# DEVELOPING LIGNIN-BASED PHENOLIC ADHESIVES FOR ENGINEERED WOOD PRODUCTS

By

Mohsen Siahkamari

# A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Forestry – Doctor of Philosophy

#### ABSTRACT

The increasing demand for sustainable wood adhesives has motivated researchers to explore alternatives to petroleum-based phenol-formaldehyde (PF) resins, which have long dominated the wood adhesive industry due to their exceptional thermal and chemical stability. However, environmental concerns and the depletion of fossil resources necessitate the development of renewable, bio-based adhesives. This thesis investigates the potential of lignin and glyoxal as sustainable replacements for phenol and formaldehyde, respectively. First, a biobased phenolic adhesive was developed by entirely replacing phenol with unmodified corn stover lignin and formaldehyde with glyoxal, a bio-based dialdehyde. The resin formulation process was optimized to achieve strong chemical, thermal, and mechanical properties. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) confirmed the successful integration of lignin and glyoxal into the polymer network, resulting in adhesives with high dry adhesion strength suitable for interior-grade wood composites. Further studies were focused on developing lignin-based resins by replacing 80-100% phenol with commercially available unmodified kraft softwood and organosolv wheat straw lignins. After extensive optimization of the resin formulation, the curing time for lignin (80%)-phenol (20%)-formaldehyde adhesives was significantly reduced from the initial 11 minutes to 5 minutes, while maintaining comparable performance to commercial PF adhesives. Additionally, replacing 80% of phenol with lignin reduced formaldehyde consumption by at least 63%, making the adhesive more environmentally friendly and sustainable. Advanced spectroscopic techniques, including FT-IR and NMR, provided valuable molecular insights into the curing mechanisms of lignin-based adhesives. Solid-state NMR confirmed the formation of methylene bridges between lignin chains when formaldehyde was used as a cross-linker. Similarly, when glyoxal was used, the analysis revealed the formation of glyoxylene bridges, highlighting the potential of both lignin and glyoxal as sustainable substitutes for phenol and formaldehyde in adhesive formulations. This work highlights the feasibility of lignin and glyoxal-based adhesives as fully biobased, eco-friendly alternatives for phenol-formaldehyde adhesive used currently in various engineered wood products, such as plywood, oriented strand board (OSB) and laminated veneer limber (LVL), contributing to the broader application of renewable materials in the adhesive industry. The findings emphasize the

importance of understanding lignin's properties and its reactions with co-monomers, such as formaldehyde or glyoxal. The successful optimization and detailed characterization contribute to the development of high-performance bio-based adhesives and paves the way for their practical application in the wood adhesive industry.

#### ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my Ph.D. supervisor, Dr. Mojgan Nejad, whose pioneering work in lignin research and dedication served as an inspiring example of hard work, collaboration, creativity, and grace. I am also deeply thankful to my committee members— Dr. Lawrence Drzal, Dr. Laurent Matuana, and Dr. James Jackson—for their invaluable guidance, expertise, and feedback, which have significantly enhanced my experience as a doctoral student and the quality of my dissertation.

I would like to extend my sincere appreciation to Dr. Tuo Wang and Debkumar Debnath for their collaboration on the solid-state NMR analysis, which was crucial to the success of this project.

A special thank you to the support staff—Katie James, Renee Tilley, Sandra Dunnebacke, and Kory McIntosh—whose constant readiness to help ensured that everyone's questions were answered. To my lab mates—Dr. Christián Henry, Dr. Saeid Nikafshar, Dr. Mona Alinejad, Sasha Emmanuel, Kevin Dunn, Sajad Bagheri, Akash Gondaliya, Enoch Acquah, Tara Allohverdi, Manasseh Tetteh, Mariia Bespalova, Maureen Afaglo, Sajad Nikafshar, Sadaf Mearaj, Hailey Becker, Laura Mihlbachler, Grace Hoglund, Alex Bakke, Anna Dunnebacke, Rachel Schenck, and Ella Yakubison —thank you for your collaboration, support, and the opportunity to learn from each of you.

I am grateful for the financial support and resources provided by the College of Agriculture and Natural Resources, the National Science Foundation (NSF), the Wood-Based Composites Center (WBC), the USDA National Institute of Food and Agriculture (NIFA), and the Center for Research & Innovation in the Bio-Economy (CRIBE).

A heartfelt thanks to my wife, Jouan, for her unconditional support and to my family, who, despite being far away, kept me motivated with their prayers and kind words. Finally, to my friends who became family. Your constant support, mentorship, and companionship were key to the completion of this work. Thank you all.

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### **CHAPTER 1:**

# Wood Adhesives for a Sustainable Future: Evaluating Phenol–Formaldehyde Resin and Innovative Substitutes

# **1.1 Introduction**

Adhesives have played an essential role in optimizing the use of wood, and their importance will continue. Nowadays, adhesives allow for nearly all types of wood to be transformed into usable products. While bio-based adhesives were historically common, synthetic adhesives became dominant in the 20th century due to their superior performance and cost-effectiveness. This change significantly boosted the bonded wood products industry, expanding markets and creating new products. The 20th century also saw major advancements in understanding wood adhesive chemistry and performance, progress that continues today. With growing interest in bio-based adhesives, especially in the 21st century, further research is expected, especially as the use of engineered wood products and bio-based materials increases.<sup>1</sup>

A wood adhesive is a polymer that interacts with wood surfaces, either physically, chemically, or both, to transfer stresses between bonded components, ensuring strong adhesion. Adhesives play a crucial role in over 70% of modern wood-based materials, including plywood, laminated veneers, particleboard, and fiberboard. They are also used in the assembly of construction materials for residential and industrial purposes, such as panelized floors and walls. Additionally, adhesives are extensively employed in non-structural applications like furniture, floor coverings, countertops, ceiling and wall tiles, and accessories.<sup>2</sup>

# **1.2 Synthetic Wood Adhesives**

The growing demand for wood-based composites has encouraged research into developing advanced adhesives. Various adhesive classes offer distinct properties and applications in the bonding industry, ranging from traditional thermosetting adhesives like phenol-formaldehyde to innovative eco-friendly options. Understanding the unique characteristics and benefits of each adhesive class is crucial for optimizing wood resource use.<sup>3</sup>

### **1.2.1** Formaldehyde-Based Wood Adhesives

Formaldehyde-based adhesives, classified as thermosetting polymers, have made substantial contributions to the progress and application of various wood-based products. The extensive utilization of these adhesives in the wood industry can be attributed to their ability to form long-lasting and resilient connections.<sup>4</sup> This discussion will primarily center on four distinct categories of formaldehyde adhesives including phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde, and phenol-resorcinol-formaldehyde adhesives.

### 1.2.1.1 Phenol-Formaldehyde Wood Adhesives

Phenol-formaldehyde (PF) polymers, synthesized in the early 20th century, are among the oldest synthetic polymers and are widely used in laminations and composites due to their durability, strong wood affinity, and polymer strength. PF adhesives demonstrate excellent resistance to delamination and achieve high wood failure rates in durability tests. However, selecting the correct formulation is crucial for optimal bond strength, as inappropriate choices can result in poor adhesion. Factors contributing to suboptimal adhesion include insufficient polymerization time, high molecular weight resins that hinder wetting and penetration, insufficient or excessive assembly time, and improper pressure during bonding. These can lead to a weak bondline or excessive adhesive penetration. Despite these challenges, PF adhesives are capable of meeting the bonding needs of most wood-based applications, provided that cost and heat curing duration are not significant concerns.<sup>5,6</sup>

Phenol-formaldehyde adhesives are produced by reacting phenol with formaldehyde or a formaldehyde precursor under controlled conditions, leading to two main pre-polymer types: novolac and resole resins. Novolac, with a formaldehyde/phenol (F/P) ratio below 1, are synthesized under acidic conditions, while resole resins, with F/P ratios above 1, are made under basic conditions. Although both processes may appear similar, they differ significantly in chemical reactions and polymer structures. In wood adhesive applications, resole resins are preferred due to their solubility, excellent wood-wetting properties, and delayed curing, which allows ample time for product assembly.<sup>5</sup>

Novolac resins are produced by reacting formaldehyde and phenol under acidic conditions, typically with formaldehyde-to-phenol ratios ranging from 0.5 to 0.8 at pH levels between 4 and 7. The process involves adding acid-activated formaldehyde to phenol, which reacts at the ortho or para positions of the phenol, forming an electrophilic reaction. This leads to the release of a water molecule, assisted by the stabilization of the phenol group in acidic conditions. The methylene group of this molecule then reacts with another phenol, forming a methylene-bridged dimer. This process continues, producing a linear novolac oligomer with a low molecular weight. Since linking step predominates in acidic conditions the polymer is formed if there was no limitation on the amount of formaldehyde used. To produce the polymers from the oligomer, additional formaldehyde is added just before application, typically in the form of paraformaldehyde. Due to their limited water solubility and high acidity, novolac oligomers are unsuitable for wood bonding.<sup>5,6</sup>

Generally, resole resins are manufactured by utilizing alkali hydroxides with a formaldehyde-to-phenol ratio ranging from 1.0 to 3.0 and maintaining a pH level between 7 and 13. The chemical reaction between base-activated phenol and formaldehyde is illustrated in Figure 1.1.<sup>5</sup> Unlike the reaction under acidic conditions, the addition of formaldehyde to phenol in basic conditions occurs rapidly, while the conversion of hydroxymethyl derivatives to oligomers is a slower process. This allows for the use of higher concentrations of formaldehyde without forming the final polymer until sufficient heat is applied.<sup>5,6</sup>

Certain hydroxymethylphenols can be combined to form a bismethylene ether bridge, which is consistently transformed into methylene-bridged species. This method is used to generate oligomers with enough reactive groups for effective curing under appropriate thermal conditions. Although fully functionalized species are shown in Figure 1.1, the formaldehyde-to-phenol molar ratio is usually kept below 3, ensuring sufficient groups to form the polymer backbone and some crosslinking sites. Once applied to wood, these compounds are converted into the final adhesive by applying heat and removing water.<sup>5,6</sup>



Figure 1.1. Chemistry of phenol-formaldehyde resins.<sup>5</sup>

Phenol-formaldehyde adhesives are highly versatile and widely used in wood bonding, provided heat can be applied during the process. In cases where environmental resistance is not required, more cost-effective adhesives are often chosen. Commercial phenol-formaldehyde products contain additives designed for specific uses, with urea being a common additive to improve flow, absorb free formaldehyde, and reduce costs. However, urea is generally not believed to integrate into the polymer backbone due to limited polymerization under basic conditions. Fillers and extenders are also important, enhancing surface adhesion and adjusting adhesive rheology for specific applications, ensuring diverse bonding needs are met.<sup>5,7</sup>

### **1.2.1.2** Resorcinol-Formaldehyde Wood Adhesives

Resorcinol-formaldehyde (RF) resins have an advantage over phenol-formaldehyde (PF) resins due to their ability to cure at ambient temperatures. This is because resorcinol reacts with formaldehyde more quickly than phenol. The two hydroxyl groups on resorcinol's aromatic ring activate the ortho and para positions, facilitating reaction. The addition and condensation reactions with hydroxymethyl resorcinol allow for cross-linking, forming a thermosetting adhesive. Resorcinol adhesives are known for their durability, resistance to bond failure, and degradation. However, the high cost of resorcinol has led to the development of phenol-resorcinol-formaldehyde (PRF) adhesives. PRF adhesives cure similarly to RF resins but are more economical. These adhesives are commonly used in wood lamination and finger jointing, offering high bond strength, water resistance, and ambient temperature curing. However, their slow curing requires longer clamping times before achieving sufficient strength for handling. In summary, RF and PRF resins provide excellent bond strength and resistance to environmental factors, making them ideal for wood-bonding applications where durability and room-temperature curing are required.<sup>4–6</sup>

### 1.2.1.3 Urea-Formaldehyde Wood Adhesives

Urea-formaldehyde (UF) adhesives have several advantages, including low cost, nonflammability, fast curing, and a light color. However, they also have notable drawbacks, such as poor water resistance and the ongoing release of formaldehyde. Despite these issues, UF adhesives are the most widely used amino resins and are typically applied in fiberboard, particleboard, and some interior plywood. The chemistry of UF adhesives involves multiple steps, starting with the reaction of formaldehyde and urea under neutral or basic conditions. This leads to the formation of primary products, such as N,N,N'-tris(hydroxymethyl)urea, bis-hydroxymethyl ureas, and mono-hydroxymethyl ureas as shown in Figure 1.2.<sup>5,8</sup> These compounds react under slightly acidic conditions and heat to generate oligomers with urea molecules linked by bismethylene ether or methylene bridges. Once the desired molecular weight for the specific application has been achieved, the polymerization process is decelerated through the increasing of pH levels and cooling. To reduce formaldehyde emissions from the resin, an additional quantity of urea can be charged. The UF resins are combined with an acid

catalyst that becomes active during the heat cure. This combination of acids and heat results in a swift curing process for UF adhesive, granting it the desired rapid-setting characteristics. Because of this rapid strength development, press times for UF adhesives are notably shorter compared to other adhesive types. To address formaldehyde emission concerns, lower formaldehyde/urea ratios, melamine addition, and scavengers are used, albeit with some impact on the ultimate strength of the final product. Specific UF formulations and bonding conditions are adjusted to meet acceptable formaldehyde emissions for end products.<sup>5,9</sup>



Figure 1.2. Chemistry of urea-formaldehyde resin.<sup>5</sup>

### 1.2.1.4 Melamine-Formaldehyde Wood Adhesives

Melamine-formaldehyde (MF) adhesives offer better water resistance than UF adhesives but have a lighter color. The MF synthesis process involves adding formaldehyde to melamine, facilitated by melamine's nucleophilic nature.<sup>10</sup> The reaction can occur under various pH conditions, with slower rates at neutral pH. Melamine can react with up to six formaldehyde groups, forming up to two methylol groups on each exocyclic amine group. These hydroxymethyl compounds then undergo condensation reactions to create the final resin.<sup>5,10</sup>

Figure 1.3 depicts the chemistry behind both addition and condensation reactions. Although the addition reaction is technically reversible, it predominantly proceeds to the right side due to equilibrium favoring product formation. Conversely, the condensation reaction, leading to the creation of oligomers and polymers, is mostly irreversible, a crucial factor contributing to the product's water resistance and setting it apart from UF adhesives. The MF adhesive requires activation for proper polymerization, involving pH reduction and temperature increase, similar to UF adhesives. Catalysts used are either acids or acid precursors that release acids upon heating to facilitate the activation process.<sup>5</sup>



Figure 1.3. Chemistry of melamine-formaldehyde resin.<sup>5</sup>

MF adhesives have limitations due to their excessive cost from melamine, leading to the development of more cost-effective melamine-urea-formaldehyde (MUF) resins. MUF adhesives offer comparable water resistance to MF adhesives at a lower price, depending on the melamine-

to-urea ratio. They are considered a less durable but more economical alternative to MF adhesives or a more water-resistant but pricier option compared to UF adhesives.<sup>11</sup>

### **1.2.2** Non-Formaldehyde Wood Adhesives

The following section discusses some non-formaldehyde wood adhesives that are widely used in the preparation of wood panels.

