Research Article

Reviewing Chemical Strategies for Improving the Sustainability and Performance of Wood Products

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Abstract | Wood is a sustainable resource with exceptional characteristics, making it a promising candidate for a bioeconomy. However, global climate change may pose significant challenges to wood-value chains. To address these issues, it is crucial to reconsider the current approach to wood procurement and processing. The ecological variety of wood, its origins, and its technological implications for the production of wooden products are the key factors to consider. Industrial procedures have been enhanced to mitigate variability in wood qualities, facilitate more effective processing, and create reliable goods. The development of innovative wood processing methodologies and environmentally friendly chemical procedures for wood modification is required due to the necessity of conserving biodiversity and the adverse effects of climate change on forests. These advancements are crucial for managing a broader range of wood resources in the coming years. This article examines the chemical and structural composition of wood and the techniques used in industrial processes to achieve uniformity and alter wood properties for environmentally friendly wood products.

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Introduction

Sustainable wood materials play a pivotal role in achieving sustainability targets during the transition towards a prospective bioeconomy. Due to an exceptional integration of CO_2 storage capacity and renewability, these substances meet fundamental criteria, encompassing diminished resource depletion and greater carbon sequestration (Makepa and Chihobo, 2024). Consequently, the expansive area of wood investigation is currently undergoing a revived surge of interest, particularly within three distinct subdomains: (i) the utilization of wood and its derived goods for engineering purposes; (ii) the fabrication of materials derived from the constituents of wood cell walls through bottom-up methodologies, and (iii) the creation of functional wood materials using top-down techniques that preserve the inherent structure. The contributions stemming from these three subfields exhibit immense potential to replace materials that are less environmentally or climatically friendly within their respective domains. However, this potential is realized at varying length scales and is accompanied by distinct challenges and prospects. Another subfield

of research centers around bottom-up methodologies that employ cell wall constituents, specifically lignin and cellulose, to facilitate the development of materials with exceptional performance (Qin *et al.*, 2024).

The complicated manipulation and arrangement of cellulose, including cellulose nanocrystals and nano- or micro-fibrillated cellulose, have resulted in the fabrication of cellulose-based materials exhibiting diverse functionalities for a wide range of applications (Laaksonen *et al.*, 2011; Wang *et al.*, 2011). Recently, lignin has been employed as a fundamental constituent for the fabrication of carbon nanotubes and shape-memory materials (Liu *et al.*, 2021). Advancements in the realm of 3D-printing and assembly techniques, such as fiber orientation with flow direction, enable the reorientation of cellulose and present novel prospects for scaling up. However, their compatibility with expansive engineering frameworks may raise concerns (Hausmann *et al.*, 2018; Mittal *et al.*, 2018). The deconstruction of the cell wall, necessary for the processing of cellulose and lignin, entails a laborious expenditure of energy and results in the unfortunate loss of the advantageous structural arrangement inherent in wood. Henceforth, it is plausible to consider cellulose and lignin-derived substances as viable candidates for esteemed applications, including but not limited to the realm of biomedicine and the fabrication of electrochemical cells (Balakshin *et al.*, 2021; Oksman *et al.*, 2016).

Chemical complexity of wood

Wood is an immensely diverse material that can be chemically modified in many different ways. Wood is abundantly provided with OH groups, which are, in essence, the focal point of each specialized chemical intervention (Wang *et al.*, 2024). However, the complex structure of wood arises from its distinctive hierarchical arrangement, characterized by significant spatial heterogeneity. At the atomic scale, the constituent components of all wood species consist primarily of the elemental entities' hydrogen, carbon, and oxygen, with corresponding ratios arising from the prevalent process of photosynthesis observed in all plants. The wood cell wall is primarily composed of structural biomacromolecules, with cellulose being a prominent constituent (Schmitt *et al.*, 2021). These biomacromolecules, including cellulose, exhibit a remarkable degree of consistency across various species. Cellulose is composed of glucose molecules, which are linked together in a linear fashion through β-1,4-glycosidic bonds. This arrangement results in the formation of cellulose fibrils, which exhibit both crystalline and amorphous regions. In the realm of the cell wall, one must acknowledge the subtle discrepancies in the structural arrangement and relative abundance of cellulose (Figure 1). However, it is imperative to recognize that lignin and hemicelluloses, which compose the intricate framework enveloping cellulose fibrils, exhibit a greater degree of diversity when comparing different wood species. Hemicelluloses are composed of various saccharide units, arranged in both main chain and side chain configurations (Madan *et al.*, 2021). Softwoods are primarily characterized by the prevalence of glucomannans, whereas hardwoods are predominantly composed of xylans (Salmén and Burgert, 2009). Hemicelluloses serve as intermediaries between lignin and cellulose in both hardwoods and softwoods, wherein lignin is generated through a radical polymerization mechanism. Even though hemicelluloses and lignin have different structures and make-ups in different types of wood, as a composite of natural fibers, the cell wall structure is consistent across all wood varieties. This is evident through the arrangement of cellulose fibrils within a hemicellulose and lignin matrix, as well as the consistent density of cell walls, approximately 1550 kg m^{-3} (Baucher *et al.*, 1998; Boerjan *et al.*, 2003).

