demethoxylation, phenolation, hydroxymethylation, and degradation pathways [47]. This section will elaborate in this order, focusing on analyzing the intrinsic mechanisms and functional complementarity of various chemical activation methods. To provide a clear framework for evaluating the diverse chemical modification strategies discussed in the following subsections, Table 2 presents a systematic comparison of the five major activation routes across key performance and practicality dimensions.

Table 2. Comparative summary of chemical modification strategies for lignin in PF resin synthesis.

Strategy	Max Phenol Substitution	Bonding Strength (MPa)	Curing Temp. (°C)	Formaldehyde Emission (mg/L)	Advantages	Limitations
Direct Substitution	30%–50% (up to 80% in some cases)	0.92–1.72 (dry)	135–145	0.64–1.13	Simple, low cost	Poor water resistance; batch inconsistency
Demethylation	60%–100%	1.07–2.94 (dry)	110–140	0.18–0.60	Significant activity increase; high efficiency, thorough removal	Reagent consumption; wastewater; equipment corrosion (acidic routes)
Phenolation	50%–80%	Comparable to pure PF	115–135	0.15–0.50	Creates new active sites, room temp., decolorization	Toxicity of phenol; high temperature; strong acid/base required
Hydroxymethylation	20%–40%	Moderate (up to ~2.7 dry)	125–140	0.22–0.60	Enhanced compatibility	Does not increase active site count; limited activation
Degradation	50%–100%	1.20–2.94 (dry)	110–145	0.20–0.80	Fundamental molecular deconstruction, green solvent, recyclable	Solvent recovery; enzyme cost; reaction selectivity

In LPF resin synthesis, the 'formaldehyde/phenol molar ratio (F/P)' requires careful definition because lignin cannot be equated to phenol monomer. Two approaches are found in the literature: Method 1—Virtual monomer approach: Lignin is converted into equivalent 'C_9 monomer' moles using an average molecular weight, which are added to the phenol moles, yielding F/(P + Lignin-monomer). This is consistent with traditional F/P logic but ignores polydispersity and uneven site distribution [48,49]. Method 2—Active site stoichiometry: The total moles of reactive aromatic hydrogens (ortho/para to phenolic OH) are quantified, and the ratio F/(P + Lignin-active-H) is calculated. This is more rigorous but lacks standardized quantification methods, limiting cross-study comparability [50,51]. We recommend that experimental reports clearly state both the phenol substitution percentage (by mass) and the F/phenol molar ratio used, and, where possible, also provide the active-site-based ratio.

From a stoichiometric standpoint, the potential formaldehyde savings from substituting lignin for phenol can be estimated. In a simplified model, each phenol molecule has three reactive sites (two ortho and one para) for hydroxymethylation, consuming up to 3 mol of formaldehyde per mole of phenol. During the subsequent curing (condensation) stage, each formaldehyde molecule forms a methylene bridge linking two aromatic rings. Therefore, for a fully cured network, the theoretical formaldehyde consumption per phenol molecule is 1.5 mol, which is consistent with the typical F/P molar ratios of 1.7–2.3 used in commercial PF resin formulations. A lignin C_9 unit contains, on average, 1–2 reactive aromatic hydrogens (depending on the H/G/S ratio). Based on the same condensation stoichiometry, its theoretical formaldehyde consumption is 0.5–1 mol per C_9 unit (i.e., 1–2 mol of reactive sites/2). Given the C_9 unit molecular weight of 180–200 g/mol vs. phenol's 94 g/mol, 1 kg of lignin theoretically consumes 5.6–11.1 mol of formaldehyde (if all reactive sites are accessible and fully condensed), whereas 1 kg of phenol consumes ~15.9 mol for complete substitution (or ~10.6 mol when considering the typical 1.5:1 F/P ratio for cured resins) [52]. Thus, substitution can theoretically save 0%–50% formaldehyde on a molar basis. This saving arises from two independent factors: (i) the lower molar formaldehyde demand per unit mass of lignin compared to phenol, due to lignin's higher C_9 unit molecular weight, and (ii) the lower number of reactive sites per C_9 unit. However, because some active sites in lignin are inaccessible due to steric hindrance, cross-linking of macromolecular chains requires additional formaldehyde to bridge chain segments; factors such as reaction-condition limitations can prevent the actual formaldehyde savings from reaching the theoretical maximum.

3.1. Direct Substitution, Chemical Derivatization, and Nanocomposite Enhancement

Direct use of unmodified lignin to partially or fully substitute phenol, due to its simple process and low cost, remains an ideal entry point for industrial utilization. The achievable substitution rate and resulting resin performance depend strongly on the lignin source. For instance, phosphate-derived pretreated PHP-lignin (PHP stands for phosphoric acid plus hydrogen peroxide, a pretreatment that combines acid hydrolysis and oxidative degradation to enrich the extracted lignin with hydroxyl groups) is rich in hydroxyl groups (Figure 2a), thereby favoring polycondensation with formaldehyde. At a 25% phenol substitution rate, the resulting PLPF resin met Chinese national standards for solid content, free phenol/aldehyde, viscosity, and bonding performance. Pressed-shaped particleboards exhibited good dimensional stability and solvent resistance [53]. Similarly, bagasse lignin PF (BLPF) resin showed significantly improved environmental performance compared with pure PF resin, with the free formaldehyde content of the resin reduced from 1.134 mg/L to 0.641 mg/L, although its solids content, degree of swelling, and storage period were slightly reduced [54]. When the substitution rate increased to 30%, the resin's molecular weight and glass transition temperature rose, while curing activity decreased [55]. In contrast, a successful 80% substitution of phenol was achieved using unmodified commercial kraft softwood (K-SW) and organic-solvent-treated wheat straw (O-WS) lignins. The resulting resin exhibited a low curing temperature of 105–110 °C, with an exothermic heat output 1/3 that of conventional resins, and reached a final curing degree of 76% (compared to only 56% for commercial PF resin). Dry bonding strength was comparable to that of commercial PF resin, though an extended hot-pressing time was still required to meet the boiling water test requirements [56]. Regarding complete substitution, soda lignin-based LPF100 resin-pressed plywood exhibited a shear strength of 0.987 MPa; bending strength and modulus of elasticity of 40 MPa and 3209 MPa, respectively; and water absorption and thickness swelling rates of 37.2% and 13.5%, demonstrating feasibility [57]. Another study indicated that a high phenol/formaldehyde molar ratio and impurity removal could impart

mechanical strength comparable to that of commercial PF and excellent water resistance to fully substituted resins [58].

These cases simultaneously reveal the decisive influence of lignin source and structure on substitution efficiency. Systematic comparisons among lignins derived from different resources—such as hardwoods, softwoods, wheat straw, and corn stover and isolated via varied processes, including the kraft, organosolv, soda, sulfite, and enzymatic hydrolysis methods, reveal that lignins rich in p-hydroxyphenyl and guaiacyl units exhibit higher reactivity toward formaldehyde [59,60]. The mechanistic basis for this differential reactivity lies in the electronic and steric effects of the aromatic substitution patterns: p-hydroxyphenyl units, with their single para-hydroxyl substitution, present the most accessible aromatic ortho positions for electrophilic attack; guaiacyl units (ortho-methoxy, para-hydroxyl) are slightly less reactive due to methoxy-induced steric hindrance; syringyl units (ortho,ortho-dimethoxy, para-hydroxyl) have their two ortho positions blocked, significantly limiting their reactivity toward formaldehyde. These lignins are more suitable for phenol replacement, enabling reduced formaldehyde usage and lower adhesive toxicity [61]. Further comparisons among enzymatic hydrolysis lignin (EHL), alkali lignin, lignosulfonate, bagasse lignin, and organosolv lignin confirm that EHL, owing to its low ash content, high molecular weight (reflecting its intact macromolecular backbone), and elevated hydroxyl content, demonstrates the highest reactivity. EHL-based phenolic resins (EHL-PF) show lower free formaldehyde, higher viscosity, and greater solid content [62]. Moreover, Kraft lignin extracted from oil palm biomass exhibits advantages over soda lignin in terms of molecular weight distribution and reactive sites, indicating greater potential for phenol substitution [63]. Specifically, the phenolic hydroxyl group content—a key indicator of the number of potential reactive sites on the aromatic ring, as a high density of phenolic -OH groups generally correlates with a greater availability of reactive ortho/para C-H positions for electrophilic substitution with formaldehyde—was 4.1076 mmol/g for kraft lignin and 2.5830 mmol/g for soda lignin, representing an approximately 59% higher reactive site density. This difference arises from the distinct pulping chemistries: kraft pulping employs sodium sulfide (Na_2S) in addition to NaOH, which promotes more effective delignification and preserves a higher proportion of phenolic hydroxyl groups than soda pulping with NaOH alone. These structure–activity relationship studies lay an important foundation for subsequent targeted chemical modification. However, direct utilization strategies still face common challenges, such as poor batch-to-batch consistency and limited water resistance, primarily due to the inherent structural heterogeneity and restricted functional group content of industrial lignins.

To address the above limitations, a series of chemical modification methods is employed to modify the lignin molecular structure, thereby enhancing its reactivity and matrix compatibility. Esterification is one effective approach: Treatment of kraft lignin and soda lignin with succinic anhydride increased carboxyl group content to 2.9 and 2.4 mmol/g, respectively, significantly improving reactivity and incorporation efficiency despite the consumption of some phenolic hydroxyl groups. This apparent paradox is explained by the fact that esterification with succinic anhydride introduces carboxyl groups via flexible aliphatic side chains, which not only enhances lignin solubility and dispersion in the resin system but also reduces the steric hindrance around the aromatic ring, thereby facilitating more effective integration into the phenolic network during curing [64]. Among these, succinylated kraft lignin maintained a gel content above 95% at a 30% substitution rate, with reduced curing activation energy and excellent thermal oxidation stability of the resin at temperatures above 600 °C. The synthesis of succinylated LPF resin is illustrated in Figure 2b,c [65]. Additionally, silanization modification can also enhance the compatibility between lignin and the resin matrix. Lignin extracted from rosewood sawdust, after dual

modification with propylation and silanization, showed significantly enhanced hydrophobicity (water contact angle of 127.7°). When incorporated into PF resin at 10 wt%, the dry shear strength of plywood increased by 56.1%, and the strength retention after boiling water treatment also improved significantly. Cohesive strength reached 5.44 MPa with a 100% wood failure rate; bending strength and modulus of elasticity increased by 38% and 27.3%, respectively; and formaldehyde emission decreased by about 20% [66]. It is worth noting that although enhanced hydrophobicity improves water resistance, it may, in principle, also hinder the copolycondensation of lignin and phenol via a formaldehyde (methylene) bridge, thereby compromising compatibility with the resin matrix. However, the improvements observed in all experiments testing mechanical properties indicate that, at the 10 wt% loading level used, the beneficial effects—particularly improved interfacial adhesion and stress transfer—outweigh the potential drawbacks. Beyond these modifications, liquefaction treatment can convert large lignin molecules into highly reactive small molecular fragments. Liquefying bagasse pulping black liquor (HL) under acidic conditions yielded a black liquefaction product (HLP), which was used to gradually replace phenol in the synthesis of modified phenolic resin (HLPF). Under optimal conditions, the resin with 40% substitution achieved a wet shear strength of 1.72 MPa, a formaldehyde emission of 0.804 mg/L (measured according to GB/T 14074–2017 using the acetylacetone method), a storage period of up to 122 days, and improved thermal stability and curing reactivity [67]. A comprehensive view of these chemical modification methods reveals that each can achieve significant improvements in specific performance dimensions, but their respective applicability and process economics still need to be weighed, and synergistic combinations between these methods remain very limited.