### 1.2.2.1 Isocyanates in Wood Adhesives

Isocyanates are widely used in wood bonding adhesives because of their ability to react with compounds containing reactive hydrogens, such as amines and alcohols. They can selfpolymerize or react with various monomers, offering versatility in creating a broad range of adhesive products.<sup>12</sup> The high reactivity of isocyanates offers advantages and disadvantages. On the positive side, it promotes rapid polymerization and generally results in high conversion rates.<sup>13</sup> One limitation to note is the rapid reaction between isocyanates and water in the wood, which can interfere with desired reactions involving wood constituents. These constituents include hydroxyl groups in cellulose and hemicellulose, as well as phenols and hydroxyl groups in lignin.<sup>12</sup> Additionally, isocyanates react rapidly with compounds in the human body, raising safety concerns during handling. Under physiological conditions, these reactions occur quickly and irreversibly, particularly during manufacturing when low molecular weight and volatile isocyanates are present. However, once isocyanate reactions have completed, the resulting ureas and urethanes are considered safe. It is important to note that during combustion, the heat can lead to the release of free isocyanate groups.<sup>12,13</sup> Isocyanates used in wood bonding are less hazardous than other types due to their higher molecular weight, which reduces volatility and the presence of free isocyanate groups. The next section will explore the main classes of isocyanates commonly employed in the wood adhesive industry.<sup>5</sup>

### **1.2.2.2** Polymeric Diphenylmethane Diisocyanate Wood Adhesives

Isocyanate adhesives have become increasingly popular due to their fast reactivity and strong bonding capabilities. Polymeric diphenylmethane diisocyanates (pMDI) are widely used in wood bonding, consisting of a blend of monomeric diphenylmethane diisocyanate and methylene-bridged polyaromatic polyisocyanates, as illustrated in Figure 1.4.<sup>14</sup> Although pMDI

adhesives are expensive, they offer benefits such as a fast reaction rate, efficient usage, and strong bonding to challenging surfaces. pMDI requires water for activation, which is not an issue when bonding with wood, but may pose challenges when used with other substrates. The chemical process involves multiple steps as the following<sup>14</sup>:

- The isocyanate initiates the reaction by reacting with water, resulting in the formation of a carbamic acid: R-NCO + H<sub>2</sub>O => R-NHCOOH
- The unstable carbamic acid decomposes, releasing carbon dioxide and yielding an amine: R-NHCOOH => R-NH<sub>2</sub> + CO<sub>2</sub>
- The amine then reacts with another isocyanate group, leading to the formation of a urea: R-NH<sub>2</sub> + OCN-R => R-NHCONH-R
- Additionally, some of the urea molecules undergo more reactions with isocyanate, producing a biuret: R-NHCONH-R + R-NCO => R-NHCON(CON—R)-R

As isocyanate reacts with water, the reactions proceed quickly if there is enough isocyanate relative to other reactive hydrogen groups. In wood bonding, water content is typically sufficient to facilitate the process. Excessive water levels, however, could hinder polymer formation by producing too many amine groups, although this issue is uncommon in wood bonding. The release of carbon dioxide during the reaction can create voids in the adhesive, potentially weakening the bond. The reactions are generally irreversible under normal conditions, resulting in strong, durable bonds between the isocyanate and wood.<sup>5</sup> There is ongoing debate among researchers about urethane bond formation with wood. Some argue that isocyanates readily form covalent bonds with hydroxyl groups on wood, while others believe the rapid reaction with water and the abundance of water molecules on the wood surface make urethane formation less likely.<sup>3,14</sup> pMDI adhesives provide notable benefits across various markets. Their fast polymerization and ability to bond effectively in the presence of high moisture levels make them well-suited for applications like oriented strand board (OSB) and bonding green or wet lumber.<sup>11</sup> The low polarity of pMDI allows it to penetrate cracks in the waxy surface of straw, making it effective for strawboard production, where traditional phenol-formaldehyde resins may struggle. However, pMDI has drawbacks, such as higher costs and strong bonding with non-wood materials, like press platens, limiting its use in OSB face layers. Additionally, safety concerns regarding isocyanates have restricted pMDI's application, but proper safety precautions can mitigate risks. Once cured, the bonded product poses no hazard due to the rapid reaction of isocyanate groups, providing a formaldehyde-free adhesive.<sup>5</sup>



Figure 1.4. Polymeric diphenylmethane diisocyanates.

## 1.2.2.3 Emulsion Polymer Isocyanates Wood Adhesives

Emulsion polymer isocyanates are a type of two-component adhesive that are frequently employed in diverse wood bonding applications.<sup>12</sup> The adhesive comprises two components: an isocyanate emulsified in water and an emulsion latex with polyhydroxyl functionalized molecules. The emulsion allows for the use of higher molecular weight polymers while keeping the solution viscosity low for easy application. After combination, the isocyanate disperses in the latex, reacting with hydroxyl groups as water penetrates the wood. During curing, polyurethane groups form through the reaction between isocyanate and hydroxyl groups. Cross-linking can be adjusted by altering the backbone structure and the number of hydroxyl groups in the prepolymer. These adhesives form durable bonds and some offer good water resistance. A major advantage is their ability to bond with plastics and non-wood substrates. However, higher costs and the need for pre-mixing are key disadvantages.<sup>5</sup>

### 1.2.2.4 Polyurethane Wood Adhesives

Polyurethanes are commonly used in coatings and adhesives, but their application in wood bonding is less prevalent. They are available in one- or two-component systems, chosen based on specific requirements. For effective wetting, low molecular weight components or solvents are often added to reduce viscosity, though care must be taken to avoid excessive volatility and health risks associated with low molecular weight isocyanates. In one-component systems, the remaining isocyanate groups react with moisture to form amines, which then create backbone and cross-linking connections. In two-component systems, the isocyanate and reactive portions must be properly mixed just before bonding. While these adhesives are less used in structural wood applications due to high wood failure rates, they are widely employed in other markets for their strength, flexibility, and ability to bond various substrates. Polyurethane adhesives have gained more acceptance in Europe than in the U.S.<sup>5</sup>

### 1.2.2.5 Epoxy Wood Adhesives

Epoxy adhesives are well-known for their environmental resistance and ability to bond various surfaces, including wood, metal, plastic, ceramic, and concrete. However, they are less commonly used in wood bonding due to their higher cost compared to most wood adhesives and, in some cases, limited durability. Many wood adhesives require heat curing, do not fill gaps, and have poor adhesion to other substrates. Therefore, epoxies are still being explored for bonding wood to other materials and repairing damaged wood structures. Aside from their cost, a significant drawback of epoxies is their limited use in applications requiring long-lasting bonds.<sup>5</sup>

Among the various epoxy resins, the most commonly used is the diglycidyl ether of bisphenol A (DGEBA), although other multifunctional epoxies are also employed. DGEBA epoxies display a range of molecular weights due to oligomerization via the epoxy group.<sup>5</sup> While these epoxies form strong, long-lasting bonds with many substrates, their durability with wood is limited. There are differing opinions about their performance in wet conditions. Most standards only allow their use in non-load-bearing applications (American Institute of Timber Construction 1990). Despite attempts to promote epoxies for restoration work, tests have shown that many

commercial epoxies do not meet the required standards.<sup>15</sup> Investigation of the failures reveals that the majority of issues arise in the epoxy interphase region.<sup>16</sup>

### **1.2.2.6** Vinyl Acetate Dispersion Wood Adhesives

Water-based adhesives such as poly (vinyl acetate) (PVAc) and poly (ethylene-vinyl acetate) (EVAc) are commonly used for bonding wood and paper products in various finished goods. PVAc is especially popular in furniture construction because it sets at room temperature, is cost-effective, and is easy to use. These adhesives work by having water absorbed into the wood or paper, making them ideal for wood-related manufacturing and construction. However, since they are not cured adhesives, their strength decreases in high humidity conditions.<sup>5</sup> The production of PVAc and EVAc dispersions uses emulsion polymerization to create stable products with small droplet sizes. Monomer addition is carefully controlled to prevent overheating from exothermic reactions. Proper surfactant management is important to avoid poor adhesion caused by a weak boundary layer. After the adhesive is applied, the beads merge to form a film on the wood surface. Adding ethylene during polymerization reduces the adhesive's polarity, making ethylene-vinyl acetate copolymers suitable for bonding less polar surfaces.<sup>17,18</sup>

PVAc is known for its flexibility as a linear polymer with an aliphatic backbone, unlike the rigid formaldehyde copolymers used in wood adhesives. These water-borne PVAc adhesives flow well into exposed wood cell lumens, although their high molecular weight limits penetration into cell walls. PVAc's high acetate content and flexible structure allow it to form strong hydrogen bonds with wood components, ensuring good adhesion. The adhesive maintains bond strength during wood expansion and contraction by flexing its polymer backbone, reducing stress at the interface. However, under high moisture conditions, PVAc may lose strength due to limited creep resistance. To improve performance, PVAc can be crosslinked to become a thermoset, increasing resistance to moisture, heat, and load. Crosslinked PVAc requires adding a cross-linker before application and is used in demanding applications like window and door construction.<sup>5</sup>

# **1.3 Bio-Based Wood Adhesives**

Protein-based adhesives have been a preferred option for wood bonding since ancient times. Early civilizations used natural adhesives from plants and animals in their bonding

practices.<sup>19,20</sup> Early bonded wood products had reasonable durability in dry conditions but softened and delaminated with high moisture levels.<sup>5</sup> In addition to protein-based adhesives, tannin and lignin have been investigated as alternative bio-based materials with promising potential for various applications including wood-based composites.<sup>5</sup>

### **1.3.1** Protein Adhesives

Protein-based adhesives, which were once the primary choice for wood bonding, had largely disappeared from the market. However, they are now experiencing a resurgence.<sup>21</sup> Since proteins vary in composition based on their source, the processes and properties of the resulting adhesives differ. For optimal performance, the protein must be unfolded to expose polar groups for better solubilization and bonding. During the setting step, hydrogen bonds between protein chains are reformed, establishing bond strength.<sup>22</sup>

Soybean flour is the most widely used protein-based adhesive, made by grinding the residue left after oil extraction from soybeans. These adhesives were crucial in developing the interior plywood industry in the early 1900s. Despite efforts to improve water resistance, soybean adhesives lacked the moisture resistance needed for exterior plywood. The demand for more durable adhesives during World War II led to the development of improved, cost-effective PF resins, causing the decline of soybean adhesives.<sup>5,22</sup>

### 1.3.2 Tannin Adhesives

Tannins are polyhydroxypolyphenolic compounds found in various plant species. They are mainly sourced from plants with higher concentrations, limiting their commercial supply to a few countries. Although tannins are more reactive than phenol, they are also more expensive. After extraction and purification, they are spray-dried into powder form.<sup>23</sup> These purified isolates exhibit water-resistant bonds when polymerized with formaldehyde. They are similar to natural resorcinol in reactivity and water resistance. However, their polymer structure differs. Formaldehyde is added mainly as single and sometimes double additions to the connected rings in tannins. The final polymer structure and properties differ from resorcinol because of lower cross-link density, despite similar reactions. Tannins, despite their advantages, have limitations compared to synthetic adhesives. Their polycyclic structure leads to fast curing and high viscosity.

Dilution to reduce viscosity causes extra steam during hot pressing. Although commercially viable in some species, tannins are less competitive than synthetic adhesives in availability and quantity. Their composition also varies due to growing conditions, making it difficult to produce consistent adhesives.<sup>5,23</sup>

### **1.3.3 Lignin Adhesives**

Lignins and tannins show notable distinctions, although both are aromatic compounds. Lignin is more abundant and cost-effective, but its' reaction with formaldehyde is notably slower. Lignin is a substantial by-product derived from pulp and paper and biorefinery industries, constituting a substantial portion of softwoods (24-33%) and hardwoods (16-24%). Native lignin is a complex polymer and requires partial degradation to separate it from cellulose and hemicellulose.<sup>24,25</sup> To become suitable adhesives, these degraded lignins must be further polymerized with formaldehyde. Lignin, despite its aromatic nature, has fewer reactive sites on the phenolic rings, which limits its reactivity with formaldehyde.<sup>5</sup> However, lignin-derived wood adhesives offer a sustainable alternative for traditional adhesives, providing advantages such as cost-efficiency and biodegradability.<sup>26</sup> Significant advancements have been made so far in both the research and practical implementation of lignin-based adhesives within the wood industry.<sup>27</sup> The prospective path of lignin-based adhesives involves the substitution of conventional adhesives and the enhancement of their performance. Further investigation is needed to characterize, modify, and incorporate lignin into various adhesive systems to reach its full potential.<sup>28</sup> Subsequent sections will provide a more comprehensive review of lignin-based adhesives, with a particular focus on their potential as alternatives to phenolic wood adhesives currently present on the market.

# 1.4 Why Phenolic Adhesives

The provided explanations regarding various wood adhesives highlight the importance of carefully assessing the optimal trade-off between cost and performance in relation to a specific application. The appropriate adhesive type is selected based on its intended use. In the subsequent sections, phenol-formaldehyde adhesives will be reviewed, offering a detailed exploration of their merits and drawbacks.

Phenolic adhesives are highly effective for wood lamination, offering durable bonds with excellent resistance to decay, moisture, and heat. However, their dark color is a drawback. Phenol-resorcinol-formaldehyde resins, though relatively expensive, cure at room temperature, while more affordable phenol-formaldehyde resins require heat curing. Melamine-formaldehyde and polyurethane adhesives, being lighter in color, also cure at room temperature. However, they do not perform as well as phenolic adhesives in standard heat and moisture-resistance tests. The durability of these adhesives is debated, especially when environmental conditions during use are not clearly defined. There are some arguments that stringent standards in the U.S. and Canada may exclude adhesives that could work well in real-world situations. However, given the importance of maintaining structural integrity in buildings, it is generally observed that more cautious and conservative approaches have been favored.<sup>29</sup>

The major advantages of phenolic adhesives are highlighted as follows:

- High mechanical strength: Wood constituents, including cellulose and lignin, are strongly bonded with phenolic resins, resulting in excellent mechanical strength and long-term durability<sup>30</sup>
- Resistance to moisture and heat: The excellent moisture and thermal resistance of phenolic resins makes them suitable for applications that involve exposure to outdoor climates and high temperatures<sup>30,31</sup>
- Low formaldehyde emissions: Phenolic resins exhibit lower formaldehyde emissions in comparison to other types of wood adhesives, such as UF adhesives<sup>30</sup>
- Compatibility with wood components: Phenolic resins have compatibility with wood components, including lignin, a naturally occurring constituent of wood. The compatibility between the adhesive and the wood components leads to robust and enduring bonds<sup>30</sup>
- Cost-effectiveness: Phenolic resins are less expensive than many other types of wood adhesives, such as MF or RF adhesives, making them a popular option in the wood industry<sup>5</sup>

Overall, Phenolic adhesives are widely favored in various industries due to their numerous advantages, particularly in applications requiring durable and robust bonds.

In 2019, the worldwide adhesives market exceeded 14.7 million tons, with the Asia Pacific region leading the sales, making up about 38% of the global total. Following were North America and Western Europe. The construction industry was the major consumer, contributing to over 26% of the global demand in the same year.<sup>32</sup> As the global demand for wood-based panels has risen, the wood adhesive industry has seen a parallel increase in production capacity. The usual adhesives employed in manufacturing wood panels primarily consist of petrochemical-based thermosets like PF, UF, MUF resins, and polymeric methylene diphenyl diisocyanate (pMDI) adhesive systems.<sup>33</sup> In 2019, the phenolic resin market was valued at around USD 12.63 billion.<sup>34</sup> Predictions indicated that the market's value has increased to approximately USD 15 billion in 2021. Among its various applications, the primary market sector for phenolic resin is its use as a wood adhesive, primarily driven by the growth of the construction industry. Within the wood adhesive market segment, the plywood manufacturing section holds the largest share.<sup>33</sup> However, the growth of the phenolic resin market faces challenges due to the variation in crude oil prices since crude oil is the main feedstock used for manufacturing these resins.<sup>33</sup>

### **1.4.1** Raw Materials

The main raw materials used in manufacturing resole phenolic resins are Phenol ( $C_6H_5OH$ ), Formaldehyde ( $CH_2O$ ), and an alkaline catalyst, commonly Sodium Hydroxide. While other phenols like cresols (monomethylphenols), xylenols (dimethyl-phenols), resorcinol (mdihydroxybenzene), and alkylated-phenols could substitute phenol, their utilization is limited due to the availability of more economical synthetic phenol.<sup>6</sup>

The majority of phenol is derived from coal tar via fractional distillation and numerous synthetic processes. There are at least six recognized commercial synthetic pathways for producing phenol, with Cumene, Raschig, Dow, and Sulfonation being the most common. However, the once-popular Sulfonation process is no longer utilized.<sup>6</sup>

### 1.4.1.1 Cumene Process

In the cumene process, benzene and propylene react in the presence of an aluminum chloride catalyst to produce isopropyl benzene (cumene). Cumene oxidizes to hydroperoxide, which is decomposed into phenol and acetone by acidification:<sup>6</sup>



Figure 1.5. The synthesis path of phenol through Cumene process.