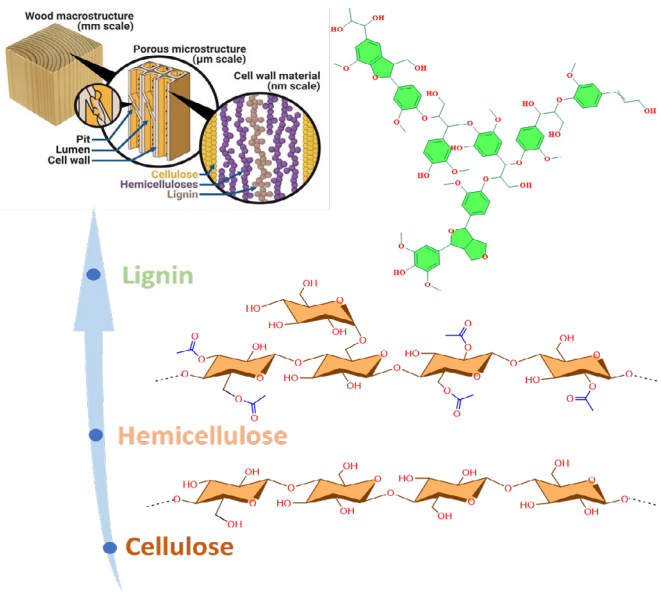

Figure 1: *A brief summary of the structure of wood at various length scales: Various types of cell wall material, including cellulose, hemicelluloses, and lignin; wood macrostructure with annual rings, and porosity microstructure with pits, which are passageways through cell walls that connect adjacent cells' lumina (singular: lumen) (Thybring and Fredriksson, 2021).*

Extractives, which are small compounds that are incorporated into the cell walls of living trees during the process of heartwood production, provide a substantial contributor to the chemical diversity observed in these plants. These compounds can fill nanoscale gaps in the structure of a cell without interacting chemically with the biopolymers that make up the structure. This results in increased hydrophobicity of the cell walls, hence slowing the disintegration of fungus (Hillis, 1968, 1971). The category of extractives can be categorized into three primary categories, namely phenolic chemicals, aliphatic molecules, and terpenes and terpenoids. According to the literature, aliphatic compounds have the ability to function as surfactants, while phenolics provide a direct antifungal impact (Zhao *et al*., 2020). The presence of extractives during wood processing and in the final products can lead to variations in wood properties, such as durability, shrinkage, swelling, coating behavior, bonding, and color (Ghofrani *et al*., 2016; Nussbaum and Sterley, 2002). However, the standard methods employed in wood processing can be utilized as a foundation for deriving inspiration from nature in order to produce wood treatments that are more environmentally friendly. These treatments may include pest repellents and preservatives, as well as techniques to enhance fire resistance. In order to accomplish this objective, it is imperative to comprehend the fundamental mechanisms governing the functionality of extractives, particularly in their interaction with tree growth, and establish appropriate methodologies for their synthetic production. However, the influence of chemical complexity on wood's treatment and usage activity cannot be reduced to the role of extractives alone. It is imperative to take into account the collective impacts of additional wood constituents and structural attributes.