To further enhance the heat resistance of lignin-based phenolic resins, nanocomposite filler reinforcement provides a new pathway. Modification of LPF with nano-SiO_2, Al_2O_3, and TiO_2 was confirmed via FT-IR and XRD, revealing the formation of chemical bond crosslinks, such as Si-O-Si, Al-O, and Ti-O, between nanoparticles and the resin matrix. SEM showed the modified resin surface became smoother and denser. TGA results indicated that at 800 °C, the char residue rates of the three nanocomposite systems increased by 4.28%, 5.38%, and 4.74%, respectively, compared with pure LPF, thereby significantly improving thermal stability, as the nanoparticles absorb more energy during degradation. Simultaneously, DSC analysis revealed that the curing temperature remained essentially unchanged, while the curing time shortened considerably, indicating that the nanoparticles act as nucleation sites or catalysts that accelerate the curing kinetics without altering the thermodynamic curing window. This decoupling of curing temperature from curing time is industrially significant, as it enables faster production cycles without increasing energy consumption [68]. While this strategy has intuitive effects, the uniform dispersion and long-term service stability of nanofillers, as well as their matching rules with chemically modified lignin, are still in the early stages of exploration.

The direct substitution strategy offers the simplest and most cost-effective entry point for industrial applications, with substitution rates of up to 80% achieved under optimized conditions. However, the inherent structural heterogeneity of unmodified lignin imposes practical limits on the consistency of performance and water resistance. Among the lignin sources evaluated, EHL and sulfate lignin—which have high hydroxyl content and low ash content—consistently outperformed other industrial lignins. From a cost-effectiveness perspective, for substitution rates $\leq$ 30%, direct substitution remains the most industrially attractive route, delivering acceptable performance with minimal process modifications. However, for higher substitution targets, chemical activation becomes necessary.

Beyond direct substitution, research on lignin-modified phenolic resins has evolved into a tiered framework encompassing chemical derivatization and composite enhancement.

Chemical modification provides a targeted route to overcome limitations in reactivity and compatibility, while nano-enhancement opens avenues for synergistic improvements in properties. However, current studies predominantly focus on individual modification methods, with limited systematic investigation into (i) synergistic effects between different chemical approaches, (ii) quantitative links between micro-mechanisms of interface evolution and macroscopic properties, and (iii) rational design principles for industrial-scale combined strategies. The following sections address these key chemical activation pathways.

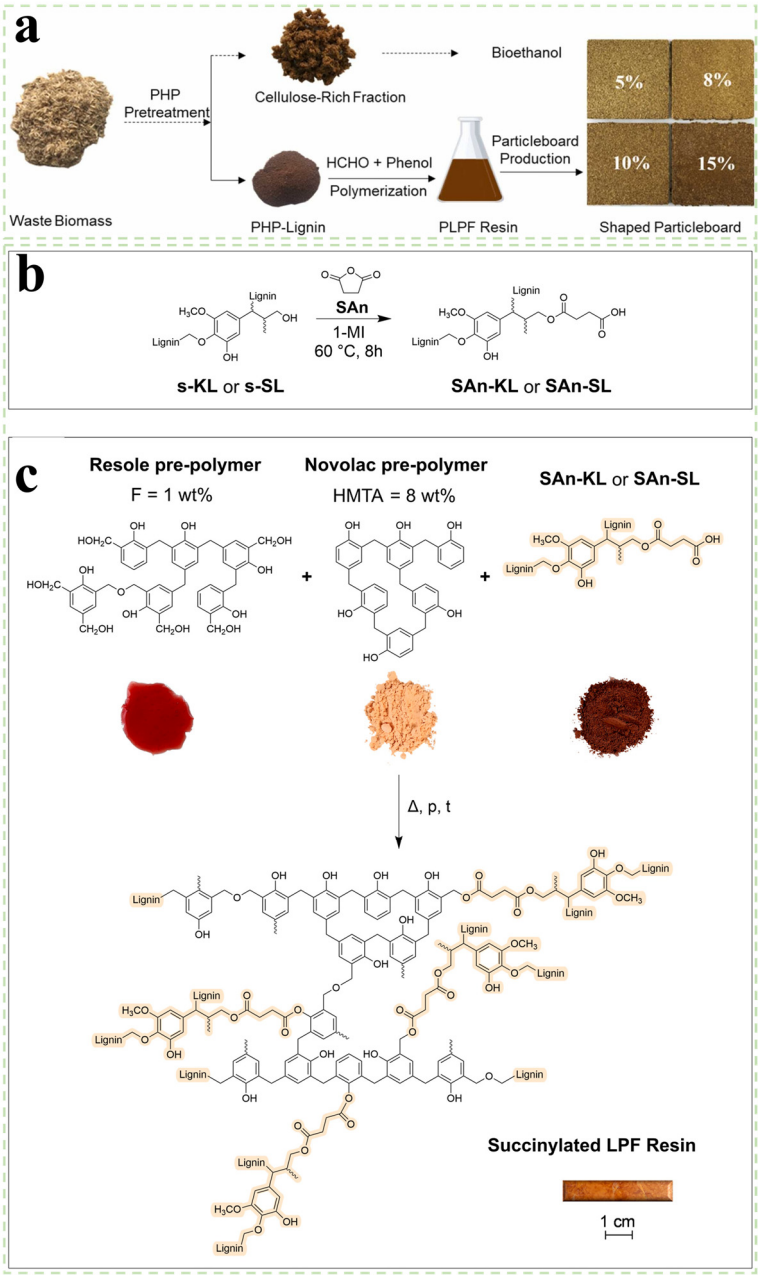


Figure 2. (**a**) Schematic diagram of phosphate-derived PLPF resin (PLPF: phosphate-derived lignin–phenol–formaldehyde resin). Reproduced with permission from reference [53]. Copyright 2024, Elsevier. (**b**) Functionalization reaction of s-KL (succinylated kraft lignin)/s-SL (succinylated soda lignin) with SAn (succinic anhydride) to prepare SAn-KL (succinic anhydride-modified kraft lignin)/SAn-SL (succinic anhydride-modified soda lignin). (**c**) Reactions occurring during synthesis of succinylated LPF resin (LPF: lignin–phenol–formaldehyde). Reproduced with permission from reference [65]. Copyright 2024, American Chemical Society.

3.2. Lignin Demethoxylation-Modified Phenolic Resins

Active sites on lignin's aromatic rings are often occupied by methoxy groups, resulting in low free phenolic hydroxyl content, which directly limits its condensation reactivity with formaldehyde. Therefore, the development of selective demethoxylation (removal of the entire -OCH_3 group to create a new C-H-active site) or demethylation (cleavage of the C-O bond in the methoxy group to generate a phenolic -OH) has become a direct strategy for enhancing lignin reactivity at the molecular level [69]. It is crucial to distinguish these two distinct pathways: demethoxylation creates a new reactive site on the aromatic ring itself, whereas demethylation transforms an existing substituent into a more reactive phenolic hydroxyl group. This review will focus primarily on demethoxylation strategies, as they directly increase the number of active sites. The development of demethylation methods has followed a clear technological trajectory—from harsh, high-temperature processes toward milder, greener catalytic and enzymatic systems. This evolution is examined below in chronological order of technological maturity.

The earliest developed demethylation methods are represented by molten sulfur-mediated reactions under alkaline conditions. These methods utilize nucleophiles like SO_3^{2-}, S, and HS^- to attack lignin's methoxy groups, generating small molecules such as dimethyl sulfide. Although this strategy can double the free phenolic hydroxyl content of sulfate lignin and alkali lignin, reactions mostly require high temperature and pressure, resulting in high energy consumption, demanding equipment requirements, and potential excessive degradation of the lignin skeleton, making selectivity control difficult [70]. This process bottleneck directly spurred the exploration of new demethylation systems under mild conditions.

To circumvent the limitations of high temperature and pressure, a series of mild chemical systems using sulfites, thiosulfates, etc., as nucleophiles have gradually become research hotspots. The combined demethylation/hydroxyethylation modification using sodium sulfite and glyoxal increased the total hydroxyl mass fraction of lignin by 88% and phenolic hydroxyl content by 15%, significantly enhancing reactivity. Its degradation was more thorough, with an exothermic peak at 77 °C and an exothermic value of 460 J/g [71]. $Na_2S_2O_3$-catalyzed lignin depolymerization has been comparatively investigated under microwave-assisted and hydrothermal conditions, both of which increase the phenolic hydroxyl content to about 22.4%. The hydrothermal method was more amenable to industrial scale-up; under optimal conditions, the resulting resin's bonding strength reached as high as 2.94 MPa, far exceeding that of undepolymerized lignin-based resin (1.31 MPa). Even with 100% phenol substitution, strength remained at 1.57 MPa, and the resin cross-section was dense and smooth with low curing temperature [72]. Sodium sulfite-catalyzed demethylation of alkali lignin under ambient pressure and low temperature reduced methoxy content from 1.93 mmol/g to 1.09 mmol/g and increased phenolic hydroxyl from 0.56 mmol/g to 0.82 mmol/g. The resulting resin cured faster and had shorter gel time, bonding strength increased from 0.92 MPa to 1.07 MPa, and formaldehyde emission decreased from 0.58 mg/L to 0.22 mg/L, offering both environmental and cost advantages [73]. Additionally, an NaOH/urea aqueous phase system can achieve demethylation under mild conditions. Demethylated lignin (DL) showed reduced -OCH_3 and increased phenolic hydroxyl. Directly synthesized DLPF resin with 60% phenol substitution met national standards, and plywood VOC emissions were significantly reduced [74]. Overall, these mild nucleophilic systems significantly reduce reaction conditions while maintaining high demethylation efficiency, but they also face issues like high reagent consumption, long reaction cycles, and product separation problems.