### 1.4.1.2 Raschig Process

The Raschig process involves passing benzene, hydrogen chloride, and oxygen over a 200°C to 300°C copper catalyst. The intermediate product consists of gaseous chlorobenzene and water. When chlorobenzene is conveyed over a heated silica catalyst at 500°C, water hydrolyzes it into phenol and HCl.<sup>6</sup>



Figure 1.6. The synthesis path of phenol through Raschig process.

### 1.4.1.3 Dow Process

The Dow process involves the utilization of a direct and highly vigorous reaction between chlorobenzene and sodium hydroxide solution at a temperature of 300 °C and a pressure of 4000 psi.<sup>6</sup>



Figure 1.7. The synthesis path of phenol through Dow process.

# 1.4.1.4 Formaldehyde Production

Formaldehyde is produced by the catalytic oxidation of methanol in a controlled process. Methanol undergoes dehydrogenation, producing formaldehyde. Methanol vapor and air are passed over a heated copper oxide catalyst at temperatures between 300°C and 600°C, forming a mixture of formaldehyde and water. The product is a 37% formaldehyde solution, which is further concentrated to 40%, creating a solution known as formalin.<sup>6</sup>



Figure 1.8. The synthesis path of formaldehyde.

Formalin includes impurities such residual methanol and formic acid, which are produced as a byproduct. Methanol is retained within the solution to serve as a stabilizing agent during the storage process, whereas formic acid is removed from the mixture.<sup>6</sup>

# 1.4.2 Toxicology

When evaluating phenolic resins, their composition (resole or novolac) and molecular weight are essential factors to consider, as these influence their physiological effects. Low to medium molecular weight resole resins contain varying levels of free phenol and formaldehyde. Once cured, phenolic resins are completely harmless. The US Food and Drug Administration (FDA) permits phenolic coatings and molded articles to come into contact with food.<sup>35</sup>

# 1.4.2.1 Toxicology of Phenol

Phenol is a potent toxic compound that induces protein degradation and tissue erosion. Phenol exposure primarily occurs in areas where it originates. Environmental concentrations are generally low compared to the threshold limit value (TLV) of 5 parts per million (p.p.m.). The LDLo (lethal dose low) for oral administration in humans is reported to be 140 mg/kg. Phenol can cause skin discoloration, blister-like red marks, and a burning sensation upon contact. It is rapidly absorbed through the skin, causing severe tissue injury. In extreme exposure cases, phenol affects the central nervous system and can be fatal. Smaller quantities primarily impact the renal, hepatic, and pancreatic systems. Inhaling or ingesting phenol causes burning sensations and symptoms like headaches, dizziness, vomiting, irregular breathing, respiratory arrest, and cardiac failure.<sup>35</sup>

### 1.4.2.2 Toxicology of Formaldehyde

Formaldehyde vapor, on the other hand, is highly irritating to mucous membranes, and its pungent odor is detectable even at concentrations below 1 p.p.m. Aqueous formaldehyde causes a similar level of irritation. This compound is commonly used for preserving medical and biological specimens.<sup>35</sup> Formaldehyde has shown mutagenic properties in bacteria, fungi, and certain insects. Studies have revealed that it forms adducts with DNA and proteins in both in vivo and in vitro test systems. As a result, the U.S. Department of Labor reduced the permissible exposure level (PEL) of formaldehyde from 3 to 1 p.p.m. in 1987, while allowing a short-term exposure level (STEL) of 2 p.p.m. for any 15-minute period. In Western Europe, permissible exposure levels (8 h) vary across countries, with Germany allowing only 0.5 p.p.m. Several toxicological investigations have indicated that formaldehyde exposure can cause a rare type of malignant nasal tumor in male and female rats, as observed in multiple inhalation experiments involving various species.<sup>35</sup> Formaldehyde is officially classified as a known carcinogen (Group 1) by the International Agency for Research on Cancer (IARC), affecting both humans and animals. This classification is based on strong evidence showing that inhaling formaldehyde can cause nasopharyngeal cancer in humans and squamous cell carcinomas in the nasal passages of rats.36,37

# 1.5 Importance of Substituting Phenol and Formaldehyde with Bio-Based Alternatives

Despite the widespread use of resole resins, significant concerns are raised regarding the toxicity of phenol and formaldehyde, along with the environmental impact of using petroleumderived sources. Additionally, fluctuations in raw material prices contribute to these concerns. A viable and efficient approach to addressing these issues is the substitution of these resins with sustainable alternatives. By using two bio-based raw materials with much lower toxicity in place of phenol and formaldehyde, eco-friendly wood adhesives can be created that are cost-effective while maintaining or enhancing performance.<sup>38</sup>

The next section explores some of the frequently used options for replacing phenol and formaldehyde in the formulation of PF adhesives. These alternative materials provide a more

eco-friendly and sustainable approach to adhesive production, contributing to a more environmentally conscious and economically viable industry.

# **1.5.1** Phenol Replacements

### 1.5.1.1 Lignin as a Phenol Replacement

Lignin is the most abundant natural aromatic polymer. It is a highly aromatic, amorphous, phenolic polymer found in vascular plants, with a complex, branched structure composed of phenol units, as shown in figure 1.9.<sup>30,39,40</sup>



Figure 1.9. The complex structure of lignin contains various types of linkages.<sup>41</sup>

The word "lignin" is derived from the Latin term "lignum," which specifically refers to wood. Lignin is typically synthesized from three hydroxycinnamyl alcohol monomers, or monolignols: *p*coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S) (Figure 1.10). This results in a randomized structure that forms a 3D network within the cell wall of plant cells.<sup>42,43</sup>

The composition of lignin exhibits variability not only across different plant species but also among various tissues within plants, as well as in various parts of the cell wall. Moreover, ecological factors, including tree age, climate, plant nutrients, and sunlight, contribute to this diversity.<sup>44,45</sup> Hardwood lignin primarily comprises G and S units with traces of H units, whereas softwood lignin is mainly composed of G units and contains lower levels of H units. In annual crops, lignin includes comparable levels of G and S units, along with a higher amount of H units compared to softwood and hardwood.<sup>46</sup>



Figure 1.10. Major units of lignin: p-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S).<sup>41</sup>

Lignin exhibits a colorless or pale-yellow appearance, but its color undergoes a transformation to a dark brown shade when subjected to treatment with acid or alkali. Moreover, the structure of lignin encompasses a diverse variety of functional groups, including aliphatic and aromatic hydroxyl, methoxy, carbonyl, and carboxyl groups. These functional groups have a considerable influence over the solubility properties of lignin.<sup>42,47</sup> The dominant inter-unit linkage

in all lignin structures is the  $\beta$ -aryl ether bond ( $\beta$ -O-4), which forms more than half of the bonding structure in both softwood and hardwood lignin. Moreover, a small portion of lignin units is connected through other C-C and C-O inter-monomeric linkages, including  $\beta$ -5,  $\alpha$ -O-4, 5-5,  $\beta$ -1,  $\beta$ - $\beta$ , and  $\alpha$ - $\beta$  linkages (refer to Figure 1.9).<sup>48–50</sup> A wide variety of lignins exists, each with unique characteristics, influenced by factors like biomass type, lignin isolation process, and subsequent downstream treatment. <sup>51</sup> An overview of some of these lignins will be provided in the following section.

### Kraft Lignin

Lignin is primarily managed by the pulp and paper industry. Kraft pulping is recognized as the most dominant among the chemical pulping processes, contributing to over 90% of the chemical pulp production. <sup>52</sup> The term "Kraft," originating from the German word for "strength," highlights the exceptional properties of the resulting pulp fibers compared to those obtained through other pulping methods.<sup>51</sup>

In Kraft pulping, wood chips undergo treatment with an alkaline solution, known as white liquor, containing NaOH and Na<sub>2</sub>S. During this process, lignin is extracted and dissolved in the alkaline liquor through nucleophilic reactions with sulfide anions. These reactions lead to lignin fragmentation, sulfur incorporation, and repolymerization. The resulting lignin-containing black liquor is separated from the pulp and concentrated using evaporators before being incinerated in a recovery boiler to produce process steam.<sup>52,53</sup>

Various industrial-scale technologies are used to isolate Kraft lignin. One simple approach involves acidifying the black liquor with H<sub>2</sub>SO<sub>4</sub> to precipitate the lignin, which is then recovered by filtration, washed, and dried. More advanced isolation methods, like the LignoBoost technology, use a two-step acidification process involving CO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> to obtain isolated Kraft lignin with improved filtration behavior, lower ash and sugar content, and reduced H<sub>2</sub>SO<sub>4</sub> consumption.<sup>53,54</sup> Another technology called LignoForce incorporates an oxidation step using air/oxygen before acidification and precipitation to remove harmful sulfur compounds.<sup>55</sup>

Currently, about 55 million tons of Kraft lignin are annually incinerated.<sup>56</sup> The production capacity of isolated Kraft lignin is approximately 150 thousand tons per year, representing less

than 1% of the lignin burned in concentrated black liquor. If 10% to 20% of the Kraft lignin in black liquor were isolated, while the remaining is used for the mill's energy requirements, the potential availability would range from 6 to 11 million tons per year. This estimate already surpasses the global market volume of phenolic resins, which is 4 to 6 million tons per year. <sup>57</sup>

### Lignosulfonates

Another category of commercially available lignins is lignosulfonates, which are mainly derived from sulfite pulping processes. Although the sulfite method holds less importance in global pulp production, lignosulfonates represent the largest volume of lignin traded worldwide. The annual production capacity is around 1.8 million tons, significantly higher than the current production capacity of Kraft lignin. <sup>58</sup>

During the sulfite pulping process, the wood is subjected to sulfite and/or bisulfite anions in an aqueous solution.<sup>58</sup> This procedure can take place under acidic, neutral, or alkaline conditions.<sup>59</sup> During pulping, interunit linkages in the wood are hydrolyzed, and more importantly, sulfonate groups are incorporated into the lignin structure. These anionic groups significantly enhance the water solubility of lignosulfonates, making them easily soluble even in acidic conditions, a unique feature among lignin types. Similar to Kraft pulping, sulfite liquor, also called red or brown liquor, can be concentrated through evaporators and incinerated to recover energy and pulping chemicals. Additionally, lignosulfonates are used for their anionic properties, functioning as plasticizers, flocculants, or metal adsorbents, and are available as either a concentrated aqueous solution or dry powder. <sup>58,59</sup>

### Soda Lignin

Soda pulping is an alternative pulping method that is similar to Kraft pulping but excludes sulfur-containing agents. Since sulfide ions are absent during this process, the lignin produced is sulfur-free, although its effectiveness is slightly reduced. Soda pulping is mainly applied to easily manageable feedstocks, such as wheat straw. <sup>60,61</sup>

### **Biorefinery Lignins**

Lignin has attracted increasing interest outside of the pulp and paper industry, as it plays a crucial role in the rising field of biorefineries.<sup>62</sup> The goal of these biorefineries is to transform

biomass feedstock into versatile intermediates for various bio-based compounds, fuels, and materials. Depending on the targeted bioproducts, the methods for biomass deconstruction vary significantly, resulting in a wide range of biorefinery lignins. Unlike the well-established pulp and paper industry, the biorefinery sector remains in its early stages, with many processes being studied and tested on a smaller scale in laboratories and experimental facilities.<sup>51</sup>

### **Hydrolysis Processes**

Cellulosic bioethanol has attracted significant attention and is now produced on a commercial scale. The typical method involves hydrolyzing the carbohydrate fraction and enzymatically fermenting the released sugars. A pretreatment step may be conducted beforehand to enhance hydrolysis and fermentation.<sup>63</sup> One commonly used method is steam explosion pretreatment.<sup>64</sup> The actual carbohydrate hydrolysis can be achieved using enzymes, inorganic acids, or supercritical water. The remaining lignin fraction, known as "hydrolysis lignins," is obtained as a water-insoluble residue and is often incinerated for bioenergy recovery. These hydrolysis lignins have low purity and contain a considerable amount of residual carbohydrates.<sup>51</sup> The economic viability of facilities focusing solely to cellulosic ethanol has been difficult, leading some companies to bankruptcy or suspending production. In response, several new biorefineries have shifted their focus to alternative sugar derivatives, like ethylene glycol, and have explored ways to valorize hydrolysis lignin.<sup>51</sup>

### **Organosolv Processes**

Another classification of biorefinery lignins is "organosolv lignins," which are derived from organosolv pulping.<sup>65</sup> Organosolv pulping, which was originally developed as an alternative to Kraft and sulfite pulping methods, has gained increased attention within the biorefinery field.<sup>66</sup> In this process raw biomass is treated with an organic solvent that may also contain water and/or trace quantities of acid/base catalysts. Numerous solvents, including methanol, ethanol, butanol, glycerol, acetone, formic acid, and acetic acid, have been investigated.<sup>65,67,68</sup> The treatment takes place at elevated temperatures (100-210 °C), resulting in solvent-assisted break down and extraction of lignin. Then lignin can be isolated as a solid powder by evaporating the solvent and/or precipitating it in water.<sup>65,67,68</sup>

### Incorporation of Lignin as a Replacement for Phenol

In various studies, lignin-based phenolic resins have been reported by researchers. Lignin is considered a suitable substitute for phenol in phenolic resin production due to its numerous phenolic hydroxyl groups. <sup>69</sup> However, its practical use is limited by steric hindrance and the high methoxy group content in its structure, which reduces its effectiveness.<sup>70</sup> In PF resin production, lignin can be used as raw, purified, or chemically modified lignin. Raw lignin has low reactivity with formaldehyde, resulting in a slow reaction rate, making purified lignin more common. Alternatively, lignin's reactivity can be improved through chemical modifications by utilizing its phenolic and aliphatic hydroxyl groups.<sup>71</sup> Methods like methylolation<sup>72</sup>, phenolation<sup>73</sup>, and demethylation<sup>74</sup> are used to improve lignin's reactivity.