Structural complexity of wood

Wood displays an exceptional range of cellular and tissue variations, leading to notable disparities in density. The remarkable diversity observed in trees can be attributed to their imperative to optimize the dual functions of wood: enabling the efficient conveyance of water from the roots to the crown while concurrently bestowing mechanical stability upon the tree, particularly in response to the challenges posed by wind loads. Softwoods and hardwoods of more recent evolutionary origin have evolved distinct mechanisms to maximize the efficiency of these processes through their tissues and axial cells. Softwoods are primarily comprised of a singular cellular entity known as the tracheid, exhibiting diverse adaptations to serve distinct purposes. Due to their thin cell walls and large lumens, the tracheids present in earlywood are ideal for transporting water efficiently in climate areas with a yearly cycle. Conversely, the tracheids observed in the latewood primarily contribute to mechanical support due to their narrow lumina and robust cell walls. In the growth rings, there are significant differences in cell densities between the beginning and ending points. The ratio of earlywood to latewood tracheids in a given growth ring can be affected by the thickness of that ring. Age, heredity, and environmental factors are among the variables that determine its thickness (Knigge and Schulz, 1966). Softwoods structural variations are strongly influenced by cellular and connective tissue levels, as demonstrated by these connections. Even within the same species, there can be noticeable changes in density from one stem to another and from one growth ring to another. This variation is mostly caused by growth ring dynamics.

Hardwoods have undergone evolutionary adaptations to maximize aqueous conveyance and enhance mechanical integrity, owing to their distinctive axial cellular and tissue arrangements. Younger hardwoods have undergone cellular differentiation, resulting in the development of distinct cell types that exhibit enhanced optimization and specialization in comparison to softwoods. The fibrous component, which plays a crucial role in providing mechanical stability, exhibits a structural resemblance to a tracheid found in the latewood. On the other hand, the vessel responsible for water transportation showcases a novel structural arrangement that relies on enhanced collective cellular functionality. Water flow is restricted in softwoods because tracheids are monolithic structures with closed ends. In juxtaposition, a container can comprise myriad discrete cellular units, wherein the perpendicular cell membranes are extracted to generate conduits spanning a magnitude of several meters. The arrangement of this structure facilitates enhanced velocity and heightened efficacy in the transportation of water (Cosgrove, 2005). Hardwoods, in addition, exhibit greater heterogeneity in growth ring structure when contrasted with softwoods. Ring-porous hardwoods, such as oak and ash, exhibit the presence of earlywood vessels with significant diameters, resulting in the formation of a ring with a lower density during the initial phase of growth. On the other hand, diffuse-porous hardwoods, including

poplar, maple, and beech, showcase a more uniform distribution of vessels throughout the growth ring. In the case of ring-porous hardwoods, the earlywood vessel ring stays pretty consistent. This makes the wood denser than it would be if the growth rings were thinner.

Chemical strategies for wood modification

The gradual advancement in knowledge regarding the characteristics and functioning of wood has brought about the recognition that the distinctive features of wood mostly derive from the chemical composition of its cell wall constituents. By altering the chemical composition of wood, it becomes feasible to modify its inherent characteristics, thereby influencing its overall functionality. The majority of studies pertaining to the chemical alteration of wood have mostly concentrated on enhancing its dimensional stability and enhancing its resistance against biological degradation.

The modification of wood cell wall polymers has the potential to reduce the rate of wood deterioration, as the majority of these processes are primarily driven by (bio) chemical mechanisms. This suggests that by modifying the chemistry of these polymers, it may be possible to eliminate or significantly decrease the extent of wood degradation, making it more beneficial for practical applications. Undoubtedly, the imposition of restrictions on access to or alteration of hydroxyl groups has significant consequences. Notably, such modifications make highly specific enzyme activities impractical and compromise the capacity to engage hydrogen bonding. The user did not provide any text to rewrite. Wood modification comprises the establishment of comparatively enduring linkages between the OH groups of wood biopolymers and functionalizing chemicals. This process helps decrease the ability of these agents to leach out of the wood. An optimal method for modifying wood should possess the following characteristics: (i) cost-effective, (ii) efficient in terms of time, (iii) environmentally benign, (iv) resulting in a material that can be safely discarded no greater environmental risks, and (v) applicable to various wood species without limitations.

Prior to the advent of the 20th century, investigations pertaining to the transformation of wood predominantly relied on empirical methodologies, particularly within the industrial domain. On one hand, this can be attributed to the complex structure of wood tissue, which encompasses both structural and chemical complexities, thereby posing significant challenges for its characterization using conventional methodologies. On the other hand, there exists a prevailing perception that wood, as an engineering material, holds a secondary position compared to more dominant counterparts such as concrete and steel. Over the years, the study of wood modification has experienced a significant boost, owing to the growing global environmental consciousness and the advent of advanced investigation techniques with enhanced precision and spatial resolution (Foston *et al.*, 2011).

