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Unlocking technical lignin: Self-crosslinking networks and the future of bio-adhesives

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Lignin, the most abundant natural aromatic polymer, faces formidable challenges for efficient valorization.[1] Commercial technical lignins, extracted via conventional pulping under harsh acidic or alkaline conditions, undergo severe depolymerization (cleaving β-O-4 linkages) and subsequent uncontrolled condensation.[2,3] Hyper-reactive intermediates rapidly form recalcitrant C–C bonds that sterically obstruct critical reactive sites (e.g., the C5 position). Consequently, in traditional lignin-phenol-formaldehyde (LPF) resin synthesis (Figure 1A), the severely depleted reactive sites on these condensed lignins prevent effective methylolation and self-crosslinking. While downstream chemical modifications—such as demethylation or phenolation—attempt to restore reactivity, they fail to resolve inherent LPF defects, including high curing temperatures, inferior crosslinking density, and toxic free-formaldehyde emissions that exceed regulatory standards.

The structural alterations of lignin inherently limit its viability in reactive feedstocks. In the synthesis of traditional lignin-phenol-formaldehyde (LPF) resins, the primary reaction mechanism relies on alkali-mediated methylolation (Figure 1A). Under alkaline conditions, this methylolation predominantly occurs at the ortho and para positions relative to the phenolic hydroxyl groups—specifically, the C1, C3, and C5 positions on the aromatic rings. However, in native lignin, alkyl side chains and methoxyl groups frequently occupy these sites. When utilizing highly condensed technical lignins as phenol substitutes, the severe depletion of accessible reactive sites prevents effective softening and self-crosslinking during hot-pressing. This depletion leads to a significant decline in crosslinking density and overall adhesive performance. Conventional approaches to circumvent these limitations predominantly rely on downstream physical and chemical modifications. These interventions include solvent fractionation, nano-processing, demethylation, and phenolation. Although these modifications enhance lignin's reactivity somewhat, they fail to fully resolve the inherent operational defects of LPF adhesives. Ongoing challenges include high viscosity, dark coloration,

