

Priority Dissolution of Hemicellulose and its Subsequent Value-added Utilization along with High Activity Lignin

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In lignocellulosic biorefineries, efficiently and cleanly deconstructing the stubborn structure of plant cell walls to achieve component separation remains a research hotspot. Among these, the high-value utilization of lignin is limited by its purity and condensed structure. Traditional pretreatment strategies have predominantly focused on “forceful cell wall disruption,” directly targeting lignin itself for removal or dissolution. However, recent research on two-step sequential biomass deconstruction is guiding us toward a more sophisticated paradigm: the preferential and deep dissolution of hemicellulose can serve as a “switch” that triggers subsequent efficient and selective dissolution of lignin.

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The efficient deconstruction and high-value utilization of lignocellulose (nature’s most abundant renewable carbon source) represents the ultimate goal of biorefineries. Lignin—a highly promising aromatic polymer—presents significant potential for selective separation and conversion, which is crucial for achieving comprehensive utilization of all fractions (Li *et al.* 2022, 2024a). Despite decades of research efforts, achieving efficient, selective dissolution of lignin under mild conditions while preserving its inherent reactivity remains a significant challenge (Zhou *et al.* 2024). We contend that past research may have overemphasized lignin itself while overlooking its critical “neighbor”—hemicellulose. This paper aims to demonstrate a central thesis: the preferential removal of hemicellulose can be a key to unlocking the selective dissolution of lignin.

Why is the removal of hemicellulose so critical?

Hemicellulose is an amorphous heteropolysaccharide that binds tightly to the surface of cellulose microfibrils *via* hydrogen bonds while cross-linking with lignin molecules through multiple covalent bonds (ether bonds, ester bonds, glycosidic bonds, and aldol bonds, among others). This structure forms a dense network between cellulose and lignin. When attempting to dissolve lignin with solvents, this hemicellulosic network acts as a formidable physical barrier, preventing effective solvent penetration and the elution of lignin fragments. The presence of lignin-carbohydrate complexes (LCC) means that dissolving lignin requires not only breaking its own ether bonds or carbon-carbon bonds, but also severing these connecting bonds. This significantly increases the difficulty and non-selectivity of chemical treatment, often leading to uncontrolled condensation reactions during dissolution that destroy lignin’s structure and reduce its reactivity.

Hemicellulose primarily fills the spaces in wood between cellulose microfibrils. Its presence markedly reduces the porosity of the cell wall micro-layers and the accessibility of solvents. Once hemicellulose is removed, it is as if a network of interconnected “nanoscale channels” has been opened within a dense wall.

The LCC bonds between hemicellulose and lignin are extremely difficult to remove completely, not merely due to the high bond energies of aldehyde, ether, and other chemical bonds, but because these bonds are concealed within lignin's dense three-dimensional network structure, making them inaccessible and difficult to attack by chemical reagents. This is analogous to a robust reinforced concrete structure, where LCC bonds act as critical "weld points" connecting the reinforcing bars (cellulose) to the concrete (lignin), while staying tightly encapsulated within. A core objective in developing efficient pretreatment technologies for lignocellulosic feedstocks is to effectively disrupt LCC structures without severely damaging the cellulose. This approach aims to "break through the armor" of lignin, thereby exposing the internal chemical bonds to subsequent reaction and cleavage.

Methods and Mechanisms for Hemicellulose Removal

Different treatment methods operate on distinct mechanisms, aiming to disrupt the structure of hemicellulose and its bonds with lignin and cellulose. Alkali treatment is the most classic and widely used method (Li *et al.* 2025b). Appropriate sulfonation of lignin under alkaline conditions swells the cell wall, thereby loosening the wood chip structure. Subsequent pre-extraction of hemicellulose with concentrated alkali yields a removal degree of 69.0% at a KOH dosage of 15%, reaction time of 1 hour, and temperature of 25 °C, with a yield of 16.4% and a relative molecular mass of 92,100 g/mol. Alkali solutions such as NaOH and KOH saponify acetyl and glucuronic acid groups in hemicellulose while breaking glycosidic bonds and partial ester linkages between hemicellulose and lignin (Zhou *et al.* 2023, 2024). This method is highly efficient, causing only minor simultaneous dissolution of lignin (<10%), though selectivity remains to be improved.

The emerging deep eutectic solvents (DES), such as choline chloride/ethylene glycol/iron chloride, demonstrate unique advantages in hemicellulose removal (Ding *et al.* 2024). DES typically possess high hydrogen bond donor/acceptor capabilities, enabling effective disruption of intramolecular and intermolecular hydrogen bond networks within hemicellulose molecules and hydrolysis of their glycosidic bonds (Li *et al.* 2024b, 2025a). DES treatment conditions are relatively mild, exhibiting good selectivity toward hemicellulose while largely preserving the structural integrity of cellulose and lignin (Ding *et al.* 2024).