Chemicals that have undergone extensive examination for the purpose of wood modification primarily consist of organic compounds. In contrast, inorganic chemicals such as metal salts, borates, and silicates are commonly employed for impregnation purposes. Organic chemicals encompass a wide range of substances, including boronates, phosphonates, silanes, isocyanates, epoxides, nitriles, alkyl chlorides, aldehydes, carboxylic acids, lactones, anhydrides, and acid chlorides (Rowell, 2006). Each of these compounds possesses distinct advantages and disadvantages, but providing a comprehensive account of these properties falls beyond the scope of this review. Even so, they all exhibit a shared tendency for reacting with hydroxyl groups present in wood. As a general principle, it can be observed that the member with the lowest molecular weight in a homologous series tends to exhibit the highest reactivity and possesses the lowest boiling point, making it particularly advantageous in practical applications. The inherent characteristics of the covalent bonding established between the wood and the reagent are also of utmost significance. If the new covalent bonding is intended to exhibit greater stability compared to the glycosidic bonds found in polysaccharides, the C-O-C bonding could be considered the most appropriate covalent bonding. Acetals and specific esters with lower stability may exhibit potential utility in facilitating the gradual or regulated liberation of a chemically bonded substance in response to environmental triggers (Rowell, 2006).

In order to attain appropriate wood modification, it is necessary to guarantee a sufficient dispersion of chemically reacted substances within the cell walls. Considering this reasoning, it is crucial that the chemical agents used to modify wood (i) can make the wood swell so they can penetrate better; (ii) react

quickly with the OH groups of cell wall polymers like lignin, hemicellulose, and cellulose, reducing biopolymer degradation in slightly acidic or neutral pH and slightly warmer conditions; (iii) don't produce any waste; (iv) form bonds that are chemically stable; and (v) keep the desirable characteristics of the original wood intact. Unfortunately, the simultaneous attainment of all these conditions is infrequently realized, particularly on an industrial scale.

Traditionally, there have been four main factors used to quantify the historical scope of wood modification: (i) proportion of weight gain, (ii) water uptake, (iii) volume gain, and (iv) antiswelling efficiency. Some of these parameters are very helpful for understanding how wood products are made and how they can be used, but when looked at all together, they don't tell us much about how the products are changed or what their natural properties are. Therefore, the utilization of advanced methodologies such as electron microscopy, scanning probe microscopy, dynamic vapor sorption, X-ray computed tomography, X-ray diffraction, NMR spectroscopy, and Raman spectroscopy has witnessed a growing trend in the examination of wood-based materials and artifacts (High and Penkman, 2020; Van den Bulcke *et al*., 2013).

The top priority in wood treatments lies in guaranteeing accessibility, specifically the permeation of the reacting reagent to sites where they actively react with wood polymers within the bulk. The use of cosolvents can be employed if the swelling of the wood matrix cannot be sufficiently induced by the modifying solvent. But in the event that their boiling point surpasses a certain threshold, the difficult process of eliminating surplus solvents and/or reagents subsequent to the treatment ensues. However, the utilization of gaseous reactants presents certain challenges in comparison to liquid reactants. This is primarily due to the necessity of employing high-pressure apparatus and the inherent difficulties associated with achieving adequate penetration. Consequently, the degree of chemical substitution attainable with gaseous reactants is typically lower when juxtaposed with their liquid counterparts (High and Penkman, 2020). The optimal approach would involve employing low-boiling-point solvents that exhibit a pronounced propensity for wood expansion. In this context, water would be prioritized considering the economic and environmental challenges linked to the utilization of organic solvents.

The OH groups present in the cell wall are predominantly exposed to moisture and engage in hydrogen bonding interactions with water molecules. As aqueous solution permeates the gaps within the lignocellulosic matrix, the cellular walls undergo expansion to accommodate the ingress of water molecules, thereby leading to a concomitant augmentation in the overall volume of the wood-water system until reaching the fiber saturation threshold. Elevated moisture levels, within a specific range, present an avenue for fungal colonization of wood, thereby initiating the decay process. If these readily available hydroxyl groups undergo chemical substitution with larger and more hydrophobic chemical moieties, the cellular barrier shall undergo expansion. Furthermore, if the substituted moieties exhibit sufficient hydrophobicity to effectively diminish the moisture content of the cellular barrier, the wood shall no longer be conducive to colonization by fungi. Consequently, the wood shall attain an elevated degree of dimensional durability and stability via acetylation, furfurylation, and cross-linking with 3-dimethylol-4.5-dihydroxyethyleneurea (DMDHEU).