Methylolation introduces hydroxymethyl groups to lignin molecules, increasing their reactive sites. Researchers have improved lignin reactivity by hydroxymethylating rice straw lignin, allowing 20-50% phenol substitution in phenol-formaldehyde (PF) resin synthesis.<sup>75</sup> Another study substituted 50% of phenol with methylolated lignin liquor from steam-treated corn stalk.<sup>76</sup> Demethylation methods using hydrogen iodide<sup>77</sup>, hydrogen chloride<sup>78</sup>, sulfur dioxide<sup>79</sup>, or sodium sulphite<sup>80</sup> has been also explored. Sodium sulphite-assisted demethylation significantly enhances lignin reactivity, leading to PF resins with faster curing rates, shorter gel times, higher reactivity, and lower formaldehyde emissions.<sup>80</sup> Additionally, phenolation of beech organosolv lignin has been reported to increase the number of potential cross-linking sites.<sup>81</sup> The extent of phenolation is influenced by factors like phenol/lignin ratio, catalyst content, reaction time, temperature, and solvent content.<sup>81</sup>

Depolymerization is another approach for lignin utilization, where complex lignin molecules are broken down into smaller molecules or oligomers to broaden their applications. Various techniques, such as base-catalyzed, acid-catalyzed, metal-catalyzed, ionic liquids-assisted, and supercritical fluids-assisted procedures, can achieve depolymerization.<sup>82,83</sup> Base-catalyzed depolymerization typically requires high temperatures and pressures<sup>82–84</sup>, while acid-catalyzed depolymerization involves harsh conditions, increasing reaction costs.<sup>85</sup> Metal-catalyzed depolymerizations, especially those employing Ni- and Pt-based catalysts, are highly selective

and cost-effective.<sup>86–88</sup> Although ionic liquids and supercritical fluids-assisted depolymerizations offer high selectivity, their high cost limits broader adoption.<sup>89–91</sup>

The incorporation of lignin into phenol-formaldehyde polymers offers several advantages, such as reducing harmful emissions of phenol and formaldehyde, thus enhancing environmental sustainability.<sup>92</sup> However, lignin's higher molecular weight and limited reactivity restrict its potential as a phenol substitute. A higher curing temperature and longer reaction time are often required due to lignin's lower reactivity. Lignins from different sources and processes can exhibit varying performances. For example, resins synthesized with high-molecular-weight lignin have higher viscosity compared to those made with low-molecular-weight lignin. Furthermore, long-chain hydrocarbon derivatives in lignin extracts can cause agglomeration during resin synthesis, reducing colloidal stability.<sup>27</sup> Lignin modification can address certain challenges, but it introduces new ones. For example, lignin phenolation and hydroxymethylation require toxic phenols or formaldehyde, while demethylation demands high temperatures and pressures, restricting widespread implementation. Additionally, lignin depolymerization leads to higher costs due to the need for elevated temperatures, pressure, and expensive catalysts. Future research should focus on developing safer, more efficient, cost-effective, and environmentally sustainable methods for incorporating lignin into phenolic polymers.<sup>27</sup>

In general, the incorporation of lignin results in a reduction in the bonding strength of wood-based panels. The extent of this reduction is directly proportional to the lignin content, meaning that higher lignin concentrations cause greater reductions, thus limiting the percentage of lignin substitution in phenol-formaldehyde resin.<sup>27</sup> However, there are some noteworthy exceptions. In a study by Kalami et al.<sup>92</sup>, plywood made with enzymatic hydrolysis lignin-based PF resin, fully substituting phenol, showed shear strength comparable to commercial PF resin. This positive result is likely due to the higher purity and reactivity of the lignin used in that study. In another investigation, Kalami et al.<sup>93</sup> used various lignin samples from different sources and isolation methods to entirely replace phenol in PF adhesive formulations. Their research demonstrated that enzymatic hydrolysis lignin from corn stover exhibited superior performance in adhesion strength and wood failure when cured under industrially accepted conditions. They

concluded that this lignin sample contained the highest amount of H lignin monomers, with two unoccupied ortho sites adjacent to the phenolic hydroxyl group, making it highly reactive and the best performer in adhesive formulation. Meanwhile, Qiao et al.<sup>94</sup> successfully replaced up to 50% of phenol with enzymatic hydrolysis lignin without compromising adhesive strength. This variation highlights the significant impact of resin formulation expertise on achieving optimal performance.

Table 1.1 provides a summary of different lignin samples integrated into PF adhesive formulations along with their respective properties and performance.

-	Table 1.1. Studies or	<ol> <li>incorporation c</li> </ol>	of diverse	e types of	lignin into	PF adhesives	for wood	l panel
ä	applications.							
Г								

Lignin type	%Replacement	t Effect on Performance	
Enzymatic Hydrolysis Corn Stover	100	Plywood exhibiting shear strengths similar to those of commercial phenol- formaldehyde resin	92
Corn Stover, Softwood, Hardwood (Isolated by various methods)	100	Corn Stover lignin obtained from Enzymatic Hydrolysis has the best performance	93
Purified lignin from black liquor	20-40	Adhesion strength was reduced. Thermal stability was improved	95
Soda lignin, pine kraft lignin, and Beech organosolv lignin	40	Higher viscosity LPF with 40% of kraft lignin replacement had similar performance to PF adhesive	96
Enzymatic Hydrolysis lignin	10-70	Adhesive strength showed a gradual increase with the addition of lignin, reaching its peak at a 50% substitution of phenol	94
Organosolv lignin	40	Higher molecular weight and lower viscosity than PF resin	97
Kraft lignin	50	Replacing 50% of phenol with lignin proved to be optimal, resulting in a binder with an adequate bonding strength	98

Table 1.1. (cont'd)

Alkaline lignin	10-50	Incorporating lignin up to 30% enhances the plywood's modulus of elasticity (MOE) and modulus of rupture (MOR). However, at 50% lignin content, the plywood showed reduced tensile strength, wood failure, MOE, and MOR.	99
Beech organosolv lignin	40	Particleboards bonded with activated resins exhibited superior mechanical characteristics compared to panels manufactured using untreated LPF resins, meeting the criteria for particle board production	100
Organosolv lignin	20-30	LPF adhesive met the criteria for particle board production	101
Kraft lignin	20-60	Comparable adhesive strength, elevated curing temperature and duration	98
Bagasse lignin	50	Substituting 50% of phenol with lignin resulted in improved bonding strength compared to standard PF resins	102
Organosolv lignin	50	The presence of extractives in alkaline organosolv lignin causes significant agglomeration and reduces colloidal stability. The adhesion strength of acid organosolv lignin resin and purified alkaline organosolv lignin resin is comparable, but less than that of PF resin	103
Corn lignin	50	An increases solid content but reduced bonding strength compared to PF resin	104

#### **1.5.1.2** Tannin as a Phenol Replacement

Another noteworthy eco-friendly alternative to phenol in PF resin synthesis is tannin, a polyphenolic compound found in tree bark and wood. Tannins are classified into two main types: hydrolysable and condensable tannins, based on their chemical properties.<sup>76</sup> The chemical structures of these two types are shown in Figure 1.11. Hydrolysable tannins consist of phenols that can be broken down into phenolic acid and carbohydrates by treatment with weak acids or bases.<sup>105</sup> Although hydrolysable tannin's structure is more complex and their reactivity is lower compared to condensable tannins, they are still used as phenol substitutes in PF resins. For instance, valonea tannin has been successfully utilized to partially replace phenol in phenol-tannin-formaldehyde resin, resulting in a resin with faster curing times and lower formaldehyde emissions.<sup>106</sup>

However, around 90% of commercially available tannins are derived from condensable tannins, which contain two aromatic rings with distinct hydroxyl groups. The reactivity of tannin is affected by the positioning of these hydroxyl groups. The success of tannin extraction from plants depends on factors such as the plant species and the solvent used for extraction.<sup>76</sup> Tanninbased phenolic resins, used as adhesives for wood panels, have seen significant innovation. Various tannins isolated from different sources (Table 1.2) have been utilized to produce resins with properties comparable to PF resin. Li et al.<sup>107</sup> investigated the reactivity of condensable and hydrolysable tannins with formaldehyde in PF resin synthesis. Resins were produced using larch (condensable) and valonia (hydrolysable) tannins, and properties such as viscosity, solid content, gel time, and free formaldehyde content were compared. The larch tannin-based resin demonstrated superior properties, including lower formaldehyde emissions. Due to their higher reactivity, condensable tannins are more commonly preferred for resin production over hydrolysable tannins.<sup>107</sup> Yi et al.<sup>108</sup> introduced a novel approach by partially replacing formaldehyde with furfural in these resins, aiming to reduce formaldehyde emissions from the adhesive. Their research presented a new method for modifying tannin to improve its interaction with furfural. To enhance reactivity, both tannin and furfural were pretreated: tannin was depolymerized, and the furan ring of furfural was opened. This pretreatment increased the substitution ratio and significantly reduced the free formaldehyde content from 5.57% to 1.42%.

Incorporating furfural also improved the resin's thermal stability. Table 1.2 provides a summary of studies on phenol substitution with tannin and the resulting performance characteristics.



Figure 1.11. Various structures for tannin: a (hydrolysable) and b (condensable) structure.<sup>76</sup>

Substitute	% Replacement	Effect on Performance	
Condensed tannin	10-30	pH and gelation time were decreased, viscosity was enhanced	109
Chestnut tannin	4-40	Higher reactivity and shorter gelation time	110
Tannin	20	Low formaldehyde content and meeting bonding strength requirements	111
Valonea tannin	30	Low formaldehyde content, higher reactivity and shorter gelation time, meeting bonding strength requirements	106

Table 1.2. Example of studies in tannin incorporation in PF adhesive formulations.

### 1.5.1.3 Cardanol as a Phenol Replacement

Cardanol is obtained from the liquid that is extracted from cashew nut shells, which are generated as a byproduct during the processing of cashew nuts. This liquid is composed of various components, including 71.7% anacardic acid, 4.7% cardanol, 18.7% cardol in trace amounts, 2.7% 2-methylcardol, and 2.2% unidentified polymeric substances. The extraction of cardanol from
cashew nutshell liquid is achieved through different methods such as pyrolysis, heat treatment, supercritical carbon dioxide extraction, or solvent-based techniques. Cashew nutshell liquid is typically enriched with a higher content of cardanol after extraction. The structure of cardanol is shown in Figure 1.12.<sup>76,112</sup>



Figure 1.12. Cardanol structure.<sup>76</sup>

Cardanol, due to its phenolic groups, has been utilized as a natural substitute for phenol in the production of PF resin. Novolac and resole resins have been synthesized with phenol partially replaced by cardanol. The degree of this substitution influences the mechanical and thermal properties of the resulting resin. In certain PF resins, the substitution of cardanol has been shown to reduce thermal stability and tensile strength.<sup>113,114</sup> A process was utilized by Parameswaran et al.<sup>115</sup>, where phenol was substituted with cardanol in varying molar ratios, along with formaldehyde, to produce resole resin. A decreasing trend in the tensile and flexural strengths of the resin was observed as the cardanol substitution increased.<sup>115</sup> A novel cardanol-based phenolic resin was formulated to improve the thermal stability and sustainability of phenolic resin. This formulation involved the copolymerization of salicylic alcohol, cardanol, and boric acid. The incorporation of boron into the resin enhanced its thermal stability.<sup>116</sup> Natarajan et al.<sup>117</sup> introduced another approach to enhance thermal stability in cardanol-based resin. They synthesized a novolac-type resin from cardanol and formaldehyde by using oxalic acid as a catalyst. To improve thermal stability, the resin was subjected to epoxidation using epichlorohydrin.<sup>117</sup> Jadhav et al.<sup>118</sup> pursued an unconventional route to craft a cardanol-based novolac resin. By employing an energy-efficient ultrasound-assisted synthesis path, they significantly reduced reaction time from 5 hours to just 30 minutes compared to traditional methods.<sup>118</sup> Furthermore, for refining the properties of cardanol-formaldehyde resin, modifications were made by substituting formaldehyde with furfural. This alteration led to an

enhancement in mechanical, chemical, and curing characteristics in the resulting cardanol– furfural resin.<sup>119</sup>

### **1.5.2 Formaldehyde Replacements**

Formaldehyde has been widely utilized as a fundamental raw material in numerous industries and manufacturing sectors. Its main applications include the production of wood composites, flooring materials, cosmetics, medicinal products, insulation materials, disinfectants, cleaning agents, preservatives, and paper. This extensive use results in widespread exposure both indoors and outdoors. However, concerns have been raised regarding formaldehyde's health risks due to its prevalent use in various industries.<sup>120–122</sup> The environmental impact of formaldehyde is equally troubling, as it negatively affects plant life and wildlife. Due to environmental and occupational concerns related to formaldehyde, various regulations and guidelines have been established to limit exposure levels. However, these restrictions differ across countries.<sup>123–126</sup>

Although formaldehyde remains essential in key industries, its harmful effects on human health have led industries and researchers to explore safer and more environmentally friendly alternatives. Bio-based substitutes are viewed as the most promising options for replacing formaldehyde. Compounds such as hydroxymethylfurfural, furfural, furfuryl alcohol, glyoxal, and vanillin have been investigated as potential bio-based alternatives in the synthesis of PF resins.<sup>76</sup>

In this section, we will delve into a discussion of several of these bio-based options, with a particular focus on glyoxal.

#### 1.5.2.1 Glyoxal as a Formaldehyde Replacement

Glyoxal, an aldehyde with two adjacent aldehyde groups in its structure, is widely considered non-toxic. Its non-volatile nature, cost-effectiveness, and biodegradability make it a suitable candidate for replacing formaldehyde in the production of phenolic adhesives. Glyoxal is naturally present in various dietary items such as wine, beer, tea, coffee, yogurt, bread, rice, soybean paste, soy sauce and oil.<sup>76</sup>

Glyoxal, the smallest dialdehyde, is commonly available as a 40 wt. % aqueous solution. Its primary applications include serving as a cross-linker or as a precursor for cross-linking agents in industries such as paper, textiles, and leather.<sup>51,127</sup> Additionally, it serves as a precursor for glycolic acid.<sup>51</sup> Glyoxal forms equilibrium between its mono- and di-hydrated forms. It can also form dimers and small oligomers through reversible condensation, with the concentration determining the prevalence of these species.<sup>51</sup> Various instances of this phenomenon are depicted in Figure 1.13.



Figure 1.13. Various hydrated forms of glyoxal.<sup>51</sup>

Glyoxal is produced through gas-phase oxidation of ethylene glycol using air and a catalyst like silver or copper.<sup>127</sup> Another approach involves the liquid-phase oxidation of acetaldehyde using nitric acid. Acetaldehyde itself can be obtained from the oxidation of ethylene or ethanol.<sup>51</sup>

Although bio-based ethanol and ethylene glycol, precursors for glyoxal, are attracting increasing interest, the current commercial availability of bio-based glyoxal remains uncertain. However, glyoxal can be produced from renewable resources using existing technology, such as bioethanol or ethylene glycol. It is important to note that 'bio-based' does not always mean a reduced carbon footprint. For instance, the oxidation of biomass-derived acetaldehyde with nitric acid may emit N<sub>2</sub>O, a potent greenhouse gas, potentially outweighing CO<sub>2</sub> reductions achieved in other areas.<sup>51</sup>

Other sources in scientific literature suggest synthesizing glyoxal from alternative carbohydrates. This could involve the direct conversion of glucose through retroaldol condensation or the indirect conversion of glycoaldehyde via autoxidation.<sup>128</sup> Additionally, galactose, mannose, fructose, ribose, arabinose, ribulose, glyceraldehyde, acetone, adenosine, mannitol, and glycerol can also be utilized to produce glyoxal.<sup>129</sup>

The use of glyoxal as an alternative to conventional hydroxymethylation, also known as methylolation, achieved by reacting lignin with formaldehyde, offers an innovative approach. El Mansouri and colleagues were the first to propose glyoxal as a substitute for formaldehyde in the hydroxyalkylation of lignin. <sup>130</sup> Since their innovative work, the glyoxalation of various lignin types has been explored.

Previous studies on sustainable adhesives have primarily used lignin and glyoxal as partial substitutes for phenol and formaldehyde, respectively. Three main strategies have been employed in earlier research to achieve this.