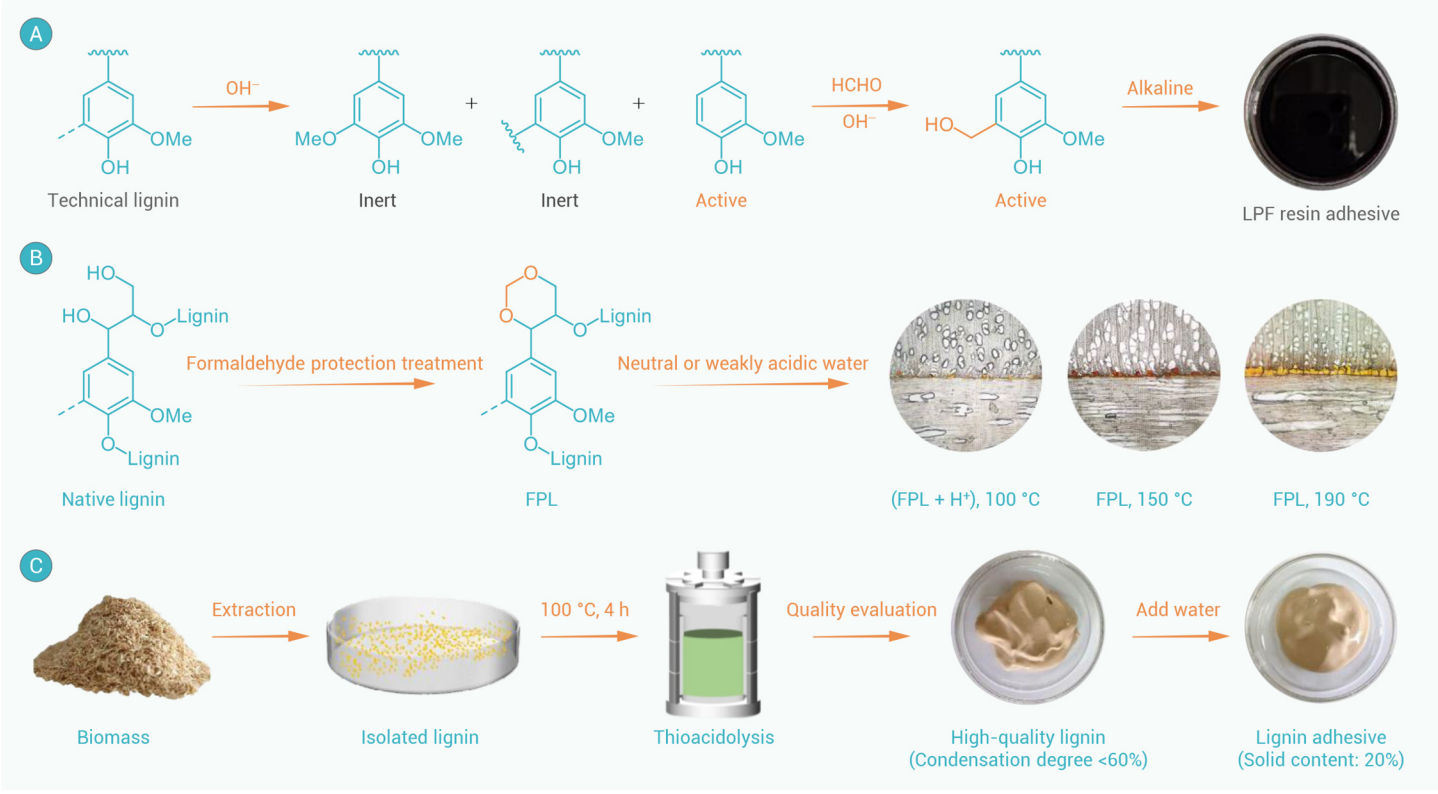


Figure 1. Pathways for synthesizing lignin adhesives (A) Traditional synthesis procedure for LPF resin adhesives under alkaline conditions. Reproduced with permission.[4] Copyright 2026, Springer Nature Limited. (B) Process of extraction from biomass and preparation of FPL adhesive. Reproduced with permission.[4] Copyright 2026, Springer Nature Limited. (C) Screening high-quality lignins extracted from biomass to prepare biobased wood adhesives. Reproduced with permission.[4] Copyright 2026, Springer Nature Limited.

and rigorous curing requirements, such as elevated hot-pressing temperatures and prolonged curing times. Additionally, these adhesives exhibit inferior crosslinking density compared to conventional phenol-formaldehyde resins. More critically, LPF adhesives often contain substantial residual free formaldehyde. This residue leads to toxic emissions that exceed regulatory standards during the manufacture and lifespan of engineered wood panels.

A recent paradigm shift redirects focus from downstream modification toward upstream structural preservation. Shuai and colleagues demonstrated that preserving the uncondensed native structure during extraction allows the resulting high-quality lignin to undergo direct self-crosslinking during hot-pressing (Figure 1B).[4] This process merely requires mixing the lignin with water, completely bypassing the need for exogenous phenol or

formaldehyde crosslinkers. The researchers evaluated lignins isolated from eucalyptus wood via diverse methodologies. These included milled wood lignin (MWL), formaldehyde-protected lignin (FPL), acetone-protected lignin (KPL), deep eutectic solvent-extracted lignin (DESL), kraft lignin (KL), and dioxane-HCl lignin (DL). They established that adhesion performance was inversely proportional to the lignin's degree of condensation. The molar yield of aromatic monomers following hydrogenolysis quantitatively reflected this condensation degree. MWL and FPL exhibited high monomer yields of 50.6% and 44.5%, respectively. These yields translated to remarkable bonding strengths that satisfied the 0.7 MPa minimum industrial requirement for plywood. In contrast, severely condensed lignins like KL and DL yielded only 5.8% and 2.9% monomers, respectively, and exhibited negligible adhesive properties. Modulating the formaldehyde loading further optimized the extraction efficiency of FPL. As the loading increased to 400 mg g^{-1} of biomass, the monomer yield rose to 44.9%. This rise correlated with a minimized condensation degree and significantly enhanced both dry and wet adhesion strengths.

Mechanistically, a sequence of physical and chemical transformations drives this self-adhesion. Water functions dually as a dispersion medium for application and as a plasticizer to soften the lignin matrix at elevated temperatures. As the hot-pressing temperature increased from 100°C to 190°C, the plasticized lignin exhibited enhanced flowability (Figure 1B). Crucially, the presence of these trace acids does not compromise the long-term durability of the wood composites; accelerated weather-resistance tests have shown that such acidic conditions actually facilitate continuous lignin crosslinking, allowing the bonding strength to slightly increase rather than degrade over multiple boiling-water cycles. This property allowed it to effectively penetrate and fill the vessels of the wood veneers. Chemical crosslinking immediately followed this physical penetration. Specifically, spectroscopic evidence delineated the precise crosslinking mechanism: gel permeation chromatography demonstrated a distinct increase in molecular weight, while solid-state NMR and FTIR spectra confirmed the acid-catalyzed consumption of aliphatic hydroxyls and residual ether bonds. Furthermore, 2D HSQC NMR elucidated the subsequent conversion of these native motifs into robust C–C linkages via reactive intermediates, validating the formation of an intractable self-crosslinked network. Ultimately, the resulting interfacial crosslinking between the applied lignin and the intrinsic lignin within the cell walls established a robust mechanical and chemical interlock. Transitioning this self-crosslinking strategy from a laboratory demonstration to scalable industrial application requires standardized evaluation protocols. To this end, Shuai and colleagues developed a systematic framework to quantify lignin quality, streamline extraction, and optimize formulation (Figure 1C).[5] To address the structural heterogeneity caused by varying biomass sources and extraction techniques, the team implemented a rapid quantitative screening protocol based on thioacidolysis. This protocol innovatively employed the effective carbon number method during gas chromatography-mass spectrometry analysis. This methodology provided a fast and cost-effective approach to quantify monomer yields. Consequently, it allowed for the precise calculation of the lignin's condensation degree without relying on expensive authentic standards. Through this systematic framework, the researchers established a definitive empirical threshold. They classified lignin with a condensation degree of ≤ 60% as "high-quality lignin". Such lignin can be directly utilized for wood adhesives without prior chemical modification.