Acetylation

Acetic anhydride forms acetate esters by a reaction with an OH groups. Wood develops its exceptional durability and structural stability when a large number of OH groups in the cell wall are uniformly acetylated throughout the wall. The chemical treatment of wood with anhydrides, such as succinic, maleic, and acetic anhydrides, alters its molecular structure, enhancing its hydrophilic characteristics and resulting in a more hydrophobic surface (Figure 2). This modification is done to improve compatibility with anhydrides, obstructing the hydroxyl groups in the wood's structure. This modification enhances the strength qualities, dimensional stability, and biological resistance to pests (Cofta *et al*., 2006; Matsuda, 2017). Cyclic anhydrides, such as maleic anhydride or succinic anhydride, are employed in chemical treatment, resulting in the formation of a carboxylic acid that bonds to the wood. Still, an additional cross-linking step can further enhance the stability of wood products (e.g., improved dimensional stability and heightened resistance to microbiological pests), in addition to augmenting hydrophobic qualities (Rowell, 2006). In addition, steric hindrance can occur during acetylation, which makes it harder for water to interact with unmodified OH groups. Therefore,

cell wall bulking is responsible for the dimensional stabilization of acetylated wood. Because bound acetyl adducts reduce the diameter of nanopores inside the cell wall and OH groups substitution reduces the number of sorption sites, the equilibrium moisture content (EMC) drops. However, the precise extent to which each of these factors contributes remains a subject of ongoing discussion. The process of acetylation, employing acetic anhydride as the reagent, has been successfully commercialized under the trademark Accoya. This chemical procedure guarantees extended longevity, convenient reutilization, and recyclability of wood without any compromises in terms of environmental impact or performance. Due to these rationales, Accoya wood is widely lauded as a viable alternative to pressure-treated timber and purportedly the sole authentic cradle-to-cradle commercial wood commodity (Van der Lugt and Vogtländer, 2014). Despite its many benefits, the Accoya process is not entirely independent of wood species. Particularly for Pinus radiata, a species that needs to be transported from countries like Chile and New Zealand to Europe for treatment.

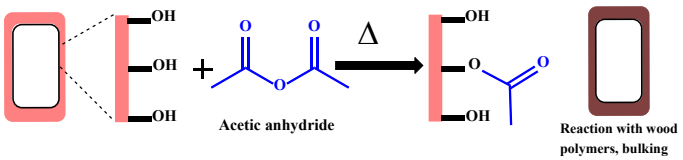

Figure 2: *Acetylation for modifying wood are depicted in this diagram. By forming acetic acid, a link is formed and nanopores are enlarged.*

Furfurylation

The utilization of furfuryl alcohol, commonly referred to as furfurylation, represents an established industrial method aimed at enhancing the resilience and dimensional integrity of wood. The furfurylation within the wood constitutes a notably intricate chemical reaction. The complexes of furfuryl alcohol are primarily found within the cavities of the wood, as well as within the cell walls. Polymerization of furfurylation occurs within the minuscule cavities of cells. The furfurylation process entails first impregnating wood with furfuryl alcohol in the presence of acid catalysts like maleic anhydride, then further heating to induce polymerization. Under specific reaction conditions, the process can lead to the accumulation of polymers within the lumina and pores of the cell wall, resulting in bulking (Figure 3). Furfurylation, according to some researchers (Larsson *et al.*, 2000; Rowell, 2005), is actually an impregnation modification procedure that gives the material characteristics more typical of a polymer-filled cell wall than a reactive cell wall. On the other hand, according to (Gérardin, 2016; Thygesen *et al.*, 2010), it's plausible that a branch of the polymer chain can link to the wood polymers through the lignin hydroxyls. Additionally, there is a possibility of link formation between the polymer and the cell wall components to some degree (Lande *et al.*, 2008; Li *et al.*, 2020).