Hydrothermal treatment utilizes high-temperature liquid water or subcritical water as the reaction medium. Under elevated temperature and pressure, the ionic product of water increases, generating high concentrations of H_3O^+ and OH^- ions that act as autocatalysts. Hydrothermal pretreatment enhances glucose release from lignocellulosic biomass and selectively removes hemicellulose, yielding hemicellulose, xylooligosaccharides (XOS), monosaccharides, and furfural (Ma *et al.* 2021). Hot water treatment demonstrates significant efficacy in hemicellulose removal, particularly for xylan dissolution. However, excessively high temperatures and prolonged durations may cause further degradation of dissolved hemicellulose into byproducts such as furfural.

Subcritical CO_2 treatment combines physical and chemical approaches. For instance, pretreatment with 5 MPa CO_2 , 80 min at 160 °C yielded a maximum xylose production of 9.8 g (including 8.4 g oligosaccharides) per 100 g raw material (Zhang *et al.* 2015). Subcritical CO_2 hydrolysis pretreatment of corn stover yielded a pre-hydrolyzed product rich in xylose, with approximately 90.2% present as xylose oligosaccharides (XOS) and functional XOS (DP < 5) accounting for about 40% (Liu *et al.* 2019). The mechanism involves: (i) CO_2 permeating into biomass pores, causing instantaneous pressure relief that physically expands and fractures the biomass structure, increasing specific surface area; and (ii) CO_2 reacting with water to form carbonic acid, lowering

system pH and catalyzing hemicellulose hydrolysis. This method is green and leaves no solvent residues, but treatment intensity is typically low. Despite methodological variations, the fundamental objective remains consistent: to preferentially degrade and dissolve hemicellulose through chemical or physical means, thereby increasing biomass porosity, disrupting LCC structure, and paving the way for subsequent lignin dissolution.

Solubility Patterns of Lignin Following Hemicellulose Removal

Once hemicellulose—the key obstacle—is removed, the dissolution behavior of lignin undergoes a fundamental, positive transformation, exhibiting high selectivity and controllability. The porous structure formed after pretreatment enables solvents to rapidly and uniformly penetrate lignin regions. Research indicates that raw materials with preferential hemicellulose removal achieve a maximum delignification of 96.5% during subsequent lignin dissolution stages (*e.g.*, ethylene glycol and ferric chloride treatment), while significantly reducing required reaction time, temperature, and chemical reagent consumption (Li *et al.* 2025b). The proportion of lignin dissolution revealed that the intercellular layer exhibited a significantly higher lignin release than the cell wall. Due to reduced mass transfer resistance, the solvent can operate under milder conditions, thereby favoring the cleavage of key bonds such as β -O-4 linkages within the lignin itself rather than inducing condensation reactions between its benzene rings. This implies that the dissolved lignin exhibits higher molecular weight, richer functional groups (such as phenolic hydroxyls), and a morphology closer to its natural structure (Li *et al.* 2025b).

By precisely controlling the extent and method of hemicellulose removal, one can “customize” the pore structure and surface chemistry of biomass. This effectively designs different “exit routes” for lignin dissolution. For instance, mild DES pretreatment may primarily open the S2 layer structure of the cell wall, guiding lignin dissolution from specific regions (Ding *et al.* 2024); whereas alkali treatment may cause more global structural disruption (Li *et al.* 2025b). This controllability enables the possibility of achieving hierarchical, directional dissolution of lignin. In essence, the dissolution of lignin after hemicellulose removal transforms from a “brute-force assault on a fortress” into a process where “channels are cleared for natural flow.” The core principle shifts from non-selective, destructive degradation to selective, protective depolymerization.

Conclusions

In summary, the prioritized removal of hemicellulose is equivalent to obtaining the “key” to unlocking the stubborn barrier of lignocellulose. Through strategies such as alkali treatment, DES, hydrothermal processing, or subcritical CO_2 , it is possible to dismantle the physical and chemical barriers formed by hemicellulose, creating a highly accessible pore structure. This pretreatment step enables subsequent lignin dissolution to proceed under milder, more economical conditions, ultimately yielding lignin products with higher yields, superior quality, and enhanced reactivity.

Looking ahead, the research focus should shift toward developing greener, integrated two-step processes combining hemicellulose removal and lignin dissolution. Achieving high-value utilization of all lignocellulosic components and advancing toward a truly sustainable bioeconomy will require deepening our understanding of how different pretreatments precisely modulate the nanostructure of biomass cell walls, and further optimizing synergies between these steps.

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