Parallel to alkaline nucleophilic routes, acidic demethylation is widely used due to its higher reaction efficiency and more thorough methoxy group removal. After modification

with dimethylformamide (DMF) and iodocyclohexane, the hydroxyl number of sulfate lignin significantly increased from 1.09 mmol/g to 1.75 mmol/g, with some molecular weight reduction [75]. When iodocyclohexane or hydroiodic acid was used as the demethylating agent, lignin's polydispersity index (PDI) decreased significantly, phenolic hydroxyl content tripled, and the prepared LPF adhesive exhibited superior dry and wet bonding strength compared to unmodified resin [76,77]. Demethylated lignin (D-Lig) obtained via Lewis acid treatment was used to synthesize D-LPF, which cured rapidly, had free formaldehyde as low as 0.18%, and reached a bonding strength of 2.19 MPa [78]. An $AlCl_3$/hydrochloric acid system has been recently reported for selective methoxy group removal with recyclable reagents. The obtained demethylated lignin had a hydroxyl content as high as 6.54 mmol/g. When substituting 75% phenol, the dry shear strength (2.46 MPa) surpassed that of traditional resin (2.36 MPa) and was maintained under excellent strength under high/low-temperature and high-humidity conditions. The lignin demethylation mechanism and the reaction of lignin-substituted phenol in phenolic synthesis are shown in Figure 3a,b [79]. Although acidic systems are efficient, equipment corrosion, wastewater treatment, and potential impacts of residual acid on resin performance remain unavoidable challenges in transitioning to green chemical processes.

To further reduce reliance on organic solvents and strong acids, aqueous-phase green demethylation processes are gaining attention. Sulfobutylation pretreatment can significantly improve the water solubility of kraft lignin, enabling subsequent demethylation to proceed under mild aqueous conditions, as shown in Figure 3c,d. Structural analysis showed that the two-step aqueous process further reduced methoxy groups by 27%. Regarding sulfur content, sulfobutylation introduces sulfonate groups (with sulfonate group content and charge density increasing by 14% and 25%, respectively); however, the subsequent demethylation step reduces the sulfur content back to levels comparable to those of the original kraft lignin. Although absolute sulfur content values (in wt%) were not reported in the study, the available data indicate that the final demethylated sulfobutylated lignin does not accumulate additional sulfur beyond the baseline level inherent to kraft lignin. The resulting resin's dry/wet bonding strength increased by 32% and 56%, respectively, and material flammability decreased, manifested as reduced smoke density and improved combustion behavior, providing a new pathway for developing sustainable water-based synthesis routes [80].

In contrast to the above chemical catalytic routes, microbial demethylation offers a milder, more environmentally friendly alternative. Bacteria and fungi secrete O-demethylase enzymes that can remove methoxy groups from lignin under ambient temperature and pressure, releasing methanol and generating structures rich in ortho-phenolic hydroxyl groups, thereby effectively enhancing the bonding strength and durability of wood adhesives [81,82]. Biological methods fundamentally avoid harmful reagents and harsh conditions and also offer the possibility of precisely analyzing the molecular mechanisms of lignin structural changes. However, low enzymatic efficiency, long reaction cycles, and substrate specificity towards different lignin sources remain major bottlenecks limiting their large-scale application.

A survey of current literature reveals that demethoxylation modification has developed into a diversified methodological framework, significantly enhancing the reactivity of lignin. However, existing research primarily focuses on the increase in phenolic hydroxyl content resulting from demethoxylation itself and the improvement of isolated resin properties. A thorough and systematic investigation into the quantitative structure–property relationships—specifically linking the degree of demethoxylation, the regioselectivity of methoxyl group removal, and associated changes in lignin molecular weight to the final resin's crosslink density and hydrothermal stability—has not been systematically estab-

lished. This knowledge gap is critical because without such quantitative understanding, the optimization of demethylation conditions remains largely empirical rather than predictive. For example, while increased phenolic hydroxyl content generally correlates with enhanced reactivity, excessive demethylation may simultaneously degrade the lignin macromolecular structure, reducing crosslink density and compromising hydrothermal stability. Furthermore, the regioselectivity of methoxyl removal (i.e., whether demethylation occurs at ortho versus para positions relative to phenolic hydroxyls) may influence the steric accessibility of the resulting reactive sites and thus the efficiency of subsequent condensation reactions with formaldehyde. Establishing these quantitative relationships would enable the rational design of demethylation processes tailored to specific lignin sources and performance targets, rather than relying on trial-and-error optimization.

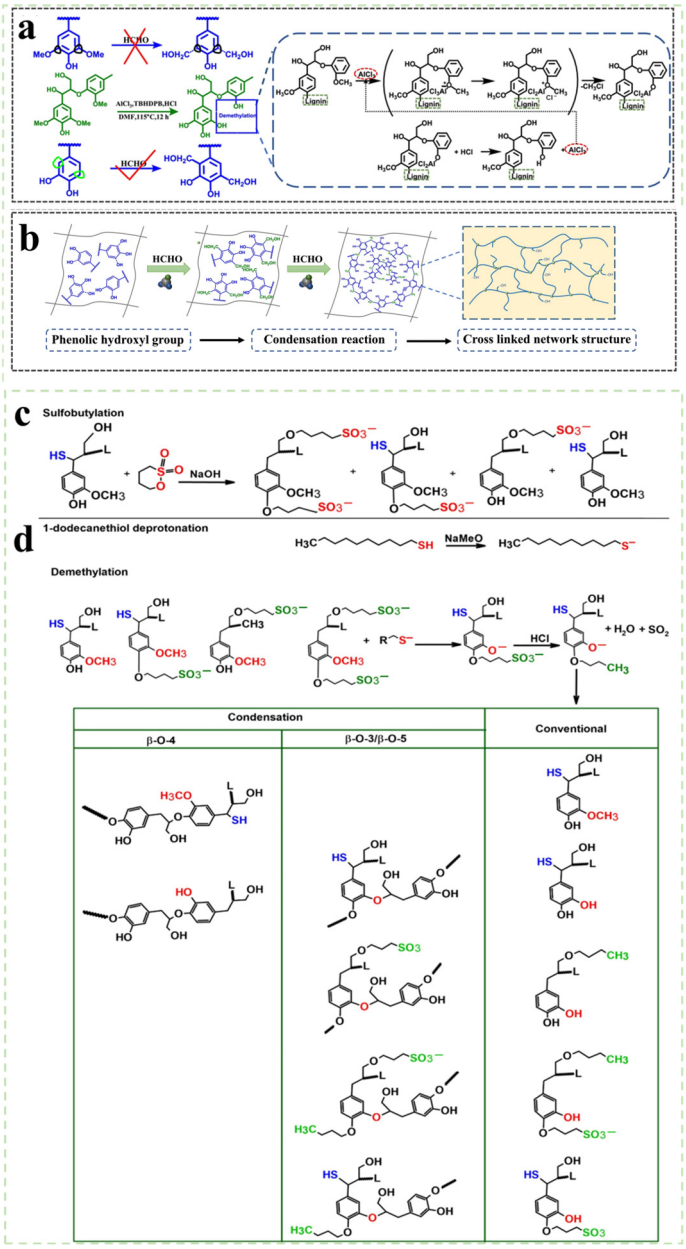


Figure 3. (**a**) Mechanism of lignin demethylation. (**b**) Reaction of lignin-substituted phenol in phenolic synthesis. Reproduced with permission from reference [79]. Copyright 2025, Elsevier. (**c**) Mechanism of lignin sulfobutylation reaction. (**d**) Proposed sulfobutyl lignin demethylation mechanism. Reproduced with permission from reference [80]. Copyright 2026, Elsevier.

Demethylation is one of the most effective strategies for directly increasing the phenolic hydroxyl content of lignin; it has been shown to achieve up to 100% phenol substitution while maintaining or even improving adhesive performance. Among the various demethylation methods, mild nucleophilic systems (Na_2SO_3, $Na_2S_2O_3$) offer the best balance between activation efficiency and industrial feasibility, as they operate at atmospheric pressure and moderate temperatures using relatively inexpensive reagents. Although acidic demethylation systems are highly efficient, they pose greater challenges for equipment corrosion and wastewater treatment. Although biological demethylation is environmentally friendly, it is limited by low efficiency and long reaction times and remains confined to laboratory-scale exploration. The hydrothermal $Na_2S_2O_3$-catalyzed system shows particular promise for industrial conversion, achieving a bonding strength of up to 2.94 MPa under optimized conditions.

To clarify the distinct chemical pathways and their implications for resin formation, it is instructive to distinguish the reactivity of the products generated by different modification strategies. Demethoxylation (removal of -OCH_3) creates a new, free C-H site on the aromatic ring. This site is highly reactive towards formaldehyde in an electrophilic aromatic substitution, forming a methylol group (-CH_2OH), which can then condense with another aromatic C-H site to form a methylene bridge (-CH_2-) during curing—this is the desired pathway for network formation. In contrast, demethylation (cleavage of the C-O bond in -OCH_3) converts the methoxy group into a phenolic -OH group. While this increases the phenolic OH content, a phenolic -OH itself does not directly react with formaldehyde. Its enhanced reactivity primarily manifests in other reactions, such as etherification or esterification, which are not the primary crosslinking reactions in PF resin curing. The primary contribution of demethylation to improvements in PF resin performance lies in the associated structural modifications and enhanced compatibility, rather than in direct participation in the formation of methylene bridges. Phenolation, on the other hand, introduces new phenol units, which provide additional reactive C-H sites. Hydroxymethylation transforms existing C-H sites into the more reactive -CH_2OH groups, which are the direct precursors to the methylene bridges. Therefore, strategies that create or protect reactive C-H sites (demethoxylation and phenolation) and those that convert them into more reactive intermediates (hydroxymethylation) are mechanistically distinct and often synergistic, whereas increasing phenolic OH content via demethylation alone does not directly add to the formaldehyde-reactive pool.

3.3. Lignin Phenolation-Modified Phenolic Resins

Building upon demethoxylation, which directly creates new active sites on the aromatic ring, lignin phenolation goes a step further by fundamentally reshaping the chemical environment and reactivity of the lignin through the covalent incorporation of entire phenol structural units into the lignin molecular skeleton. Lignin phenolation refers to the electrophilic or nucleophilic substitution reaction between lignin and phenol or its derivatives under acid or base catalysis, accompanied by modifications such as hydroxyl methylation and etherification, thereby achieving directional grafting of phenol structures onto lignin molecules [83]. This strategy simultaneously increases both the number of active sites and their spatial accessibility, making it one of the most effective pathways to enhance lignin reactivity and achieve high or even full phenol substitution, although phenolation does consume phenol during the activation step (typical lignin-to-phenol mass ratios of 1:1 to 1:3, with 30–60 wt% of the added phenol becoming covalently incorporated into lignin). The unreacted phenol, which is not covalently bonded to the lignin, is typically recovered from the reaction mixture by distillation or solvent extraction at the end of the phenolation process and can be recycled for subsequent reactions, thereby mitigating the

economic and environmental impact of this initial "investment." Importantly, this initial "investment" of phenol yields a substantially higher "return" in the final resin: while unmodified kraft lignin typically replaces only about 25% of phenol, phenolated lignin can achieve substitution rates of 45% or higher, resulting in a net positive saving of phenol throughout the process. Current research is continuously evolving from traditional strong acid/strong base catalytic systems towards milder, greener novel phenolation strategies.