The first strategy involves the use of lignin as a partial substitute for phenol, reaching up to 50% by weight, alongside a complete substitution of formaldehyde with glyoxal.<sup>131,132</sup> For instance, a study demonstrated replacement of phenol with lignin at the rate of 50% by weight, combined with a full replacement of formaldehyde with glyoxal, resulting in a resin with improved tensile strength compared to a reference phenol-formaldehyde resin.<sup>132</sup> The second approach involves preparing lignin-glyoxal resins, which are then blended with petroleum-based cross-linking agents like pMDI (polymeric 4,4'-diphenylmethane diisocyanate) to enhance adhesion strength.<sup>130,133</sup> An example of this method includes mixing a lignin-glyoxal resin with 40–60% pMDI by weight, resulting in adhesives with satisfactory internal bond strength suitable for particleboard applications.<sup>130,133</sup> Other studies have incorporated up to 60 wt. % of lignin-glyoxal resin into solutions of tannin extract and hexamethylenetetramine (hexamine), performing as a hardener, to enhance adhesion strength.<sup>134,135</sup> In one instance of this approach, an adhesive was developed with a dry adhesion strength of 1.4 MPa, surpassing industry standards (e.g., EN 314-2) for interior grade plywood.<sup>134</sup> The third strategy involves formulating lignin-glyoxal resins using alternative cross-linking agents such as epichlorohydrin, polyacrylic

ester, an aqueous polyurethane emulsion, or a commercial diglycidyl ether of bisphenol-A (DGEBA) epoxy resin.<sup>136,137</sup>

However, a recent study<sup>38</sup> has adopted an alternative approach, marking the first instance of simultaneously substituting both petroleum-based phenol and formaldehyde with unmodified lignin and glyoxal. This study highlights the significant potential of glyoxal in producing environmentally friendly adhesives that demonstrate remarkable performance while being significantly less toxic, a critical requirement for interior wood panel applications. The ligninglyoxal adhesive exhibited dry adhesion performance comparable to both lignin-formaldehyde and conventional phenol-formaldehyde adhesives available commercially. However, the developed adhesive did not pass the accelerated wet adhesion test, which assesses the adhesive's durability under prolonged environmental conditions, often crucial for outdoor applications. This underscores the need for further investigation into the interactions between lignin and glyoxal to optimize the resin synthesis process more precisely.

In the reaction between lignin and formaldehyde, formaldehyde is added to an alkaline lignin solution, leading to three distinct reactions, as shown in Figure 1.14. The primary reaction is the Lederer–Manasse reaction, where hydroxymethyl groups (–CH<sub>2</sub>OH) are incorporated into the C5 position of the aromatic rings in lignin.<sup>138</sup> However, concurrent side reactions can take place, including the Cannizzaro reaction, where two formaldehyde molecules react in an alkaline environment to produce formic acid and methanol. Another side reaction, the Tollens reaction, leads to the substitution of lignin's side chains with aliphatic methylol groups.<sup>51</sup> Glyoxalation involves similar reactions, including the incorporation of glyoxal at vacant ortho positions in lignin, the Cannizzaro reaction of glyoxal, and the substitution of glyoxal at lignin's side chains.<sup>51,139</sup>



Figure 1.14. Various reactions during the reaction of lignin with formaldehyde (left) and glyoxal (right) including: A (Lederer-Manasse), B (Cannizzaro), and C (Tollens) reactions.<sup>51</sup>

A key factor in synthesizing phenolic resole resins is the prevention of aldehyde side reactions, especially the Cannizzaro reaction. Aldehydes that lack an alpha-hydrogen undergo a disproportionation reaction in an alkaline environment, resulting in the formation of alcohol and carboxylic acid products.<sup>140</sup> Glyoxal, with its two adjacent carbonyl groups, easily initiates an intramolecular Cannizzaro reaction when introduced into an alkaline solution, as illustrated in Figure 1.15 B.<sup>51</sup> This reaction can proceed even under mild alkaline conditions, resulting in the formation of glycolic acid.<sup>51</sup> Since the Cannizzaro reaction of glyoxal occurs within the same molecule, without requiring two aldehyde molecules, the possibility of glyoxal's side reaction exceeds that of formaldehyde. Moreover, the close proximity of the two carbonyl groups with partial positive charges makes glyoxal more prone to this side reaction.<sup>38</sup>

The glycolic acid produced from the Cannizzaro reaction of glyoxal lowers the resin's pH. Without proper control of the resin's alkalinity, this pH decrease can interfere with the electrophilic substitution reactions between lignin and glyoxal during phenolic resole resin synthesis. At the same time, excessive alkalinity can negatively impact the adhesive's performance, especially under moisture exposure. Therefore, it is essential to adjust the reaction medium's pH to achieve optimized properties.<sup>141</sup>



Figure 1.15. Proposed mechanism for the Cannizzaro reaction of formaldehyde (A) and glyoxal (B).<sup>38</sup>

# 1.5.2.2 Furfural as a Formaldehyde Replacement

Furfural is an organic compound characterized by a furan ring with an aldehyde functional group at the 2-position. It is industrially significant in resin manufacturing, acts as a lubricant, and is involved in the synthesis of various organic compounds such as furfuryl alcohol (FFA), tetrahydrofuran, and methylfuran.<sup>142</sup> Furfural is derived from non-edible wood waste, where

pentosans in lignocellulosic residues are converted into pentoses through acid hydrolysis, followed by steam stripping for dehydration to produce furfural. However, the economic feasibility of this method was limited by low yields and high production costs, causing plant closures in the 1990s. In response, global companies implemented modified procedures to improve yields from lignocellulose biomass.<sup>143</sup> Another approach involves using ionic liquids to produce furfural from lignocellulosic materials, as outlined in a recent review by Peleteiro et al.<sup>144</sup> Figure 1.16 provides a schematic representation of the furfural synthesis process from biomass.



Figure 1.16. Synthesis path for furfural.<sup>76</sup>

Various aldehydes, including furfural, have been used in the development of phenolic resins. Oliveira et al.<sup>145</sup> conducted the preparation of phenol-furfural resin and performed extensive structural analysis using nuclear magnetic resonance (NMR) and MALDI-TOF spectroscopy. This analysis revealed that linear oligomers predominated over cyclic ones within the structure. They also successfully created composites using phenol-furfural resin and sisal fibers. Thermal evaluations, including thermogravimetric analysis, differential scanning

calorimetry, and electron microscopy, demonstrated the strong adhesion between the resin and sisal fibers.

Cheng et al.<sup>146</sup> outlined the synthesis of phenol-formaldehyde adhesives using furfural as a crosslinking agent. As furfural content increased, the number of methylene bridges connecting phenol and furfural also rose, enhancing the bonding strength of the modified resin. This improvement resulted in a significant increase in wet tensile strength, reaching 2.8 MPa, compared to 1.5 MPa in traditional PF resin. In another study,<sup>147</sup> formaldehyde was fully replaced by furfural and glucose. The research team formulated resole-type resins with different molar ratios of glucose to furfural. They then evaluated key characteristics such as bonding strength, free phenol content, pH, and resin solid content. The properties of the resin met the wood adhesive standards specified in GB/T 14732-2006. Dongre et al.<sup>148</sup> conducted a study where lignin and furfural were used as replacements for the usual phenol and formaldehyde components in PF resins. Lignin, obtained from the acid hydrolysis of hot water extract, substituted phenol, while furfural replaced formaldehyde. These two components were blended and cross-linked. Notably, the composite created under a pH of 1 and containing 16% furfural demonstrated tensile properties comparable to the tensile strength observed in PF resin.

### **1.5.2.3** Hydroxymethylfurfural as a Formaldehyde Replacement

Hydroxymethylfurfural (HMF) is regarded as a promising substitute for formaldehyde, with significant potential due to its ability to serve as a source for various chemicals and liquid fuels. This organic compound consists of a furan ring and functional groups, including aldehyde and alcohol. These functional groups provide HMF with high reactivity and water solubility. HMF acts as a precursor in the production of a wide range of compounds such as liquid alkanes, cosmetics, polymers, and pharmaceuticals.<sup>149–152</sup> The industrial value of HMF is substantial, especially in its role in producing biofuels such as dimethylfuran (DMF) and ethoxymethylfurfural (EMF), which are used in self-driving vehicles.<sup>153,154</sup>

This aromatic aldehyde is present in dried fruits, honey, coffee, and flavoring agents. The proportion of HMF in these natural sources varies, and catalytic dehydration has been widely used to extract HMF from them.<sup>155</sup> HMF can also be produced from lignocellulose and cellulose

using organic solvents and ionic liquids.<sup>156</sup> In recent years, significant progress has been achieved in the development of catalysts with the ability to transform biomass into HMF.<sup>157,158</sup> This process includes depolymerization or hydrolysis, which breaks the bonds between polymers, facilitating the action of catalysts.<sup>159</sup> Figure 1.17 illustrates the schematic diagram for synthesizing HMF from cellulose.



Figure 1.17. Schematic diagram for synthesizing HMF from cellulose.<sup>76</sup>

Zhang et al.<sup>160</sup> conducted a study aimed at developing a phenolic resin by replacing formaldehyde with HMF. Their innovative method resulted in the formulation of a series of novolac PF resins, where formaldehyde was substituted by HMF. HMF was generated in situ from glucose and then reacted with phenol to synthesize the resin. Using the common curing agent hexamethylenetetramine (HMTA), the resin was cured and used to fabricate fiberglass-reinforced composites. The composite's thermal, mechanical, and curing properties were evaluated by varying the HMTA concentration. The findings demonstrated the feasibility of HMF-modified PF resins for producing environmentally friendly composites, with zero formaldehyde

emissions upon heating. In another study, phenol was replaced with a depolymerized hydrolysis lignin and formaldehyde with HMF, resulting in a resin made entirely from renewable materials. The resin was then cured with HMTA. Notably, this alternative resin demonstrated exceptional thermal stability, resisting decomposition up to temperatures of 315°C.<sup>161</sup> However, it is important to recognize that despite HMTA's common use in curing novolac-type phenolic resins, concerns have been raised about its environmental impact due to its tendency to decompose at room temperature that release toxic substances.<sup>162</sup> In a separate study, bisphenol A diglycidyl ether (DGEBA) was used as an alternative to HMTA to crosslink the phenol–hydroxymethylfurfural resin. A novolac phenol–hydroxymethylfurfural resin was synthesized by reacting phenol with in-situ generated HMF from glucose. This resin was then cured using DGEBA as a formaldehyde-free curing agent. The cured resin exhibited excellent thermal and mechanical properties, making it suitable for use in fiber-reinforced plastics and composites.<sup>163</sup>

# 1.6 Research Gaps and Objectives

Despite significant advancements in lignin-based adhesives, no studies have simultaneously replaced both phenol and formaldehyde with unmodified lignin and glyoxal while testing the resulting adhesive against industry standards. Previous research has often focused on partial substitutions or modifications of lignin to enhance reactivity, but the potential of using unmodified lignin in conjunction with glyoxal remains underexplored. This gap presented an opportunity to assess the performance of fully bio-based adhesive formulations in addressing sustainability goals without compromising its application at industry scale.

In addition, while lignin-based adhesives have shown promise at the laboratory scale, their scalability and compatibility with industrial processes remain uncertain. Issues such as cost efficiency, process optimization, and compliance with performance standards for wood products require further investigation. Addressing these challenges will not only bridge critical gaps in adhesive research but also contribute to advancing sustainable material solutions for the engineered wood products industry.

Another important gap in current research is the limited understanding of the molecular interactions between lignin with formaldehyde and glyoxal. As a safer and more sustainable

alternative to formaldehyde, glyoxal offers significant potential in adhesive applications. However, insufficient studies on its reaction mechanisms with lignin hinder the optimization of adhesive formulations. Without a deeper understanding of these interactions, it remains difficult to achieve adhesives with performance characteristics comparable to conventional phenolformaldehyde resins. Filling this knowledge gap is essential for advancing the development of lignin-glyoxal systems.

Efforts to address key challenges in sustainability, scalability, and performance are driving significant changes in the adhesive industry. The simultaneous replacement of phenol and formaldehyde with unmodified lignin and glyoxal is aimed at bridging the gap between environmental responsibility and industrial practicality. An innovation in this area is expected to reduce reliance on petroleum-based raw materials while minimizing health and environmental risks associated with formaldehyde emissions. The replacement of at least 80% of phenol with commercially available lignin, along with the significant reduction of formaldehyde usage, is viewed as addressing the urgent need for scalable solutions compatible with industrial manufacturing processes. Additionally, fundamental knowledge is needed through investigations into the molecular interactions and reaction mechanisms of lignin with formaldehyde and glyoxal to optimize adhesive formulations. These efforts are considered crucial for the development of bio-based adhesives that meet industry standards, enabling their widespread adoption in engineered wood products and contributing significantly to a sustainable and resilient materials economy.

The objectives of this study are outlined below, aimed at delivering clear and practical outcomes:

**Objective 1:** To evaluate the potential of lignin-glyoxal adhesives as substitutes for traditional phenolic adhesives in interior-grade engineered wood products, with a focus on determining whether they can be cured at the same temperature as commercial phenol-formaldehyde and lignin-formaldehyde adhesives, without compromising performance.

**Objective 2:** To investigate the feasibility of developing lignin-based adhesive formulations with 80-100% phenol replacement with unmodified commercially available lignins, while ensuring the adhesive can be cured at the same press parameters currently used in plywood industry.

**Objective 3:** To analyze the molecular structure and reaction mechanisms of lignin-formaldehyde and lignin-glyoxal resins before and after curing, focusing on whether formaldehyde and glyoxal form effective methylene or glyoxylene linkages with lignin to establish a stable 3D network.

Chapter 2 has been published as a peerreviewed paper in "ACS Sustainable Chemistry & Engineering" journal

### **CHAPTER 2:**

# Lignin-Glyoxal: A Fully Bio-Based Formaldehyde-Free Wood Adhesive for Interior Engineered Wood Products

# 2.1 Introduction

Phenolic-based adhesives were first developed in 1911 and are still made from fossil fuelbased phenol and formaldehyde. The resole resin is the most widely used phenolic resin, prepared with an alkaline catalyst and a molar ratio of formaldehyde to phenol greater than one. Resole resins are used to manufacture various engineered wood products such as oriented strand board, plywood, and laminated veneer lumber.<sup>7</sup> Although resole resins have been used for decades due to their durability and high water resistance, the toxicity of formaldehyde and the carbon footprint of petroleum-derived phenol and formaldehyde are still major concerns that should be addressed.<sup>164</sup>

Replacing phenol and formaldehyde with two bio-based raw materials with significantly lower toxicity is an important step toward formulating greener wood adhesives while simultaneously improving the final products' life cycle impacts. Currently, the only commercial wood adhesive that is fully bio-based is a soy-based adhesive adapted for interior grade plywood (*i.e.*, Columbia Forest Products). Over the past century, soy-based adhesives have received more attention than any other class of bio-based raw materials to produce greener, formaldehyde-free adhesives.<sup>165,166</sup> There are several reasons for using soy-based adhesives, including low price, high availability, and high biodegradability.<sup>167</sup> However, there are processing challenges to using soy-based adhesive for interior plywood productions, including low solid contents requiring more extensive drying, high viscosity, and poor overall adhesion strength. The weak performance of soy-based plywood in humid environments and long curing times during hot-pressing due to excess water are some of the disadvantages of this class of bio-based adhesives.<sup>166</sup> Extensive work has been performed during the past decade to address these shortcomings through strategies that include incorporating nanoscale reinforcing fillers, modifying the soy protein structure, and using crosslinking agents.<sup>166</sup> Recent studies showed that despite these efforts in altering the structure of soy protein and the use of petroleum-based phenol-formaldehyde resin as a crosslinking agent, the dry adhesion strength of soy-based adhesives still remained low (approximately 2 MPa).<sup>168,169</sup>