Furthermore, the protocol optimized the engineering parameters of the precipitation and isolation steps, yielding a structurally preserved adhesive platform that demonstrated clear operational advantages over traditional LPF resins across four key areas. First, it enabled mild curing conditions. By circumventing strongly alkaline environments, the FPL adhesive could be hot-pressed under neutral or weakly acidic conditions. Adding trace sulfuric or phosphoric acid as a crosslinking catalyst significantly reduced the required hot-pressing temperature from 170°C to 100°C and shortened the pressing time from 15 to 2 min. This acidic curing environment also mitigated the dark coloration typical of LPF resins, yielding a visually appealing, light-colored glue line. Second, the platform yielded competitive thermomechanical properties. Seven-layer plywood pressed with FPL adhesives at 110°C for 20 min (glue spread 100 g m^{-2}) achieved a modulus of elasticity of 6716 MPa and a modulus of rupture of 32 MPa, fully satisfying industrial requirements. Thermoset sol-gel analysis indicated a sol fraction of less than 5%, confirming a highly water-resistant crosslinked network that outperformed urea-formaldehyde resins in multi-cycle boiling water tests. Third, it achieved zero added formaldehyde emissions. Because the extracted lignin is insoluble in neutral or acidic aqueous solutions, solid-liquid separation fundamentally eliminated the risk of free formaldehyde pollution. Emission tests revealed that FPL-bonded plywood emitted only 0.2 mg L^{-1}, easily surpassing the stringent European E0 grade requirement of ≤ 0.5 mg L^{-1}. In contrast, traditional urea-formaldehyde plywood failed severely at 9.98 mg L^{-1}. Finally, the strategy improved logistical efficiency. High-quality lignin can be stored and transported as a solid paste and reconstituted with water on-site to a functional solid content of 20% to 33%. The protocol specified the slow dropwise addition of the spent pretreatment liquor into deionized water, acting as an anti-solvent, at a volume ratio strictly greater than 2:1. This critical parameter prevented the formation of sticky agglomerates, ensured sufficient lignin recovery, and facilitated the removal of unreacted modifying agents via simple water washing. Together, these formulation strategies circumvent the shelf-life stability issues inherent to liquid adhesives and drastically minimize transportation costs.

Beyond logistical efficiency, evaluating the industrial translation of this strategy requires critical assessment. Unlike conventional LPF routes that utilize readily available industrial technical lignins, this paradigm demands dedicated protective extraction facilities, where initial capital costs and large-scale solvent recovery remain significant bottlenecks. Furthermore, distinct operational trade-offs exist: while FPL yields highly reactive lignin, it introduces toxic reagents upstream; conversely, KPL offers a greener solvent profile but requires stringent reactor pressure and temperature control. Compared to other bio-based alternatives, this uncondensed lignin route offers superior hydrothermal durability over soy-protein adhesives and circumvents the geographic supply limitations of tannin-based systems, despite necessitating more complex upstream processing. Nevertheless, the biorefinery concept of coproduction—generating lignin adhesives alongside cellulose-rich solids—can effectively offset these upfront extraction costs. In conclusion, this systematic research transforms lignin's historical structural limitations into synthetic advantages via native preservation and water-plasticized self-crosslinking. While offering performance metrics rivaling petroleum-based resins, future research must address the scalability of upstream solvent recovery and continuous extraction protocols. Ultimately, overcoming these engineering challenges will firmly establish lignin as a highly tunable, sustainable resource for advanced polymer materials.

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AUTHOR CONTRIBUTIONS

All authors contributed to the manuscript and approved the final version.

DECLARATION OF INTERESTS

The authors declare no competing interests.