Acid catalysis is a classic route for phenolation. Early research on oxalic acid-catalyzed phenolation of lignosulfonate found that the ortho position of phenol was significantly more reactive than the para position. This regioselectivity rule laid the theoretical foundation for directional control of subsequent phenolation processes [84]. At the application level, solid acid-catalyzed phenolation (SACP) treatment of enzymatically hydrolyzed lignin (EHL) for phenolic foam preparation showed that SACP effectively depolymerized lignin and increased its reactivity: under optimized conditions (140 °C, 4% HZSM-5—a zeolite-based solid acid catalyst with the ZSM-5 (Zeolite Socony Mobil-5) framework type, widely used in catalytic cracking and biomass conversion, 2 h), the weight-average molecular weight (Mw) of EHL decreased from 6695 to 2418 g/mol without condensation. The treated lignin could substitute for 50% phenol, and the resulting material exhibited good thermal insulation and compressive strength [85]. Combining phenolation of acid-insoluble lignin from rice husk with three-step resin polymerization effectively enhanced its reactivity. The product outperformed unmodified systems in appearance, thermal stability, water resistance, and UV resistance, which is attributed to enhanced covalent interactions between PF resin and lignin [86]. Acid-catalyzed phenolation studies on resinol lignin models and eucalyptus alkali lignin revealed finer structural evolution: syringaresinol phenolation generated new naphthalene products, indicating cleavage of the resinol structure's C1–Cα bond during phenolation, releasing syringol or guaiacol. Additionally, diphenylmethane products formed between phenol and these phenols were detected. Resinol structures were converted to phenanthrene compounds via ring-opening and formaldehyde elimination, confirming the formation of naphthalene structures during phenolation (Figure 4a) [87]. These findings not only enhance understanding of phenolation reaction pathways but also provide a molecular-level basis for regulating product structure.

Phenolation can also proceed effectively under alkaline conditions. Characterization and phenolation evaluation of four industrial lignins obtained from different biorefining processes found that despite varying sources and structures, all could undergo alkaline phenolation to increase active sites and be successfully integrated into LPF resin synthesis [88]. Research on preparing PF resin from phenol-liquefied lignin under alkaline conditions with formalin found its gel time at 135 °C significantly shortened and DSC exothermic peak temperature lower, indicating that introducing phenol-liquefied lignin effectively improved curing efficiency [89]. Compared to acid catalysis, alkaline phenolation typically involves milder conditions but also shares common issues like high alkali catalyst usage.

To overcome limitations of traditional phenolation such as high temperature, strong acids/bases, and phenol toxicity, novel phenolation strategies have emerged. Among them, the method of introducing polymeric phenol (i.e., a low-molecular-weight, water-soluble phenol oligomer prepared by enzymatic or chemical oligomerization of phenol monomers) into lignin via graft copolymerization is particularly noteworthy (Figure 4b). This process enables polyphenolation of hardwood organosolv lignin at room temperature without requiring strong acids/bases, increasing lignin active sites by more than tenfold [90]. Additionally, polyphenolation significantly reduced the dark color characteristic of industrial lignin, overcoming its barrier for application in light-colored materials. This graft copolymerization phenolation method, combining efficiency, mildness, and decolorization effects, holds promise for widespread application in activating various industrial lignins.

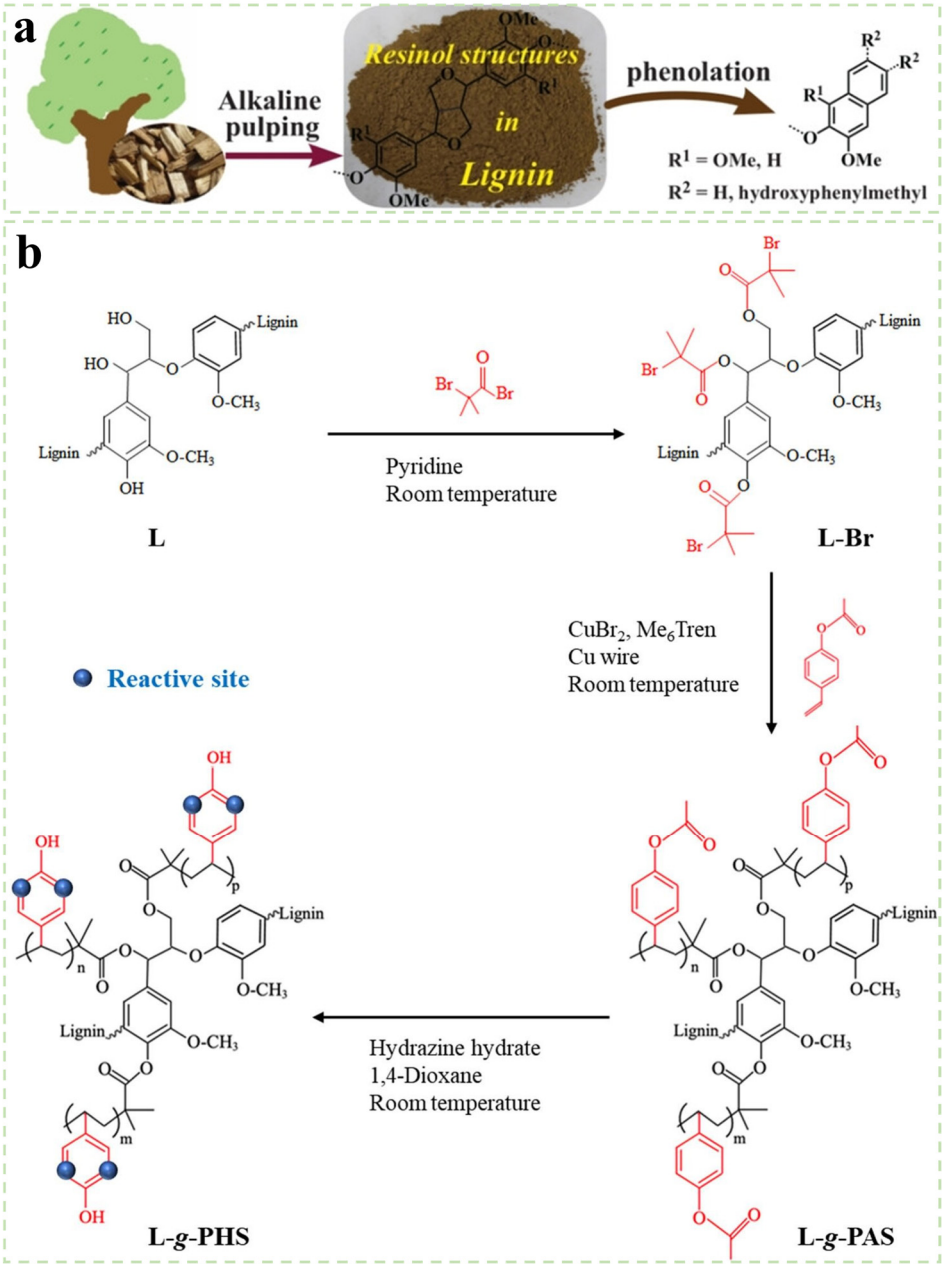


Figure 4. (**a**) Formation of naphthalene structures during phenolation. Reproduced with permission from reference [87]. Copyright 2020, John Wiley and Sons. (**b**) Mechanism diagram of introducing polymeric phenol into lignin via graft copolymerization. Reproduced with permission from reference [90]. Copyright 2024, Elsevier.

The key contribution of the phenolization strategy lies in simultaneously increasing both the number of active sites on the lignin and the accessibility of the reaction space, enabling it to participate in the copolymerization of the resin at a higher proportion. However, current research has largely focused on how the phenolation process itself enhances the reactivity of lignin, while there is a lack of in-depth quantitative analysis regarding its actual cross-linking behavior during subsequent resin curing—particularly how phenylated sites contribute to three-dimensional network formation and their impact on cross-linking uniformity and resistance to moisture and heat. Furthermore, determining how to achieve precise control over the degree of phenolization while significantly enhancing activity—thereby avoiding molecular degradation caused by over-phenolization—is a scientific question that must be addressed for this field to advance toward rational design. Such degradation

occurs when excessively harsh conditions (e.g., temperatures ≥150 °C or overly high acid charges) promote excessive cleavage of lignin's ether bonds (β-O-4 and α-O-4), resulting in extensive fragmentation that compromises the macromolecular integrity and ultimately reduces the crosslinking density and mechanical performance of the final resin.

Phenolation effectively enhances lignin reactivity by covalently grafting phenol units and increasing the number of active sites and their spatial accessibility. This strategy achieves high substitution rates (50%–80%), with resin performance comparable to that of pure PF systems. From a practical standpoint, acid-catalyzed phenolation offers higher reaction efficiency and more thorough structural modification, but requires careful management of hazardous reagents and reaction conditions. The recently developed graft copolymerization method, which introduces polymeric phenols at room temperature without the use of strong acids or bases, represents a significant advancement in green phenolation technology. However, its scalability and applicability to different industrial lignins still require further validation. A key challenge is achieving precise control over the degree of phenolation to avoid excessive degradation while maximizing the enhancement in activity.