As the most abundant natural aromatic polymer, lignin as a phenol substitute in adhesive applications has been the subject of significant recent research.<sup>92</sup> Lignin can comprise 15-35% of the dry mass of wood and other vascular plants.<sup>92</sup> Industrially processed lignin is commonly used as a low-value fuel to generate energy for pulp and paper mills. However, lignin is a viable alternative to fossil-derived feedstocks for many polymeric resin applications.<sup>170</sup> Lignins are natural polyphenolic compounds that can react with formaldehyde through an electrophilic aromatic substitution.<sup>96</sup> Consequently, developing lignin-based phenolic resins requires lignins with one or two vacant sites in the *ortho* positions to the phenolic hydroxyl groups to react with formaldehyde.<sup>96</sup>

Compared to phenol, lignin has fewer available sites for reaction with formaldehyde per aromatic unit due to (1) the presence of methoxyl groups at ortho positions to the phenolic hydroxyl group in guaiacyl and syringyl monomers, (2) inter-unit linkages (e.g., 5-5,  $\alpha$ -O-5,  $\beta$ -5 linkages) at positions ortho to a phenolic hydroxyl group, (3) phenolic groups involved in interunit linkages (e.g., β-O-4 linkages) between lignin monomers, and (4) steric hindrance associated with the lignin higher-order structure.<sup>93</sup> To address this issue, a wide range of lignin functionalization approaches have been investigated, including phenolation,<sup>70</sup> methylolation,<sup>138</sup> and demethylation.<sup>79</sup> However, these approaches all require additional processing steps and extra energy and chemicals, which add to the final cost of products and may not be appealing for the resin industry.<sup>171</sup> In prior work, we demonstrated that unmodified biorefinery-derived lignin could be used to completely replace phenol and showed that the formulated adhesive exhibited adhesion strength comparable to a commercially formulated phenolic adhesive.<sup>92</sup> This success was achieved due to the source of lignin, containing substantially higher phenolic groups, including two open ortho sites relative to other lignins tested and processing history (dilute acid pretreatment) of the lignin.<sup>172</sup> Furthermore, we also found that by replacing 100% of the phenol with lignin, the formulated adhesive contained 50% less formaldehyde on a weight basis compared with the resin formulated with phenol and formaldehyde.<sup>93</sup>

Despite this achievement in reducing formaldehyde consumption, the use of formaldehyde has remained a significant concern both for industry and consumers. Options explored include substituting formaldehyde with other compounds such as propionaldehyde,<sup>173</sup> glutaraldehyde,<sup>174</sup> gossypol,<sup>175</sup> and glyoxal.<sup>133</sup> However, there were some issues with volatility, toxicity, and solubility for propionaldehyde and glutaraldehyde.<sup>51</sup> On the other hand, glyoxal, the simplest dialdehyde with two adjacent carbonyl groups, proved to be a promising candidate for formulating formaldehyde-free adhesives, as it exhibits significantly lower toxicity than formaldehyde.<sup>51</sup> Specifically, formaldehyde is categorized as carcinogenic, mutagenic, and reprotoxic by the ECHA (European Chemicals Agency) and has measured values for LD<sub>50</sub> (500-800 mg/kg),<sup>176</sup> an order of magnitude lower than glyoxal (2960-8979 mg/kg).<sup>177</sup> Furthermore, there are multiple routes for the production of glyoxal from bio-based feedstocks or intermediates, including sugars, ethanol, and ethylene glycol.<sup>51</sup> In addition, glyoxal has been proven to be an appropriate replacement for formaldehyde<sup>131,133</sup> as a non-volatile, biodegradable, and low-cost monomer.131,178

Prior work on sustainable adhesives has used lignin and glyoxal to partially replace phenol and formaldehyde, respectively. Three general strategies were used by previous studies. In the first category, lignin is used as a partial phenol replacement up to 50% by weight, while formaldehyde was entirely substituted by glyoxal.<sup>131,132</sup> As one example of this approach, one study demonstrated up to 50% phenol substitution by weight with lignin and completely replaced formaldehyde with glyoxal to develop a resin with higher tensile strength than a reference phenol-formaldehyde (PF) resin.<sup>132</sup> For the second approach, lignin-glyoxal resins are prepared and mixed with petroleum-based crosslinking agents such as pMDI (polymeric 4,4'diphenylmethane diisocyanate) to improve adhesion strength.<sup>130,133</sup> As an example of this strategy, a lignin-glyoxal resin was mixed with 40-60% pMDI by weight, and the resultant adhesives had shown to have adequate internal bond strength required for particleboard applications.<sup>130,133</sup> In other studies, up to 60 wt.% of lignin-glyoxal resin was mixed with tannin extract solution and hexamethylenetetramine (hexamine) that act as a hardener to improve adhesion strength.<sup>134,135</sup> In one study using this approach, an adhesive was generated with a dry adhesion strength of 1.4 MPa, which was reported to be higher than industry standards (*i.e.*, EN

314-2<sup>179</sup>) for interior grade plywood.<sup>134</sup> In the third approach, lignin-glyoxal resins were prepared using other crosslinking agents such as epichlorohydrin, polyacrylic ester, an aqueous polyurethane emulsion, or a commercial diglycidyl ether of bisphenol-A (DGEBA) epoxy resin.<sup>136,137</sup>

The goal of the current study is to evaluate the possibility of replacing 100% of both phenol and toxic formaldehyde with two bio-based compounds. For this, phenolic resins are formulated using an unmodified biorefinery corn stover lignin and glyoxal, and their properties and performance are compared with a commercially formulated phenol-formaldehyde resin.

# 2.2 Experimental

### 2.2.1 Materials

POET LLC (Sioux Falls, SD) kindly provided the lignin cake. The lignin cake is a mixture of lignin with residual unhydrolyzed plant cell wall polysaccharides (primarily cellulose) and ash that is generated as a byproduct of lignocellulosic ethanol production via dilute acid pretreatment and enzymatic hydrolysis of corn stover. Lignin was isolated from the lignin cake by extraction in NaOH for further analysis and resin formulation. For this purpose, 100 g of lignin cake was dissolved in 1000 mL 0.5 M NaOH for 30 min while stirred at 350 rpm. Next, the insoluble fraction was separated by centrifugation (Kendro D-37520 Osterode) at 4150 rpm for 5 min, and the supernatant containing the extracted lignin was saved. The pH of the supernatant was adjusted to 2 by dropwise addition of 1 M H<sub>2</sub>SO<sub>4</sub>. Next, the suspension was heated up to 85 °C and kept at this temperature for 30 min. The suspension was then vacuum filtered, and the filtered lignin was washed first with 500 mL distilled water at 60 °C and then 500 mL room temperature water. The insoluble fraction (recovered lignin) was dried in a vacuum oven for 24 h at 50 °C. Lignin properties were determined as outlined below and were measured in triplicate. An adhesive producer kindly provided the commercially available phenol-formaldehyde resin. Glyoxal (40 wt.% in water), formaldehyde (37 wt.% in water), and all other reagents were purchased from Sigma-Aldrich and Fisher Scientific, Inc. and used as received.

### 2.2.2 Methods

#### 2.2.2.1 Ash Content of Lignin

The ash content of lignin was determined using TAPPI-T 211 om-93 test method.<sup>180</sup> First ceramic crucibles were dried and weighed. Then 2 g of oven-dried lignin was added to each crucible (3 replicates). Samples were placed in a muffle furnace (Thermolyne Furnatrol) and heated to 525°C with a heating rate of 5 °C/min. After 4 h, samples were cooled to 100 °C and then placed in a desiccator. The samples were weighed after reaching room temperature, and ash mass fraction was determined by dividing the weight of ash by the weight of oven-dried lignin.

# 2.2.2.2 Lignin Molecular Weight Measurement

Gel permeation chromatography (GPC) was used to measure the number average molecular weight (M<sub>n</sub>), weight average molecular weight (M<sub>w</sub>), and polydispersity index (PDI) of the isolated pure lignin. For this purpose, each sample was acetylated to ensure its solubility in tetrahydrofuran (THF), which was used as the mobile phase.<sup>181</sup> For acetylation, 1 g lignin was added to a 40 mL solution of a mixture of pyridine (20 mL) and acetic anhydride (20 mL) and mixed at room temperature for 24 h using a magnetic bar and digital magnetic stirrer (600 rpm). Next, 150 mL of 0.1 M HCl was used to precipitate acetylated lignin. Precipitated particles were separated using vacuum filtration and washed three times with low concentration hydrochloric acid solution (0.05 M) and deionized water. After this step, the acetylated sample was dried for 16 h using a vacuum oven at 40 °C.<sup>181</sup> Next, the acetylated sample was dissolved in HPLC grade THF at a concentration of 5 mg/mL and filtered using a syringe filter (PTFE, 0.45 μm). The filtrate was used for GPC analysis. A Waters GPC system (Waters e2695 Separation Module) was then used to analyze the filtrate at a flow rate of 1 mL/min, using three 300 mm × 7.8 mm Waters columns in series including 1- Styragel HR 4 THF, 2- Styragel HR 3 THF and 3- Ultrastyragel THF. Monodisperse polystyrene (162, 370, 580, 945, 1440, 1920, 3090, 4730, 6320, 9590, 10400, 16200 Da) were used as calibration standards. The filtrate solution (25 µL) was injected into the instrument and was detected using a 2414 Refractive Index Detector, which was constantly maintained at the same temperature as the columns (35 °C). Data was collected and analyzed using Empower GPC Software.

#### 2.2.2.3 Lignin Hydroxyl Content

The phenolic and aliphatic hydroxyl content of lignins were determined by <sup>31</sup>P NMR according to the procedure published by Asgari and Argyropoulos with slight modifications.<sup>182</sup> For this, a mixture of 325  $\mu$ L of anhydrous pyridine/ deuterated chloroform (1.6:1 v/v) and 300  $\mu$ L anhydrous dimethylformamide (DMF) was prepared, and 40 mg of oven-dried lignin was dissolved in the prepared solution. Next, 100  $\mu$ L of cyclohexanol with a concentration of 22 mg/mL (in anhydrous pyridine and deuterated chloroform with a ratio of 1.6:1.0 (v/v)) was added to the mixture. Then 50  $\mu$ L of chromium (III) acetylacetonate solution with a 5.6 mg/mL concentration in the mixture of (1.6:1.0 v/v) anhydrous pyridine and deuterated chloroform was prepared and added to the sample. The cyclohexanol serves as an internal standard, and chromium (III) acetylacetonate is a relaxation reagent. Finally, 100  $\mu$ L of phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (TMDP)) was added to the mixture. Samples were analyzed in an Agilent DDR2 500 MHz NMR spectrometer, equipped with 7600AS, running VnmrJ 3.2A, a relaxation delay of 5 s, and 128 scans. The number of various hydroxyl groups was calculated based on the ratio of the area under the internal standard peak compared to the integrated areas attributed to various hydroxyl groups.

#### 2.2.2.4 Resin and Adhesive Preparation

Lignin-based resins were formulated by incrementally increasing the percentage of formaldehyde replacement with glyoxal from 0 to 100% (0, 20, 40, 60, 80, and 100%). Using the same procedure reported by Kalami et al.<sup>93</sup>, the molar ratio of lignin to formaldehyde or glyoxal or their combination was kept constant at 1:2 (two moles of aldehyde per one mole of the phenolic hydroxyl group in lignin) for all the resins. First, 25 g lignin was dissolved in 85 mL of 1M NaOH in a beaker and transferred to a 250 mL three-necked round bottom flask equipped with a thermometer, stir bar, and condenser. For maintaining a uniform temperature around the flask, a dry bath stacker was used. Then, the corresponding formaldehyde/glyoxal mixture was gradually added to the lignin solution. The temperature was increased steadily from room temperature to 65 °C in 30 min while stirring at 600 rpm using a digital hot-plate stirrer. Once the solution temperature reached 65 °C, it was kept at 65 °C for 30 min, after which 40 mL 1M NaOH solution was next added to the flask. Then the temperature was increased gradually to 90 °C,

where it was held constant for 2 h. The formulated resin was next cooled down to room temperature, and some of the resin was stored in a freezer to prevent further polymerization for adhesive preparation. The remaining resin was used to measure its chemical and physical properties.

The incremental replacement of formaldehyde with glyoxal was performed to investigate the changes in the properties of the formulated resins and evaluate the performance of biobased adhesives as the glyoxal amount was increased in the system. In addition, a series of ligninformaldehyde (LF) and lignin-glyoxal (LG) resins and adhesives with optimized formulations were prepared. The goal was to formulate lignin-based resins to have similar properties to a commercial phenol-formaldehyde resin. This was achieved by reducing the amount of the alkaline solution used to dissolve lignin initially, which resulted in lignin-based resins with closer pH and solid content to commercial PF resins. All formulated resins and adhesive properties and performance were measured and compared with commercially available phenol-formaldehyde resins and adhesives.

The developed resins were used to formulate lignin-based adhesives using the same procedure recommended for commercial phenol-formaldehyde glue mix by industry, as previously reported by Kalami et al.<sup>92</sup> First, 6.5% (all on the weight basis) wheat flour was dissolved in 18% of distilled water. Then 6.5% plywood extender (Modal) was added to the wheat flour mixture while stirring with a glass rod. Next, a combination of 3% NaOH and 66% thawed resin was added to the mixture and stirred for 5 min using a high-speed mixer at 800 rpm until it became homogeneous. Properties of the formulated resins and adhesives were determined according to recommended ASTM test methods and plywood standard test methods as described in detail below. These properties were tested in triplicates except solid content that was tested with five replicates.

# 2.2.2.5 Resin Molecular Weight Measurement

The molecular weights of optimized resins were determined, following the procedure described earlier for molecular weight analysis of lignin. The resins were also acetylated to enhance their solubility in THF before GPC analysis.

#### 2.2.2.6 Resin Solid Content

The solid content was measured with five replicates for each sample, according to ASTM D4426-01.<sup>183</sup> Briefly, 1 g of the resin was measured in each labeled pan and placed in an oven for 105 min at 125 °C. Next, samples were cooled to room temperature in a desiccator and weighed. The percent solid content was calculated by dividing the weight of oven-dried resin by the initial weight of the resin multiplied by 100.

#### 2.2.2.7 Resin pH, Viscosity, and Gelation Time

The pH of resin and adhesive was measured using a Mettler Toledo S220 digital pH meter at room temperature after stirring the samples for 10 s at 400 rpm. The rheology of the formulated resins was analyzed by a Discovery HR-1 hybrid rheometer (TA Instrument) with a 40 mm parallel plate geometry and 1000  $\mu$ m gap at 23 °C. The viscosity of resins and adhesives was determined at a constant shear rate of 1000 (s<sup>-1</sup>) using the rheometer.

A Brookfield Gel Timer was used as a special configuration of the Brookfield DV2T Viscometer to measure the gelation times of the commercial and optimized resins accurately. The gel timer was equipped with an adjustable stop, a glass rod, and a coupling assembly that uses the rotational method to measure gelation time. As the thermoset material begins curing, the required torque for turning the glass rod immersed in the sample shows a sudden increase. According to the manufacturer procedure, for measuring the gel time at 100 °C, 10 g of each resin was poured into a 50 mL beaker, and the beaker was placed in a boiling water bath. The water bath was positioned on a hot plate to keep the water temperature at 100 °C. Then the instrument was run at a fixed speed of 1 rpm to determine the gelation point at which the torque begins a rapid increase. After finding the required torque corresponding to the gel point, a new set of fresh samples were run to find the accurate time needed to reach the determined torque. This time was recorded automatically by the instrument and is considered as the gelation time. This test was repeated three times for each sample, and the gel time was recorded as the average of three recorded times.