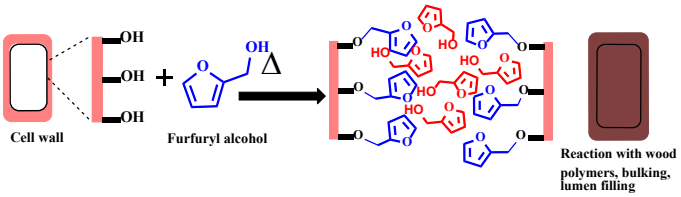

Figure 3: *Furfurylation for modifying wood are depicted in this diagram. Filling of the lumen and the formation of bonds may result from furfurylation.*

The impregnation solution remains stable even at room temperature due to cyclic anhydrides catalysts. Heating initiates the polymerization process, with two condensation reactions competing in the first stage (González *et al.*, 1992). The high wood cell-wall bulking in furfurylated wood indicates grafting events at early stages. Furfuryl alcohol polymer chains may have cross-linking patterns (González *et al.*, 1992). Grafting to lignin and hemicelluloses is expected to be dominant with catalytic systems used for furfurylation of wood. Consequently, it is quite likely that a guaiacyl unit of lignin which is the most common unit in lignins from softwoods and the furfuryl alcohol will undergo a grafting reaction. Various levels of furfurylation, typically quantified as percentages of weight gain values, might result in distinct outcomes. Two examples of wood products with a percentage of weight gain falling within the range of 20 to 50 are kebony and visor wood. Similarly, kebony also falls within the percentage weight gain range of 30 to 100. The user's text is too short to be rewritten academically (Sandberg *et al.*, 2017).

Cross-linking

The process of acetylation is free from the development of cross-links, however in furfurylation, cross-linking may occur depending on the specific parameters of the process. The fundamental mechanism of cross-link production is a crucial aspect of the wood modification technique known as Belmadur. The initial investigations were conducted in the late 1950s;

however, it was not until the early 2000s that this procedure was refined and implemented on a pilot scale specifically for Scots pine by the corporation BASF. Despite these advancements, widespread adoption in the market was not achieved. The essential component of this procedure is DMDHEU, a chemical compound that has been extensively utilized in the textile sector over a significant period of time. DMDHEU has the ability to infiltrate the cellular walls of wood, engaging in a chemical reaction with the hydroxyl groups present in the polymers of the cell walls (Figure 4). This interaction leads to a permanent expansion of the cell wall structure. Consequently, the dimensional durability and stability of wood are notably enhanced (Emmerich *et al*., 2019). Nevertheless, it is important to note that cross-linking in cell wall gives rise to fracture-prone behavior in wood, which may present challenges in many applications.

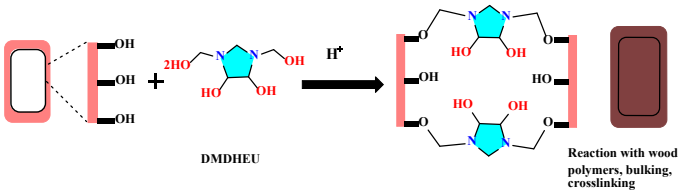

Figure 4: *DEDHEU crosslinking for modifying wood are depicted in this diagram. When DMDHEU is used to cross-link, there is an accompanying increase in mass.*

Conclusion

The sophisticated composition of wood, which is considered to be among the most common biomaterials found on our planet, experienced extensive modification throughout the course of tree history, spanning around 270 million years. The process of optimization has resulted in the achievement of a high level of efficiency in the transportation of water and nutrients, as well as the mechanical stability and durability of wood. The distinctive structural composition and notable directional dependence of wood reflect upon it a diverse range of exceptional characteristics, hence presenting possibilities for the development of practical materials. Chemical modifications facilitate a wide array of applications, encompassing the energy storage and conversion, advancement of high-performance structural materials, remediation of the environment, nanofluidics, nanoionics, and light and thermal control. The implementation of green chemical practices is of utmost importance in the field of sustainable wood modification, particularly in light of the increasing variety of available wood supplies. The proposed methodology promotes the utilization of environmentally friendly chemicals and solvents, prioritizing the employment of catalysts above stoichiometric reagents. The objective is to select chemicals that have a limited adverse impact on the environment, human health, and safety (EHS), while also avoiding the use of poisonous and hazardous substances. Green chemistry promotes the utilization of low pressure and temperature conditions in order to minimize energy consumption during chemical reactions. The aforementioned approach holds particular significance in the forthcoming period, given the improbability of discovering compounds that are entirely environmentally friendly and sustainable.

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Novelty Statement

The ecological diversity of wood, its origins, and technological implications are crucial for producing reliable products. Industrial procedures are improved to mitigate variability, facilitate efficient processing, and combat climate change.

Author's Contribution

Salim Saifullah: Conceptualization, methodology, data curation, data interpretation, data visualization, and writing first draft and writing revised drafts.
Muhammad Ilyas, Muhammad Farooq and Sanam Zarif Satti: Data curation, Data interpretation, Data visualization, and writing first draft.

Conflict of interest
The authors have declared no conflict of interest.

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