3.4. Lignin Hydroxymethylation-Modified Phenolic Resins

Unlike demethoxylation and phenolation, which aim to "create" active sites, lignin hydroxymethylation takes a more direct approach. It does not increase the total number of active sites on aromatic rings but transforms existing reactive aromatic C-H sites into more reactive hydroxymethyl (-CH_2OH) functional groups. Specifically, under alkaline conditions, formaldehyde undergoes electrophilic aromatic substitution at the ortho and para positions of lignin's aromatic rings relative to the phenolic hydroxyl groups, thereby introducing highly reactive hydroxymethyl groups. These groups can further condense with phenol or other active intermediates to construct lignin-phenol-formaldehyde copolymer resins [91]. A crucial mechanistic question is the regioselectivity of formaldehyde addition. Under the typical alkaline reaction conditions, formaldehyde preferentially reacts with the hydrogen atoms at the ortho and para positions of phenolic hydroxyl groups on the lignin aromatic rings [92]. This is the desired pathway, as it creates highly reactive hydroxymethyl groups directly on the aromatic nucleus. These hydroxymethyl groups are the key reactive intermediates that subsequently condense with other aromatic C-H sites (from phenol or other lignin units) to form stable methylene bridges (-CH_2-) during resin curing, which constitute the core of the three-dimensional polymer network [50]. However, formaldehyde can also react, to a lesser extent, with aliphatic hydroxyl groups present on the lignin side chains, forming less stable hemiacetal or acetal linkages. In contrast, phenolic hydroxyl groups, although also capable of forming hemiacetal or acetal species, are much less reactive towards formaldehyde in this context, and such reactions are not considered to be the main pathway for hydroxymethylation (methylolation). The formation of hemiacetals or acetals from both aliphatic and phenolic hydroxyl groups is generally an undesired side reaction that consumes formaldehyde without contributing to the formation of the crosslinked polymer network. However, precisely because its essence is functional group transformation rather than site creation, hydroxymethylation's contribution to overall lignin reactivity enhancement is relatively limited. This inherent property determines that it is more suitable as an auxiliary activation method rather than a substitute for demethoxylation or phenolation.

To fully realize the potential of the hydroxymethylation route, researchers first systematically analyzed the reaction mechanism. Using softwood kraft lignin, phenol, and paraformaldehyde under NaOH catalysis as a model system, two-dimensional NMR spectroscopy detected clear hydroxymethylation signals, directly confirming the participation of guaiacol units in lignin during hydroxymethyl addition. More crucially, the study found

that reaction conditions guide product structure: at higher temperatures and lignin concentrations, the formed hydroxymethyl groups further condense to form methylene bridge bonds, and methylene cross-links also form between lignin and phenol molecules [93]. This mechanistic understanding reveals the two-stage characteristic of hydroxymethylation reactions, "addition first, condensation later," laying a theoretical foundation for precise regulation of process parameters to balance activation and prepolymerization, avoiding excessive self-condensation. It should be noted, however, that this mechanistic study is based on a softwood lignin model system. The regioselectivity of hydroxymethylation and its influence on subsequent condensation behavior for structurally more complex hardwood lignins or industrial mixed lignins require further clarification.

Different lignin sources, with varying impurity contents, molecular weight distributions, and aromatic ring substitution patterns, directly affect hydroxymethylation efficiency and product performance. A systematic comparative study of typical industrial lignins from South America, selecting sodium lignosulfonate, kraft lignin, and organosolv lignin, quantitatively characterized phenolic hydroxyl and reactive aromatic hydrogen content and reactivity via UV-Vis spectroscopy. It confirmed that all three possess basic potential for phenol substitution, with sodium lignosulfonate considered the optimal candidate due to its excellent hydrophilicity and high reactive hydrogen abundance [94]. This screening approach based on raw material structural characteristics provides a methodological reference for industrial lignin selection.

At the process level, researchers have gradually improved the resin properties of hydroxymethylated lignin by adjusting reaction conditions and substitution ratios. Using coniferous lignin ammonium sulfonate as the raw material, the optimal molar ratio of formaldehyde to lignin (calculated based on the C9 phenylpropane unit with an average molecular weight of ca. 190–200 g/mol) was determined to be 2.5:1; when the modified lignin replaced 30% of the phenol, the performance of the plywood met the application requirements [95]. Studies on the hydroxymethylation of organic-solvent-extracted lignin further revealed that the relative molecular mass of the modified lignin significantly influences the apparent activation energy of LPF during curing, indicating that molecular weight is a key parameter for regulating curing behavior [96]. Generally, lower-molecular-weight lignins are preferred because they exhibit higher reactivity and a lower apparent activation energy due to greater solubility and a higher concentration of accessible reactive end groups. Methylated lignin sulfonate achieved a 20% phenol substitution rate while maintaining the resin's water resistance and mechanical properties [97]. Although these studies have advanced the optimization of the hydroxymethylation process from different perspectives, they mostly involve empirical parameter screening; the interaction patterns among key process variables—such as formaldehyde-to-lignin ratio, reaction temperature, catalyst loading, and lignin source—have not yet been systematically elucidated. For instance, the optimal formaldehyde dosage may vary with the phenolic hydroxyl content of a given lignin, while the optimal temperature may depend on the acid or base catalyst used. Without understanding such cross-variable interactions, the optimized conditions established for one lignin source cannot be reliably extrapolated to another, thereby limiting the transferability of the optimization results.

It is worth noting that, to reduce the environmental and health risks associated with traditional formaldehyde-based systems, replacing formaldehyde with the less toxic glyoxal for lignin modification via a similar hydroxymethylation pathway has emerged as a new approach. Regarding the reaction paths, formaldehyde, as a monoaldehyde, undergoes the classic Lederer–Manasse reaction to form hydroxymethyl groups, which subsequently condense into methylene (–CH_2–) bridges. Glyoxal, as a dialdehyde, follows a similar initial glyoxalation route but is more prone to side reactions such as the Cannizzaro

reaction and glyoxal-induced recondensation [98]. Owing to its bulkier structure and lower reactivity, glyoxal generally requires longer reaction times or higher catalyst loadings to achieve comparable degrees of modification, which helps explain the performance gap between glyoxal- and formaldehyde-based systems [99]. In contrast, the reaction of lignin with ethylene glycol follows a fundamentally different mechanism: under alkaline conditions, ethylene glycol acts primarily as a solvent and liquefying agent, promoting the cleavage of ether bonds (e.g., β-O-4 linkages) in the lignin structure [49]. When corn stover lignin reacts with ethylene glycol under NaOH catalysis, the resulting ethylene glycol-modified lignin shows significant improvements in hydroxyl content, degree of activation, and thermal stability, although its molecular weight increases—presumably due to a secondary polycondensation reaction between the lignin and ethylene glycol. In this system, ethylene glycol acts not only as a solvent and liquefying agent to promote the cleavage of ether bonds (e.g., β-O-4 linkages) in the lignin structure, but also as a reactant that can undergo condensation with the generated lignin fragments. Plywood prepared using this method exhibits a dry strength of 2.73 MPa, demonstrating good application potential [100]. Regarding catalytic activation, converting lignin into an active prepolymer via methylation and blending it with pure phenolic resin produced an adhesive that cured more readily than traditional NPF (novolak phenol–formaldehyde resin—a thermoplastic phenolic resin that requires a curing agent such as hexamethylenetetramine for crosslinking), with both dry and wet tensile and shear strengths exceeding industry standards [101]. Hydroxymethylation modification of kraft paper lignin has also confirmed that a 60% increase in hydroxyl content facilitates the condensation reaction. As the substitution rate increases, the viscosity of the HKLPF resin rises due to an increased number of hydroxymethyl groups participating in polycondensation, thereby extending the molecular chains and increasing branching. In phenolic resin synthesis, viscosity is a key process parameter for terminating the condensation reaction: once the target viscosity is reached, the reaction is stopped by cooling or by adjusting pH. For HKLPF, the bonding strength reached its maximum at a 30% substitution rate, beyond which further increases in viscosity did not yield additional improvement [102]. Although the glyoxal route represents a significant step forward in reducing toxicity, it still lags behind the formaldehyde-based hydroxymethylation system in terms of reaction efficiency, control of secondary condensation, and the moisture and heat stability of the final resin; the underlying mechanisms also require further investigation.

In summary, hydroxymethylation effectively enhances lignin's participation in phenolic condensation systems by introducing aldehyde functional groups in place of the existing aromatic hydrogens. However, the inherent limitation of this method is that it converts rather than increases the total number of active sites; thus, if the resulting methylol groups are insufficient for adequate crosslinking, the overall reactivity remains constrained. In this context, combining hydroxymethylation with "site-increasing" modification strategies such as demethoxylation and phenolation—which create additional aromatic active sites—holds promise for synergistic enhancement in both functional group transformation and site-creation dimensions, achieving greater breakthroughs in lignin activity.

3.5. Lignin Degradation-Modified Phenolic Resins

The aforementioned strategies of demethoxylation, phenolation, and hydroxymethylation focus on modifying functional groups based on lignin's original molecular skeleton. However, these methods do not fundamentally address the severe steric hindrance caused by the high molecular weight of native lignin. The large molecular volume not only shields potential reactive sites but also hinders the effective embedding of lignin molecules into the phenolic resin crosslinking network [103]. Therefore, appropriately breaking down lignin

macromolecules, reducing molecular weight, and simultaneously increasing the number of accessible active sites offer another efficient pathway to enhance lignin reactivity. Compared with phenolation's "site addition" and hydroxymethylation's "efficiency enhancement," the degradation strategy addresses the more fundamental dimension of "deconstruction," often offering greater overall activation efficiency [104]. Currently, lignin degradation methods mainly include oxidative degradation, chemical hydrolysis, ionic liquid/deep eutectic solvent methods, plasma treatment, and biological enzymatic methods, overall showing a trend from harsh high-temperature/high-pressure conditions towards milder, greener catalytic systems.

Lignin's chemical reactivity is primarily concentrated in side-chain aliphatic hydroxyls, terminal phenolic hydroxyls, and active benzene-ring positions [105]. Selective oxidation can directionally cleave ether bonds, generating new phenolic hydroxyl groups and releasing methanol, significantly reducing molecular weight while increasing active functional groups, and typically proceeds under relatively mild conditions with a lower environmental burden [106]. Laccase-mediated oxidative modification is a typical example: after laccase oxidation treatment, lignin reactivity significantly improved, enabling the direct preparation of a 100% lignin-based formaldehyde resin without added phenol and achieving greatly improved adhesive bonding performance [107]. The phenol-assisted depolymerization (PAD) process further expands the application space of oxidative degradation, as shown in Figure 5a. Distinct from phenolation—which grafts phenol onto the lignin macromolecule to increase its reactivity—PAD selectively cleaves the robust C–C methylene linkages in condensed lignins. Here, "condensed lignins" refer to lignin structures formed during pulping or pretreatment processes in which lignin units have undergone irreversible C-C coupling (e.g., 5-5′, β-5, β-β, and α-5 linkages) that resist cleavage by conventional hydrolytic methods. In the PAD system, phenol serves primarily as a solvent and scavenger to facilitate depolymerization, with the cleavage targeting the inter-unit C-C bonds rather than formaldehyde-derived methylene bridges (which are typically formed during PF resin synthesis). This process achieved monomer yields up to 40% and biphenol yields up to 42%. The residual polyphenol fraction could be directly used to synthesize lignin-formaldehyde adhesives, meeting plywood application requirements [108]. Although this residual fraction is oligomeric, its molecular weight is substantially lower than that of the original lignin due to cleavage of methylene linkages during PAD, thereby increasing the density of reactive sites. Oxidative degradation offers clear advantages in mildness and environmental friendliness, but precise control of the selective cleavage of specific ether bonds and the quantitative relationship between oxidation depth and product distribution remain weak points in current research.