#### 2.2.2.8 Resin Free Formaldehyde Content

The hydroxylamine hydrochloride method was used to determine the free formaldehyde content of the formulated resins following the European Standard DIN EN ISO 9397 test method.<sup>184</sup> When formaldehyde reacts with hydroxylamine hydrochloride, hydrochloric acid is formed. Then a potentiometric titration is used to determine the amount of produced hydrochloric acid. 5 g of resin was weighed and added to 100 mL distilled water to determine free formaldehyde content. Then, using 0.1 N HCl, the pH was adjusted to 4.0 while stirring the solution at 350 rpm. Then 20 mL of 10 wt.% hydroxylamine hydrochloride was added to the resin solution. After 5 min, the solution was titrated to a pH of 4.0 using 0.1 N NaOH solution. Then the percent free formaldehyde of each resin was calculated using Equation 2-1.

% Free Formaldehyde Content = 
$$\frac{V(NaOH) \times N(NaOH) \times 30.03}{w(g)} * 100$$
 Equation 2-1

V is NaOH volume (L), N is NaOH normality, 30.03 is the formaldehyde molecular weight, and w is the amount of resin (g).

#### 2.2.2.9 Resin Alkalinity

The alkalinity of the samples was measured according to the procedure recommended by Lorenz and Christiansen.<sup>185</sup> According to their procedure, different amounts of resin or adhesive (2 to 10 g), based on the expected amount of NaOH in the sample, were added to 100 mL distilled water. Then 0.1 N hydrochloric acid solution was used to titrate the solution to a pH of 3.5. The alkalinity measurement is based on the volume of hydrochloric acid and the amount of resin or adhesive used.

$$\% Alkalinity = \frac{V (HCl) \times N(HCl) \times 40}{w (g)} * 100$$
 Equation 2-2

V is HCl volume (L), N is HCl normality, 40 refers to NaOH molecular weight, and w is the amount of resin (g).

#### 2.2.2.10 Resin Water Resistance

Water resistance was evaluated by placing approximately 5 mL of resin in 3 aluminum dishes (5 mL each). Next, 0.5 g sawdust was mixed with the resin, and samples were cured in an oven for 1 h at 130 °C. Afterward, the cured samples were cooled. Each sample was submerged in a beaker containing about 100 mL of distilled water and was monitored visually for up to one week at room temperature.<sup>92</sup>

#### **2.2.2.11** Thermal and Thermomechanical Properties of Adhesives

The curing temperature of optimized resins was analyzed using a differential scanning calorimeter (DSC Q2500, TA Instrument). Resin samples were freeze-dried (Labconco Freezone 4.5) before being analyzed to remove any excess water. Next, about 13 mg of each freeze-dried sample was placed in a high-volume pan sealed with a lid. Each sample was then heated from room temperature to 250 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 10 mL/min.

The thermomechanical properties of the adhesives were measured using a TA Instruments dynamic mechanical analyzer (Q800) in dual cantilever mode under airflow. The scanning process was conducted from 50 to 175 °C using a fixed frequency of 1 Hz and a low heating rate of 3 °C/min to minimize the effect of thermal lag. The hardwood strips (60 mm × 13 mm × 0.6 mm) were oven-dried for 1 h at 105°C and then stored in a desiccator before the DMA test. A thin adhesive layer was placed between wood strips to prepare a specimen sandwich for each dynamic mechanical analysis (DMA). To maintain a balanced composite design, the wood strips in the specimen were matched for grain, thickness, and weight. 220-grit sandpaper was used to sand the bonding surfaces along the grain slightly, and a paper towel was used to clean the surfaces before applying adhesive. A uniform adhesive layer (115 g/m<sup>2</sup>) was applied to each wood strip. The specimens were assembled in short assembly times and wrapped in aluminum foil to retain moisture content during the analysis.

# 2.2.2.12 Adhesion Performance

Lap shear strength and percent wood failure tests were performed to determine the adhesion strength of the formulated adhesives. For measuring lap shear strength, 0.12 g of the

prepared adhesive was applied on one-fourth (25.4 x 25.4 mm<sup>2</sup>) of the Douglas-fir veneer samples (25.4 mm x 102 mm x 5.6 mm) according to ASTM D5868-01.<sup>186</sup> The single-lap joint samples were prepared using a digital hot press (Carver, Inc., Model 3895.4PL1000). By adjusting the temperature of the press plates and the required pressure, the automatic press instrument provides the necessary conditions for curing the adhesive between the veneer samples. Two veneers were pressed at 175 °C under 1400 kPa—pressure for 4 min following the recommended press parameters by the industry for commercial adhesives. An Instron 5565 Universal testing machine with a loading rate of 12.7 mm/min was used to measure the adhesion strength of developed adhesives. The adhesion strength was recorded as tensile strength at maximum load.

In addition to dry shear strength, the wet shear strength test was conducted following the PS 1-09 Structural Plywood standard<sup>187</sup> to evaluate the performance of the formulated adhesives when exposed to long-term moisture. In this test, single-lap-joint veneer samples are first soaked in boiling water for 4 h and placed in an oven at 65 °C for 20 h. Samples are then submerged in boiling water for another 4 h. Then the adhesion strength of samples was measured right after the second water immersion test (in boiling water) using an Instron machine.

The percent wood failure of all the lap shear samples was determined quantitatively with the image analysis method using ImageJ software.<sup>188</sup> The 100% wood failure means that adhesive performed so well that force only caused the wood to break (fail), not the adhesive layer. This analysis was conducted to determine the percentage of the veneer samples detached due to adhesive failure or wood failure. For this purpose, the photos of veneer samples were adjusted in Photoshop by cropping the area for analysis to specific dimensions of 19 × 19 mm<sup>2</sup>. Then the contrast and color were adjusted by first selecting "auto contrast" and then "auto-color" in the "image" tab. Using the "adjustment" tab under the "image" function, the brightness and contrast were set to 100. Next, images were saved as a tiff file for ImageJ analysis. In the ImageJ software, adjusted images were converted to binary. The percent area of dark sections in the results corresponds to adhesive failure percent. Next, the percent wood failure was calculated by subtracting the percent area from 100%.

# 2.3 Results and Discussion

### 2.3.1 Lignin Characterization

The measured structural and chemical properties of the corn stover lignin sample isolated from lignin cake in the lab are summarized in Table 2.1. These results show that the isolated lignin has a relatively low molecular weight, which in our previous work demonstrated an improved reactivity with formaldehyde relative to lignins with higher molecular weights.<sup>93</sup> Additionally, the relatively narrow molecular weight distribution leads to homogeneous resins with reproducible properties and high adhesion performance.<sup>93</sup>

The information acquired from <sup>31</sup>P NMR is needed to determine the total phenolic hydroxyl content of lignin accurately. This information is necessary to calculate the amount of formaldehyde/glyoxal needed for formulating resin with a 2:1 molar ratio of formaldehyde (or glyoxal) to lignin (based on its total phenolic OH content).

The reaction between formaldehyde or glyoxal occurs in the vacant *ortho* positions to the phenolic hydroxyl group within the lignin structure.<sup>96</sup> Therefore, lignin's phenolic units (corresponding to a lignin polymer chain end) with more vacant *ortho* positions have more active sites for the reaction with the aldehyde. For the preparation of lignin-based phenolic resins, aldehydes can only react with the *p*-hydroxyphenyl and guaiacyl units of lignin, which have two and one reactive sites, respectively. The presence of high content of *p*-hydroxyphenyl in the lignin will result in lignin-based phenolic resins with desirable properties since a *p*-hydroxyphenyl unit has double the number of reactive sites of a guaiacyl unit. The <sup>31</sup>P NMR results showed that the isolated lignin had a high *p*-hydroxyphenyl content (0.74 mmol/g) significantly higher than the average *p*-hydroxyphenyl content (0.18 mmol/g) of eight other commercial lignins recovered from various biomass processing methods utilizing hardwood, softwood, and annual crops analyzed in our previous study.<sup>93</sup> The higher number of reactive sites will increase the reactivity with aldehydes, making this lignin a desirable biopolymer for replacing phenol in the phenolic resin formulation.<sup>175</sup>

Techniques		Measured Lignin Properties	Range of Properties in the Previous Study <sup>93</sup>	
Ash Content (%)		0.57 ± 0.01	0.1 - 11.4	
GPC Analysis Results	囨 <sub>n</sub> (Da)	1,710 ± 20	1,300 – 2,400	
	М <sub>w</sub> (Da)	3,690 ± 25	3,100 - 9,350	
	PDI	2.2 ± 0. 1	2.3 - 4.0	
Hydroxyl Functional Groups of Lignin <sup>31</sup> P NMR Analysis Result (mmol/g)	Aliphatic Hydroxyl	2.24 ± 0.03	0.98 - 2.38	
	Syringyl	0.57 ± 0.02	0 - 2.40	
	Guaiacyl	0.75 ± 0.03	0.06 - 2.18	
	Condensed Phenolic	$0.18 \pm 0.02$	0.09 - 1.43	
	<i>p</i> -Hydroxyphenyl	0.74 ± 0.05	0.01 - 0.81	
	Carboxylic Acid	$1.19 \pm 0.02$	0.02 - 0.93	
	Total Phenolic	2.25 ± 0.08	0.16 - 4.16	
	Total Hydroxyl Content	5.68 ± 0.03	1.16 - 6.43	

Table 2.1. Measured lignin properties (average of three replicates ± standard deviation).

# 2.3.2 Resin Properties

Properties of formulated resins were analyzed, and several key findings can be highlighted (Figure 2.1). First, increasing glyoxal addition reduced the pH and alkalinity of the formulated resins (Figure 2.1A). This outcome is likely due to the side reaction of glyoxal in an alkaline medium, which is more prominent than formaldehyde's side reaction, leading to the production of glycolic acid and consequently decreasing both the alkalinity and pH.<sup>51</sup> Concurrently, increasing glyoxal substitution resulted in increased resin viscosity and solid content (Figure 2.1B). This trend has been observed in previous studies<sup>189</sup> and may be attributable to the decreasing pH reducing the solubility of unreacted lignin in the resin, resulting in increasing resin viscosity. Additionally, the higher solid content of glyoxal-containing resins is potentially due to the higher molecular weight of glyoxal than formaldehyde.



Figure 2.1. Measured properties of formulated resins as a function of glyoxal replacement of formaldehyde (average of at least 3 replicates ± standard deviation).

One of the crucial points in synthesizing phenolic resole resins is preventing the side reaction of aldehydes (Cannizzaro reaction). An aldehyde without an alpha-hydrogen undergoes a disproportionation reaction in an alkaline medium, resulting in alcohol and carboxylic acid formation.<sup>140</sup> Glyoxal, with two adjacent carbonyl groups, readily undergoes an intramolecular Cannizzaro reaction in an alkaline solution (Figure 2.2).<sup>51</sup> This reaction can occur even in mild alkaline conditions and forms glycolic acid.<sup>51</sup> Since the Cannizzaro reaction of glyoxal occurs on the same molecule and there is no need for two aldehyde molecules, the side reaction of glyoxal may be more likely to proceed than the formaldehyde side reaction. Also, the vicinity of the two carbonyl groups with partial positive charge makes glyoxal more prone to this side reaction. The produced glycolic acid decreases the pH of the resin. If the alkalinity of the resin is not appropriately controlled, the drop in pH will disrupt the electrophilic substitution reactions between lignin and glyoxal in the production of phenolic resole resins. Consequently, the pH of the reaction medium should be adjusted to favor the electrophilic substitution reaction in an alkaline medium. At the same time, high alkalinity will negatively impact the adhesion performance of the adhesive, especially in the presence of moisture.<sup>141</sup> To reiterate, alkalinity is the ability of a solution to neutralize acids and depends on the total number of anions present in the solution. In the resole resin solutions, aldehydes can also react with the catalyst (sodium hydroxide) and be converted to their conjugated bases (reducing the pH). In glyoxal-containing resins, a higher rate of Cannizzaro reaction leads to the production of glycolic acid, which can

consume hydroxyl ions and produce glycolate anions (Figure 2.2B).<sup>190</sup> Thus, controlling the pH in a glyoxal-based resin is crucial to ensure the reaction is happening in an alkaline condition.



Figure 2.2. Proposed mechanism for the Cannizzaro reaction of formaldehyde (A) and glyoxal (B).

# 2.3.3 Adhesive Properties and Performance

Viscosity, solid content, and pH of lignin-based adhesives were determined and are presented in Figure 2.3. Also, the adhesion performance of the formulated lignin-based adhesives was assessed by measuring the lap shear strength and analyzing the percent adhesive or wood failure.



Figure 2.3. Measured adhesive (glue-mix) properties as a function of glyoxal replacement of formaldehyde (n=3).

Figure 2.3 shows the measured properties of adhesives as formaldehyde was substituted by glyoxal. The key trends are that increasing glyoxal substitution increases the adhesive viscosity, increases the solid content, and decreases the pH. Previous studies had reported that when 50% (or less) of the phenol was substituted with lignin, the adhesive product exhibited comparable adhesion strength to commercial adhesives while lignin substitutions greater than 50% significantly dropped the adhesion strength.<sup>104,191</sup> Figure 2.4 illustrates the adhesion performance results for lignin-based adhesives in the present work. As formaldehyde was replaced by glyoxal, dry shear strength reduced from 3.4 to 2.6 MPa, and the percent wood failure decreased from 80% to 62% (shown in green symbols in Figure 2.4).



Figure 2.4. Adhesion performance of lignin-based adhesives as a function of glyoxal replacement of formaldehyde.

As Figure 2.4 illustrates, the adhesion performance of the lignin-glyoxal (LG) adhesive is considerably lower than the lignin-formaldehyde (LF) adhesive formulated in this study or previous studies.<sup>92,93</sup> These changes indicate the importance of controlling the resin synthesis pathway so that the resulting resins have optimal properties.

One of the most critical aspects of resin synthesis is adding the alkaline catalyst to the resin solution. The catalyst accelerates the reaction between the vacant *ortho* positions to the phenolic hydroxyl group of the lignin's aromatic rings and the aldehyde while maintaining the viscosity of the aqueous reaction mixture below the gelation point of resin until the completion of the resin synthesis. In the optimized resin formulations, by controlling the amount and concentration of sodium hydroxide, which acts both as the solvent for lignin and as the catalyst, the pH of the lignin-based resins was optimized to achieve lignin-based resins with similar properties and performance to commercial resins. This was achieved by dissolving lignin in the lowest amount of sodium hydroxide to produce resins with similar pH and solid content to the phenol-formaldehyde resin.

The formation of resole phenolic resins consists of three stages. In the first step, methylolphenol is formed by adding aldehyde to the phenolic ring. The next stage involves chain growth or condensation by joining phenolic rings and forming a prepolymer (Figure2.5). The last stage is the curing reaction or crosslinking that happens by applying heat.<sup>35</sup> The first two steps of the reaction, leading to the formation of a prepolymer, are pH and temperature-dependent. Temperatures below 60 °C and the pH range of 8-9 favor the addition reaction of aldehyde to the phenolic ring and formation of methylolphenols, while temperatures above 60 °C and the pH range of 9-11 benefit the condensation reaction of methylolphenols in which dimeric, trimeric, and higher oligomers are formed.<sup>7,35</sup> In different reaction conditions such as different pH, temperature, and aldehyde content, methylolphenols undergo different degrees of condensation.<sup>7</sup>



Figure 2.5. Formation of prepolymer based on the reaction of lignin precursor (phydroxyphenyl) with formaldehyde.<sup>192</sup>

In this study, the GPC analysis of lignin-formaldehyde and lignin-glyoxal resins following prepolymer formation (which coincides with the resin synthesis step), but prior to curing was

conducted to verify prepolymer formation with the appropriate degree of condensation. Acetylated samples were fully soluble in THF resin. Comparing the molecular weight properties of the optimized resins with the lignin used to synthesize these resins shows that both the  $\overline{M}_n$ and  $\overline{M}_w$  of the LF and LG resins are increased when the lignin is incorporated into the prepolymer (Table 2.2). The weight average molecular weight of the resins is almost three times greater than that of lignin and confirms the condensation reaction and prepolymer formation.