Chemical hydrolysis is a traditional degradation method, typically promoting cleavage and rearrangement of C-C and C-O bonds in lignin macromolecules under high temperatures or pressures, thereby achieving deep depolymerization [109]. Depolymerized lignin from hydrolytic treatment can serve as a biophenol to replace part of the phenol used in synthesizing resol phenolic resin, thereby reducing the resin curing temperature while maintaining good bonding and water resistance [110]. This reduction in curing temperature is attributed to the significantly lower molecular weight and the increased availability of reactive sites in the depolymerized lignin, which enhances its reactivity with formaldehyde and allows the crosslinking reaction to proceed more efficiently at lower temperatures. In that study, the hydrolytically depolymerized Kraft lignins (DKLS) had weight-average molecular weights (Mw) of 800, 1200, and 1700 g/mol, as determined by GPC, all substantially lower than the original Kraft lignin (Mw~10,000 Da), indicating extensive depolymerization. The products were predominantly oligomeric, and the paper did not report specific quantitative data on the yields of individual monomeric phe-

nol derivatives. Low-temperature depolymerization of alkaline lignin in an NaOH/urea aqueous solution yields low-molecular-weight aromatic compounds for phenolic resin preparation, exhibiting excellent properties such as fast curing, low formaldehyde emission, and high bonding strength [111]. MALDI-TOF-MS analysis in the cited study showed that the molecular weight of alkaline lignin decreased significantly after depolymerization in the NaOH/urea system. The primary molecular weight distribution shifted from approximately m/z 1500–2000 to m/z 700–1100, with the main peak decreasing from m/z 1785 to m/z 729, indicating efficient depolymerization and a more uniform molecular weight distribution. Bio-oil obtained from the liquefaction of hydrolyzed lignin in an ethanol/water cosolvent was used to prepare BPF resin, which exhibited a low curing temperature, high dry bonding strength, and dry and wet strengths that meet plywood adhesive requirements, but had a higher free formaldehyde content and slightly lower thermal stability than pure PF resin [112]. Chemical hydrolysis is a mature process, but high energy consumption costs, equipment requirements, and insufficient reaction selectivity are driving its transition towards low-temperature catalysis and green solvent systems.

Ionic liquids, as novel green solvents, are liquid compounds composed of inorganic or organic cations and anions that remain liquid at room temperature, offering advantages such as good biomass solubility, low toxicity, and low volatility, thereby providing new options for efficient biomass processing [113]. Studies show that 1-octyl-3-methylimidazolium acetate can catalyze the efficient conversion of more than 96% of lignin model molecules into phenolic compounds under mild conditions, demonstrating excellent catalytic cracking efficiency [114]. Furthermore, acidic deep eutectic solvents (DES, e.g., choline chloride/p-toluenesulfonic acid or choline chloride/lactic acid) can catalyze the degradation of industrial alkaline lignin. The resulting phenolic monomer mixture replaced 50 wt% of phenol and underwent ternary co-condensation with phenol and formaldehyde to prepare a bio-based phenolic resin, TCALPF (ternary co-condensation acid-catalyzed lignin-phenol-formaldehyde resin), and the degradation-condensation mechanism was elucidated. This DES system had a recovery rate of >85%, maintained catalytic activity after 5 cycles, and, after 4 cycles, the resin cost was only approximately half of pure phenolic resin [115]. To further enhance comprehensive resin performance, a dual functionalization strategy combining DES modification with MoS_2 nanosheet composite was applied to alkaline lignin (Figure 5b). At 20% lignin substitution, DES modification depolymerized lignin and exposed more reactive sites, increasing adhesive dry/wet bonding strength from 1.58/1.43 MPa to 1.91/1.58 MPa. Further introduction of 20% MoS_2@MAL (molybdenum disulfide nanosheets supported on modified alkali lignin) increased the strength to 2.42/1.86 MPa, and the limiting oxygen index reached 27.8%, simultaneously achieving significant improvements in both bonding and flame-retardant properties [116]. The MoS_2 nanosheets, when composited with the DES-modified lignin, serve both as a reinforcing nanofiller that improves mechanical properties through stress transfer and as a flame-retardant additive that promotes char formation during combustion, thereby enhancing the limiting oxygen index. Ionic liquid and DES systems represent the forefront of degradation modification, transitioning towards green chemical engineering, but their large-scale application still faces challenges such as solvent recovery, energy consumption, and long-term cycling stability.

Plasma treatment provides a novel physical field-assisted means for lignin degradation. However, this technology is still in the early stages of laboratory research, and industrial applications have not yet been reported. After plasma treatment, alkali lignin undergoes significant degradation; original groups are destroyed, and aromatic rings become enriched with radicals and oxygen-containing functional groups such as hydroxyl, carbonyl, carboxyl, and acyl groups, thereby comprehensively enhancing reactivity. Introducing

this modified lignin into the phenolic resin system reduced the resin's free formaldehyde content due to the increased number of reactive sites (e.g., phenolic hydroxyls and other oxygen-containing groups) in the plasma-treated lignin, which can chemically bind and consume more free formaldehyde during resin synthesis and curing, while simultaneously enhancing bonding strength, toughness, and thermal stability [117]. The plasma method offers unique advantages, such as short treatment time and no need for chemical reagents, but current research is still in its early stages and lacks a systematic understanding of the structure–property relationships among plasma type, treatment parameters, lignin structural evolution, and final resin performance.

Biological methods utilize enzymes produced by microorganisms to degrade lignin. In natural environments, lignin can be completely degraded through synergistic actions of various microorganisms [118]. Enhancing the activity of biological enzymes is crucial to biological lignin degradation. Lignin peroxidase (LiP), laccase, and manganese peroxidase are the most extensively studied [119]. LiP exhibits high efficiency in lignin depolymerization and delignification due to its high redox potential [120]. Laccase, with its phenoloxidase activity, is considered a suitable biocatalyst for lignin depolymerization. Recently, researchers successfully developed an alkaliphilic fungal laccase with high redox potential through enzyme-directed evolution strategies. This enzyme can effectively oxidize, demethylate, and depolymerize eucalyptus lignin, increasing phenolic hydroxyl and carbonyl content [121]. Furthermore, laccase can promote phenol liquefaction of lignin, and the resulting lignin-based phenolic resin exhibits better thermal flow and curing properties. Biological enzymatic methods offer mild conditions, high specificity, and environmental friendliness, but long reaction cycles, high enzyme costs, and insufficient adaptability to complex industrial lignin substrates remain major bottlenecks hindering their industrialization.

This degradation strategy overcomes the fundamental limitations posed by lignin's high molecular weight and steric hindrance, thereby enabling more comprehensive activation through molecular cleavage. This method consistently yields high phenol substitution rates (up to 100%), significantly improves bonding strength, and reduces curing temperature. However, the trade-off between activation efficiency and process practicality varies by method. Oxidative degradation, particularly laccase-mediated systems, offers the mildest conditions and best environmental compatibility, but suffers from low reaction rates and high enzyme costs. Chemical hydrolysis is industrially mature, but high energy consumption and limited selectivity constrain its efficiency. Ionic liquid and DES systems represent the most promising frontier in sustainable degradation; they have demonstrated catalyst recoverability (>85%) and potential for cost reduction (down to approximately half of the cost of pure PF resin), but solvent recovery and long-term stability remain challenges.

Before discussing the synergistic combination of physical and chemical modification, we must first answer a fundamental question: Given a specific lignin feedstock and a specific application goal, which modification strategy should be prioritized as the starting point? Figure 6 systematically presents the complete mapping relationships among 16 decision paths as a heatmap. Readers can quickly identify the recommended modification strategy based on their specific conditions—lignin source, phenolic hydroxyl content, target phenol substitution rate, and investment capacity. This heatmap replaces the traditional complex branching decision tree, condensing four layers of decision logic into a single-page matrix for easy reference and cross-path comparison.

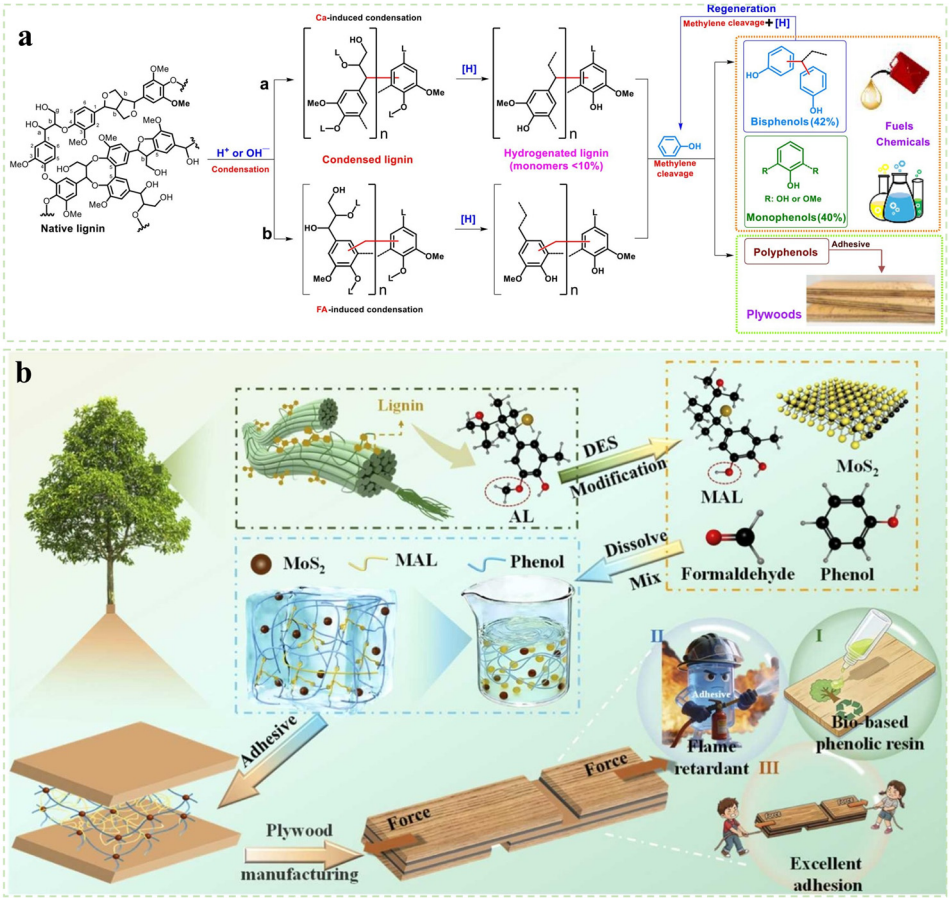


Figure 5. (**a**) The overall mechanism of phenol-assisted depolymerization (PAD) involves the cleavage of methylene bonds in condensed lignin. Reproduced with permission from reference [108]. Copyright 2023, Elsevier. (**b**) Schematic diagram of lignin-phenolic resin adhesive preparation process. Reproduced with permission from reference [116]. Copyright 2026, Elsevier.

After determining the recommended strategy based on Figure 6, Figure 7 presents the quantitative evaluation results for eight representative strategies as a radar chart to provide an intuitive understanding of their overall performance across the three dimensions of "reactivity enhancement," "achievable substitution rate," and "industrial feasibility." Overall, this radar chart reveals a clear "reactivity–substitution rate–industrial feasibility" trade-off: the strategy most easily implemented on an industrial scale (DS) yields only limited performance improvements, while the strategies with the most significant performance improvements (AD, PH) face the greatest challenges in industrial-scale production. This figure complements Figure 6—while Figure 6 addresses the question of "which strategy to choose," Figure 7 provides an intuitive comparison of "how each strategy performs across the dimensions." Used together, the two figures provide comprehensive decision support for strategy selection.

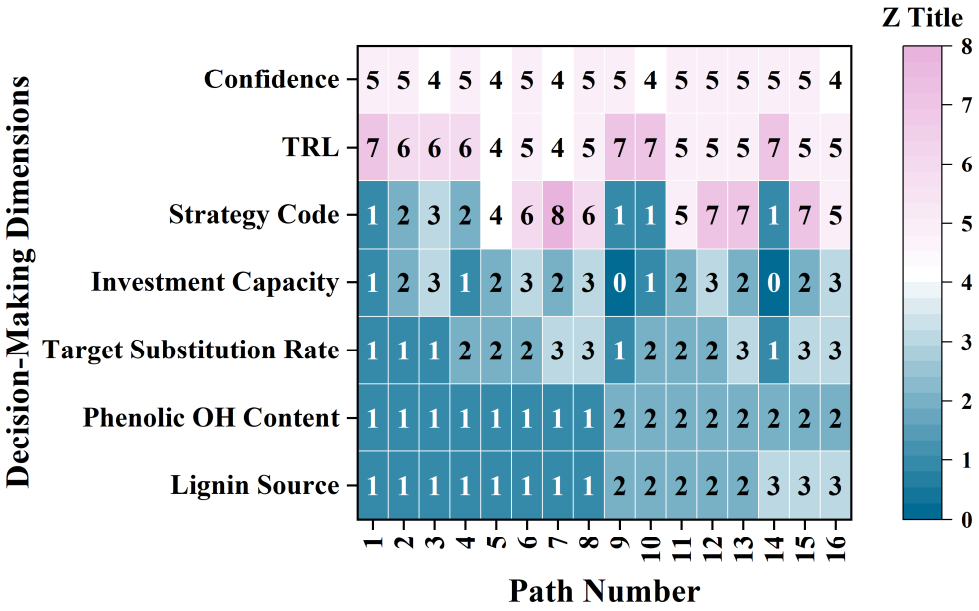


Figure 6. Heat map for selecting lignin modification strategies (16 decision paths). Each column represents an independent decision path (16 in total), with the values for the four decision dimensions shown in the columns—lignin source (1 = sulfate method, 2 = organic solvent method, 3 = enzymatic hydrolysis), phenolic hydroxyl content (1 = low, <3.5 mmol/g; 2 = high, ≥3.5 mmol/g), target phenol substitution rate (1 = <30%, 2 = 30%–50%, 3 = >50%), and investment capacity (1 = low/no new equipment, 2 = medium/existing equipment can be retrofitted, 3 = high/new production line can be installed, 0 = any)—as well as the corresponding recommended strategies, technology readiness levels (TRLs), and confidence levels. Color coding: The color changes in the cells for each decision dimension reflect the numerical value of that condition; recommended strategies are categorized into 8 types (1 = DS = Direct Substitution, 2 = HM = Hydroxymethylation, 3 = SF = Solvent Fractionation, 4 = US = Ultrasonic Depolymerization, 5 = MW = Microwave-Assisted Activation, 6 = AD = Demethylation, 7 = PH = Phenolation, 8 = DG = Degradation). Confidence indicates the strength of the recommendation (5 represents the highest confidence, based on a comprehensive evaluation of evidence from the literature). Reading example: Path 1 (sulfate method + low reactivity + <30% substitution rate + low investment) → Direct substitution recommended (DS, TRL 7, confidence 5/5). Data Source: The strategy recommendations for each path are derived from a comprehensive analysis of Tables 1–3 in the main text. This heatmap presents the full decision logic of the traditional decision tree in a matrix format and can be used as a standalone strategy query tool. (The methodology for constructing these decision paths, including the assignment of TRL and confidence scores, is detailed in the Supplementary Note on Quantitative Assessments and Scoring Methodology at the end of Section 4.)

Table 3. Quantitative environmental and economic indicators for LPF resin production strategies.

Strategy	Formaldehyde Emission Reduction	Energy Consumption (kWh/kg Resin)	Estimated CO_2 Reduction (%)	Solvent Recovery Required	Green Chemistry Score
Direct Substitution	30%–50%	0.8–1.2	15–25	N/A	7/10
Demethylation (alkaline)	50%–70%	1.2–1.8	20–35	Medium	6/10
Demethylation (acidic)	60%–80%	1.5–2.0	25–40	High	4/10
Phenolation (acid)	40%–60%	1.5–2.5	20–30	High	4/10
Graft Phenolation	50%–70%	1.0–1.5	25–35	Medium	7/10

Table 3. *Cont.*

Strategy	Formaldehyde Emission Reduction	Energy Consumption (kWh/kg Resin)	Estimated CO_2 Reduction (%)	Solvent Recovery Required	Green Chemistry Score
Hydroxymethylation	40%–60%	1.0–1.5	15–25	Low	7/10
Hydrolysis Degradation	50%–70%	2.0–3.0	20–30	Low–Medium	5/10
DES/Ionic Liquid	50%–70%	1.5–2.5	25–35	>90%	8/10
Combined Ultrasound + Demethylation	60%–80%	2.5–4.0	30–45	N/A	6/10
Conventional PF (reference)	—	0.8–1.0	—	N/A	3/10

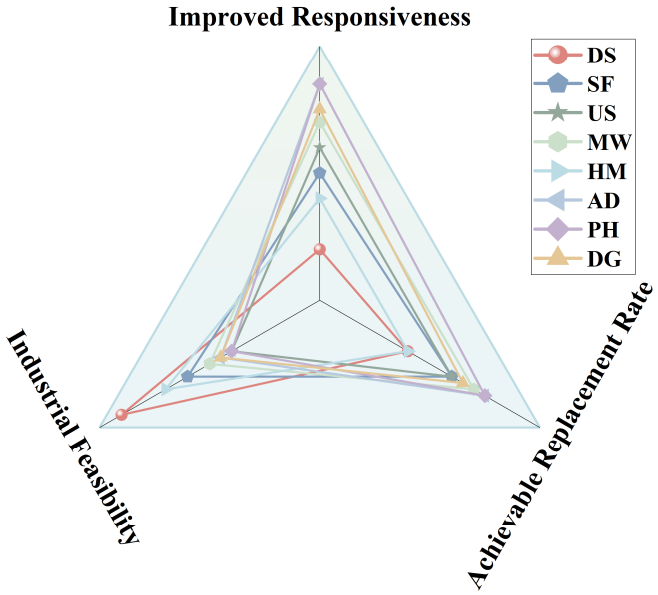


Figure 7. Comparison of lignin modification strategies in a radar chart comparing three performance dimensions (reactivity enhancement, achievable substitution rate, and industrial feasibility). Strategy abbreviations: DS = direct substitution; SF = solvent fractionation; US = ultrasonic depolymerization; MW = microwave-assisted activation; HM = hydroxymethylation; AD = demethylation (combining alkaline and acidic methods); PH = phenolation; DG = degradation. (Scores for "Reactivity Enhancement," "Achievable Substitution Rate," and "Industrial Feasibility" are semi-quantitative assessments by the authors, based on the literature and detailed in the Supplementary Note on Quantitative Assessments and Scoring Methodology at the end of Section 4.)

3.6. Synergistic Pathways: Integration of Physical and Chemical Strategies

Although most current research focuses on individual modification techniques, a growing body of evidence suggests that strategic combinations—or synergistic pathways—can yield superior results. For example, microwave-assisted phenolation of acid-insoluble lignin not only reduces reaction time but also enhances uniformity of phenolation, leading to improved resin properties. Similarly, ultrasound-assisted depolymerization followed by hydroxymethylation can sequentially address lignin's high molecular weight and limited active sites, resulting in a greater net increase in reactivity than either treatment alone. The use of deep eutectic solvents (DESs) represents another powerful synergistic platform: DES simultaneously depolymerizes lignin and exposes reactive sites, which can then be further activated by demethylation or phenolation in a one-pot or sequential process.

Despite these promising examples, systematic investigation of synergistic effects remains in its early stages. Critical knowledge gaps include: (i) quantitative understanding of how physical pretreatment parameters influence subsequent chemical modification efficiency; (ii) optimization of reaction sequences and conditions for maximal synergy; and (iii) structure–property relationships governing the performance of synergistically activated lignins. Addressing these gaps represents a key direction for advancing lignin-based phenolic resin technology toward industrial-scale applications.

3.7. Industrial Perspectives and Scale-Up Challenges

Despite decades of research and significant advances in lignin modification chemistry, the industrial adoption of LPF resins remains limited. A critical examination of the barriers to scale-up reveals a complex interplay of technical, economic, and logistical factors.

(1) Reagent Costs and Economics

The cost of chemical modification agents varies substantially across strategies. Direct substitution incurs minimal additional reagent costs, making it economically attractive for substitution rates $\leq$ 30%. Demethylation using Na_2SO_3 or $Na_2S_2O_3$ involves moderately priced reagents but requires careful dosage optimization to balance cost and efficiency. Phenolation, while effective, requires relatively expensive phenol and acid catalysts, which impose significant cost burdens on large-scale production. Degradation via DES systems offers favorable economics when the solvent recovery rate exceeds 85%. However, DES systems require additional capital investment for solvent recovery infrastructure.

(2) Lignin Feedstock Availability and Variability

Industrial lignin is primarily sourced from the pulp and paper industry (kraft and sulfite lignins, ~50 million tons/year globally) and emerging biorefineries (organosolv, enzymatic hydrolysis lignins, ~2–5 million tons/year) [122]. Kraft lignin, the most abundant and lowest-cost option ($200–400/ton), suffers from high polydispersity, sulfur contamination, and condensed structure [123]. Organosolv lignin ($500–800/ton) offers higher purity and reactivity but limited commercial availability. The inconsistency in lignin properties across batches and suppliers remains a primary barrier to industrial adoption, as resin manufacturers require consistent feedstock quality for reliable product performance.

(3) Solvent Recovery and Waste Management

Chemical modification processes often generate significant solvent waste. For DES systems, recovery rates > 85% have been demonstrated with maintained catalytic activity over multiple cycles. However, industrial implementation requires integrated recovery systems, which add to capital and operating costs. Acidic and alkaline modification processes generate wastewater that requires neutralization and treatment, with environmental compliance costs varying by jurisdiction.

(4) Process Scalability and Energy Impact

Among the chemical strategies discussed, direct substitution and hydroxymethylation are the most compatible with existing PF resin manufacturing infrastructure and require minimal process modifications. Demethylation using mild nucleophilic systems (Na_2SO_3/$Na_2S_2O_3$) operates under ambient pressure and moderate temperatures, facilitating straightforward scale-up. Phenolation and degradation processes typically require more specialized equipment and carry higher energy footprints. Microwave-assisted and ultrasound-assisted processes, while energy-efficient at the laboratory scale, present challenges for industrial-scale energy delivery and process control.

(5) Compatibility with Existing PF Manufacturing Infrastructure

The synthesis protocols for LPF resins—typically using similar temperature profiles, catalysts, and reactor configurations—can be adapted with minimal capital investment. However, the higher viscosity of LPF resins compared to neat PF resins may require modifications to pumping systems and spray-drying equipment. In principle, the resin viscosity at a given solids content can be adjusted by controlling the degree of condensation, as is standard practice in PF resin production. However, the incorporation of lignin can alter the viscosity–temperature relationship and the response to the degree of condensation. While several studies have reported the viscosity of LPF resins at different substitution rates [54,67,73], systematic quantitative studies that establish a general model linking the degree of condensation, lignin content, and final viscosity are lacking. This represents a key knowledge gap for industrial process design. Additionally, the increased water content in certain lignin feedstocks can affect resin solids content, requiring longer curing times or higher press temperatures.

(6) Environmental Considerations

LPF resins offer potential advantages for reducing formaldehyde emissions, with many studies reporting 30%–70% lower emissions than conventional PF resins. This reduction is attributed to a combination of factors: (i) the partial replacement of phenol with lignin reduces the total moles of phenolic components in the formulation, thereby decreasing the stoichiometric demand for formaldehyde; (ii) specific reactive sites on lignin can react with and chemically bind formaldehyde more effectively than phenol, leading to a lower free formaldehyde content in the final resin; (iii) the macromolecular structure of lignin may also physically hinder the diffusion of free formaldehyde, further contributing to the observed reduction. Quantitative LCA studies specifically addressing LPF resins remain relatively scarce. However, available data from related biorefinery and bio-based polymer studies suggest that replacing 30%–50% of phenol with lignin can achieve a 20%–40% reduction in global warming potential (GWP), primarily due to avoided fossil resource consumption and lignin's biogenic carbon content. Formaldehyde emission reductions translate to significant indoor air quality benefits, particularly in wood-based panel applications. It should be noted, however, that conventional PF-bonded wood panels already meet ULEF standards with extremely low formaldehyde emissions. Reducing emissions from this already low level to even lower values provides a relatively small incremental benefit to indoor air quality. The more significant advantages of LPF resins are therefore the reduction in fossil phenol consumption and the valorization of renewable lignin resources, with the reduction in formaldehyde emissions representing an additional, secondary benefit. These environmental advantages must be balanced against increased energy consumption for certain modification methods (e.g., ultrasound-assisted processes) and the environmental burden of reagent production and solvent recovery [124]. Table 3 summarizes quantitative environmental and economic indicators for different LPF resin production strategies, including the formaldehyde emission reduction rate, energy consumption, CO_2 reduction potential, required solvent recovery rate, and green chemistry score.

3.8. Industrial Applications: Current Status and Examples

Despite the substantial research efforts summarized above, the industrial-scale adoption of lignin-modified PF resins remains limited relative to the vast academic literature. Nevertheless, several notable examples of commercial or near-commercial implementation exist. Sunbake Co. (Tokyo, Japan) has been a pioneer in the commercial production of lignin-phenol-formaldehyde (LPF) resins for plywood applications, utilizing kraft lignin as a phenol substitute and achieving production scales of several thousand tons annually. In

the Nordic region, particularly in Norway, Borregaard has developed lignin-based PF resin products leveraging its lignosulfonate production platform, with applications in wood adhesives for exterior-grade panels. In China, several biorefinery demonstration projects have explored using enzymatic hydrolysis lignin from cellulosic ethanol production for PF resin synthesis, although these remain primarily at the pilot scale (100–1000 tons/year). More recently, companies in Finland and Sweden have initiated technology licensing programs for LPF resin production, targeting the European wood panel industry, where stringent formaldehyde-emission regulations create market pull.

4. Supplementary Note on Quantitative Assessments and Scoring Methodology

To ensure transparency and reproducibility of the quantitative comparisons presented in this review (Tables 1–3 and Figures 6 and 7), we provide the following methodological clarifications. The numerical values in Tables 1 and 2 are derived from a comprehensive analysis of the literature cited in the corresponding sections. Ranges (e.g., Mw reduction of 40%–70%) represent the span of reported values across multiple studies. The values in Table 3 (Energy Consumption, Estimated CO_2 Reduction, and Green Chemistry Score) are estimated by the authors using the best available data from the reviewed literature and general principles of green chemistry and life cycle assessment. The "Green Chemistry Score" is a semi-quantitative indicator (1–10) assigned by the authors based on an integrated assessment of five criteria: atom economy, use of hazardous reagents, reaction condition severity, waste generation, and solvent recyclability. A score of 10 represents an ideal green process. For example, DES/Ionic Liquid degradation receives a high score due to its excellent solvent recyclability (>90%), mild reaction conditions, and high atom economy. At the same time, acidic demethylation is rated lower due to its reliance on corrosive reagents and the high volume of waste generated. The "Formaldehyde Emission Reduction" is estimated from reported values in the studies cited in the main text, reflecting the potential environmental benefit of each strategy.

For Figure 6, the 16 decision paths were constructed by identifying the most critical variables that influence the selection of a modification strategy: lignin source, phenolic hydroxyl content, target substitution rate, and investment capacity. The recommended strategies were assigned based on a holistic evaluation of the literature synthesized in this review, cross-referencing the advantages, limitations, and reported outcomes of each method (summarized in Tables 1 and 2). The Technology Readiness Level (TRL) was assigned according to the standard definitions (TRL 1–3: basic research; TRL 4–6: validation in lab/pilot environment; TRL 7–9: industrial demonstration and deployment), based on the scale at which the strategy has been demonstrated in the reviewed literature. The "Confidence" score (1–5) reflects the strength of the evidence base supporting the recommendation, as assessed by the authors. A score of 5 indicates that the recommendation is supported by numerous studies with consistent findings.

For Figure 7, the scores for "Reactivity Enhancement," "Achievable Substitution Rate," and "Industrial Feasibility" are semi-quantitative (0–10) assessments by the authors, synthesized from the literature. "Reactivity Enhancement" integrates data on increases in active sites (e.g., phenolic OH content), reductions in molecular weight, and reported improvements in reactivity from the cited studies. "Achievable Substitution Rate" is based on the maximum phenol substitution rate successfully reported for each strategy in the reviewed literature. "Industrial Feasibility" is a composite assessment based on criteria such as equipment and infrastructure compatibility, ease of scale-up, reagent cost and availability, waste management challenges, and the potential for integration with existing PF manufacturing. This representation is intended to provide an intuitive visualization

of the trade-offs between performance enhancements and practical applicability, guiding strategic decision-making for research and development.

5. Conclusions and Perspective

This review surveyed physical and chemical lignin modification strategies for the synthesis of phenol-formaldehyde (PF) resin. Unmodified lignin substitutes phenol at 25%–50% without severe performance degradation, whereas chemically activated lignin, via demethylation, phenolation, or controlled degradation, achieves 60%–80% substitution with comparable or superior bonding. Membrane fractionation and steam explosion offer the highest industrial potential, while ultrasound and microwave methods require further development. Alkaline demethylation and acid phenolation optimally balance efficiency and scalability, whereas deep eutectic solvent (DES) and enzymatic methods represent frontiers in green chemistry.

Despite these advances, industrial lignin heterogeneity remains the primary obstacle to consistent resin performance. Urgent standardization of protocols for quantifying phenolic hydroxyls, assessing molecular weight distribution, and assessing reactivity is required for reliable quality control. Furthermore, quantitative structure–property relationships linking specific lignin features (e.g., S/G ratio, degree of condensation, phenolic OH content) to final resin performance remain to be established, hindering rational feedstock selection. Future research should prioritize five directions:

(1) Hybrid modification strategies: Systematically mapping multidimensional parameter spaces (pretreatment severity × modification conditions) to identify synergistic physical–chemical combinations, guided by computational design.
(2) Artificial intelligence and machine learning: Leveraging existing datasets for predictive modeling to rapidly screen feedstocks and conditions, alongside AI-assisted spectral interpretation (2D NMR, FTIR) and molecular dynamics for cross-linking network analysis.
(3) Multi-scale mechanistic understanding: Utilizing Density Functional Theory (DFT) and ab initio molecular dynamics (simulations based on quantum mechanical first principles without empirical parameters) to elucidate molecular-level reaction pathways—from bond cleavage during demethylation to cross-linking during curing—for rational catalyst design.
(4) Standardization and certification: Developing standardized testing protocols and obtaining regulatory certifications through academic–industrial–regulatory collaboration.
(5) Biorefinery integration: Co-valorizing cellulose and lignin fractions, guided by techno-economic analysis (TEA) and life cycle assessment (LCA) to ensure economic viability and verifiable sustainability.

In conclusion, lignin-based phenolic resins represent a concrete, technologically feasible pathway for the high-value utilization of forest biomass and the reduction in dependence on fossil resources. While significant challenges remain, the convergence of advances in green chemistry, computational modeling, and biorefinery integration brings industrial-scale LPF resin production within reach. The synergistic activation strategies outlined in this review provide a roadmap for this transition, and we anticipate continued progress toward the sustainable, economically viable manufacturing of bio-based phenolic resins in the coming decade.

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Y.W. and J.S.; funding acquisition, F.X. and J.S. All authors have read and agreed to the published version of the manuscript.

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