Sample	囨 <sub>n</sub> (Da)	M̄ <sub>w</sub> (Da)	PDI			
Lignin	1,710	3,690	2.2			
Lignin-Formaldehyde Resin	2,680	10,420	3.9			
Lignin-Glyoxal Resin	2,720	11,050	4.1			

Table 2.2. The molecular weight of lignin and lignin-containing prepolymer.

Table 2.3 summarizes the measured properties for optimized resins and adhesives.

Resin Properties								
Sample	Commercial PF	Optimized LF	Optimized LG					
рН	11.7 ± 0.1	$10.1 \pm 0.1$	9.8 ± 0.1					
Alkalinity (%)	6.7 ± 0.1	2.3 ± 0.2	3.6 ± 0.2					
Viscosity (mPa·s)	660	270	200					
Free Formaldehyde Content (%)	0.45 ± 0.02	$0.49 \pm 0.04$	0					
Solid Content (%)	44.3 ± 0.2	25.2 ± 0.2	30 ± 0.2					
Gelation Time (min)	8.4 ± 0.2	7.3 ± 0.2	7.7 ± 0.2					
Adhesive Properties								
Sample	Commercial PF	Optimized LF	Optimized LG					
рН	12.9 ± 0.1	12.7 ± 0.1	13.2 ± 0.2					
Viscosity (mPa·s)	460	1,300	960					
Free Formaldehyde Content (%)	0.22 ± 0.02	0.27 ± 0.04	0					
Solid Content (%)	43.8 ± 0.1	31.4 ± 0.2	38.3 ± 0.2					

Table 2.3. Properties of PF and lignin-containing prepolymer resins and adhesives (n=3).

Flow curves of the scanning shear rate of three different resins (LF, LG, and commercial PF) are illustrated in Figure 2.6. PF resin has relatively exhibited Newtonian behavior over the range of the shear rate at which the viscosity measurement (red, sort dash line) was conducted. On the other hand, the viscosity of the LF resin (blue, short dot line) gradually decreased with increasing shear rate, and shear thinning behavior was observed over the entire range of shear rates (Figure 2.6). For the LG resin, the decrease of viscosity (solid green line) at different shear rates was remarkably higher, which could be assigned to the dissociation of phenolic interaction and chain disentanglement.<sup>193,194</sup>



Figure 2.6. Rheological behavior of phenol-formaldehyde (PF), lignin-formaldehyde (LF), and lignin-glyoxal (LG) resins at different shear rates.

Differential scanning calorimetry (DSC) was used to determine the curing temperature of the resins, which can be used to determine the press parameters. Phenolic-based resins typically exhibit two exothermic peaks in their DSC spectra. The first peak occurs at a lower temperature due to the reaction between free formaldehyde and the phenolic ring, while the second peak that is more distinct indicates a crosslinking reaction during the curing process.<sup>195</sup> In this study, high-volume pressure sealed pan was used, which can suppress the liberation of water during the curing reaction due to its internal pressure capability. As a result, the DSC data shows a well-delineated exothermic peak that can be integrated to determine the heat released from the

curing reaction. The DSC analysis of the commercial PF and the optimized LF and LG adhesives showed that the peak cure temperature occurs in the temperature range of 140 to 170 °C (Figure 2.7 and Table 2.4). Based on DSC analysis results, PF and LF adhesives had relatively similar onset and peak curing temperatures (142°C and 146°C), while LG adhesive reached its peak at a significantly higher temperature (167 °C). A previous study has also reported that the ligninphenol-glyoxal resin had a higher cure temperature than PF resin.<sup>196</sup> Our results show that formaldehyde-based resins (PF and LF) had lower cure temperatures than glyoxal-based resin, which can be attributed to the higher reactivity of formaldehyde than glyoxal with phenol or lignin.<sup>196</sup> Additionally, the amount of heat generated during the curing reaction indirectly relates to the reactivity of the resin, from which we can conclude that LF and LG adhesives had similar reactivities, and their reactivities were significantly lower than that of PF adhesive as expected. This can be attributed to the fact that phenol provides more reactive sites than lignin in PF adhesives.<sup>136</sup> The curing rate is also determined by the difference between onset and peak curing temperatures. In this study, to ensure performance comparisons occur under identical conditions, the pressing temperature of 175 °C was applied during the curing of all samples used for adhesion analysis.



Figure 2.7. DSC-determined heat flow of the commercial phenol-formaldehyde, optimized lignin-formaldehyde, and optimized lignin-glyoxal adhesives.

Sample	Onset Temperature (°C)	Peak Temperature (°C)	Enthalpy (Normalized) (J/g)	ΔT (°C)
Commercial PF	111	142	133	31
Optimized LF	109	146	51	37
Optimized LG	130	167	45	37

Table 2.4. Curing properties of commercial phenol-formaldehyde (PF), optimized lignin-formaldehyde (LF), and optimized lignin-glyoxal (LG) adhesives.

To evaluate adhesive performance and efficacy of optimized formulations and curing processes, it is crucial to understand strength development and cure kinetics in wood-adhesive composites. DMA is an analytical tool used to evaluate polymer cure developments. A linear heating rate was used in this study to elucidate the vitrification events and determine the curing degree at the vitrification and endpoint of the curing process. The effects of temperature change on storage modulus (G') and tan  $\delta$  are depicted in Figures 2.8A and 2.8B, respectively. Figure 2.8A comprises three phases: thermal softening of the uncured wood-adhesive interface, adhesive curing, and thermal softening of the cured wood-adhesive system.<sup>197</sup> At room temperature, the adhesive layer becomes semi-solid after the liquid adhesives are applied to the dry wood surface. As the temperature rises, the adhesive-wood system gradually softens, and the G' decreases until a minimum G' plateau is reached, suggesting a competitive interaction between adhesive softening and curing.<sup>197</sup> With subsequent G' increase, the adhesive curing prevails over the softening. In this case, the onset of the mechanical cure is described as the rise in storage modulus G'min. The PF and LF adhesives begin mechanical curing at 112 °C and 117 °C, respectively, faster than LG adhesive, which begins curing at 123 °C. These results are consistent with the DSC data that shows PF and LF adhesives cure at lower temperatures than LG adhesive.


Figure 2.8. Storage modulus (A) and tan  $\delta$  (B) plots of the commercial phenol-formaldehyde, optimized lignin-formaldehyde, and optimized lignin-glyoxal adhesives.

The tan  $\delta$  peak can reveal key insights into the curing process in polymeric systems. In the tan  $\delta$  curve, the peak represents the vitrification point, which means the polymer reaches the glass transition temperature.<sup>198,199</sup> The peak also corresponds to the temperature at which the maximum rate of mechanical curing is achieved.<sup>200</sup>

Equation 2-3 can be used to determine the degree of mechanical cure ( $\beta$ ) at any time.<sup>201</sup> In this case, G' (t) is the storage modulus at time t.

$$\beta = \frac{G'(t) - G'(min)}{G'(max) - G'(min)}$$
 Equation 2-3

In Table 2.5, the adhesives' degree of cure is displayed at the vitrification point and the end of the curing process. All the adhesives exhibit almost the same degree of mechanical cure at the point of vitrification. However, at the end of the curing process, the curing degree for LF and LG adhesives (0.93 and 0.90) were higher than the PF adhesive (0.77). At the end of the curing process, PF may have a lower degree of curing due to more reactive sites in phenol than lignin for crosslinking. In other words, although there is more curing reaction for PF adhesive (based on the enthalpy difference determined by DSC analysis), relatively higher unreacted sites remain in the phenolic structure of phenol than in the phenolic structure of lignin in lignin-based adhesives. The DMA data shows that over 90% of the reactive sites in LF and LG adhesives are crossed-linked during the curing process in this study.

Table 2.5. Mechanical degree of cure for commercial phenol-formaldehyde (PF), optimized ligninformaldehyde (LF), and optimized lignin-glyoxal (LG) adhesives.

Sample	G' <sub>min</sub> (MPa)	G' <sub>max</sub> (MPa)	G' at the Vitrification point (MPa)	G' at the endpoint (MPa)	Degree of cure at the Vitrification point	Degree of cure at the endpoint
Commercial PF	832	1,831	1,056	1,600	0.22	0.77
Optimized LF	801	1,340	912	1,302	0.21	0.93
Optimized LG	603	1,150	737	1,096	0.24	0.90

After optimizing the resin synthesis parameters, the adhesion performance of lignin-glyoxal (LG) adhesive improved significantly. The results are shown in Figure 2.9, which illustrates the reduction in the performance gap between the LG and LF adhesives. The adhesion strength of the LG adhesive improved from 2.6 to 3.9 MPa after optimizing resin formulation, and the percent wood failure increased from 62% to 90%. The dry adhesion strength of the optimized LG adhesive was even greater than previously reported LF adhesives.<sup>92,93</sup>



Figure 2.9. Dry adhesion performance of phenol-formaldehyde (PF), optimized ligninformaldehyde (LF), and lignin-glyoxal (LG) adhesives.

Next, a water-resistance test was carried out as a quick evaluation of the formulated resin's performance in the presence of moisture. After the formulated lignin-glyoxal resin and sawdust mixture were immersed in water for one week, it remained intact and did not dissolve (Figure 2.10A). However, despite the acceptable performance of the LG adhesives in a dry environment

and good water-resistance test results, the LG adhesive could not successfully pass the wet shear strength test (boiling water test) related to adhesion performance in a wet environment. In this test, single-lap-joint veneer samples soaked in boiling water (Figure 2.10B) detached after the first 4 h of the boil test (Figure 2.10C). For this reason, these adhesives are recommended for interior wood products similar to soy-based adhesives.



Figure 2.10. Adhesion performance in a wet environment. Water-resistance test after one week (A), single-lap joint samples immersed in water (B), and single-lap joint samples detached after boiled water test (C).

Chapter 3 has been submitted as a journal paper in "ACS Sustainable Chemistry & Engineering" journal

#### CHAPTER 3:

# Advancing Wood Adhesive Sustainability: Unmodified Technical Lignins as Phenol Substitute

## 3.1 Introduction

Phenol-formaldehyde (PF) resins, developed in the early 20<sup>th</sup> century, represent a traditional and widely used class of synthetic polymers for wood adhesive applications. Their exceptional durability arises from strong wood affinity, high polymer strength, and remarkable adhesive stability. PF adhesives evidently achieve high levels of wood failure and resist delamination in numerous durability tests. While cost and cure time constraints might exist, PF adhesives effectively address the bonding needs of a wide range of wood species and products.<sup>5,6</sup>

PF adhesives rely on the controlled reaction of phenol with formaldehyde (or precursor) under specific conditions to generate a resin that undergoes further polymerization during the curing. Two key pre-polymer types exist: novolac (F/P ratio < 1, acidic synthesis) and resoles (F/P ratio > 1, basic synthesis). Despite similar starting materials, their distinct chemical pathways and resulting polymer structures lead to different properties. In wood adhesives, resoles are preferred due to their solubility, superior wood-wetting ability, and heat-activated curing, enabling efficient and convenient product assembly.<sup>5</sup>

Resole PF resins are typically synthesized using alkali hydroxides with an F/P ratio of 1.0-3.0 and a pH of 7-13 (Figure 3.1).<sup>5</sup> Key to their formation is the base-catalyzed reaction between phenol and formaldehyde. Unlike the slower oligomerization step, the initial phenol addition occurs rapidly, allowing higher F/P ratios without premature polymerization. This translates to controlled curing upon heat activation, facilitating efficient application in wood adhesives.<sup>5,6</sup>



Figure 3.1. The chemical reaction of phenol-formaldehyde resins.

Despite the long-standing use of PF resole resins attributed to their durability and exceptional water resistance, concerns persist regarding the toxicity of formaldehyde and the environmental impact associated with petroleum-derived phenol and formaldehyde, including non-renewability, as well as air and water pollution, and their carbon footprints. Addressing these concerns is viable by substituting phenol with a bio-based raw material possessing lower toxicity and cost, either fully or partially, and reducing formaldehyde usage. This represents a significant improvement in formulating eco-friendly wood adhesives.<sup>38</sup>

Lignin, the most abundant aromatic natural polymer, is an amorphous phenolic polymer found in vascular plants. It has a complex, branched structure composed of phenolic units, as shown in Figure 3.2.<sup>40,41,48</sup> Lignin is derived from three main monolignols—*p*-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S)—which form a complex, three-dimensional network within plant cell walls, as shown in Figure 3.2.<sup>42,43</sup> Lignin composition varies remarkably

across plant species,<sup>46</sup> and in addition to its source, the isolation process that separates lignin from biomass plays a significant role in shaping its characteristics.<sup>51</sup>



Figure 3.2. The complex structure of lignin contains various types of linkages.<sup>41</sup>

Lignin-based phenolic adhesives have been extensively studied as eco-friendly substitutes for conventional petroleum-derived phenolic resins. Lignin, which is abundant in nature and chemically similar to phenol, is considered as its renewable alternative. It has been shown that replacing phenol with lignin reduces toxicity and reduces the carbon foot-print of the resulting materials.<sup>46</sup>

Kalami et al. (our group's previous studies) replaced 100% of phenol with lignin in phenolic adhesive formulations by using nine different lignin samples. Notably, an enzymatic hydrolysis corn-stover lignin, although not widely accessible, exhibited comparable performance to PF resin in these studies. This performance was attributed to the enhanced reactivity of lignin, resulting from the source and isolation process, which provided more vacant ortho positions for the reaction with formaldehyde.<sup>92,93</sup>

Despite progress made, a major challenge in the field is the lack of studies utilizing commercially available lignins (technical lignins) for developing high-performance lignin-based phenolic resins that meet industrial application requirements. Enzymatic hydrolysis lignin, often used in many of the studies, is derived from lab or pilot-scale processes and has relatively high reactivity with formaldehyde.<sup>93</sup> However, its availability is limited due to dependence on biofuel production processes.<sup>51</sup> Commercially available lignins, such as kraft and organosolv lignins, offer more industrial-scale options. Kraft lignin, produced through sodium hydroxide and sodium sulfide treatment in the kraft pulping process, is available in large quantities and has been used to partially (20-60%) replace phenol.<sup>52,53</sup> Organosolv lignin, generated using organic solvents like ethanol, is sulfur-free with higher purity, making it ideal for applications requiring higher purities.<sup>65,67,68</sup> Focusing on commercial lignins, even for partial substitution, is essential to bridge the gap between research and practical application. To address this issue, further investigation is needed to develop lignin-based phenolic resins using commercially available lignin and ensure that the resin formulation obtained is suitable for large-scale adhesive manufacturing, and wood panel productions.

This study represents the use of two unmodified commercially available lignin samples, Kraft softwood (K-SW), and organosolv wheat straw (O-WS) to develop lignin-based phenolic resins in close collaboration with industry partners. The innovation lies in adhering to industry standards, ensuring the formulations can be scaled up effectively. The goal was to replace at least 80% of phenol with lignin in the resin formulation, with significant efforts focused on optimizing resin and adhesive formulations and curing conditions to align with these standards while meeting the required performance.

# 3.2 Materials and Methods

#### 3.2.1 Materials

Fortum and West Fraser graciously supplied the O-WS and K-SW lignin samples. The properties of lignin were assessed following the outlined procedures and measured in triplicate. A commercial phenol-formaldehyde resin was generously provided by an adhesive producer. Phenol (99.5% pure), formaldehyde (37 wt. % in water), and other necessary reagents were obtained from Sigma-Aldrich and Fisher Scientific, Inc. and used without further modification.

#### 3.2.2 Methods

#### 3.2.2.1 Ash Content of Lignin

The ash content of lignin was assessed following the TAPPI-T 211 om-93 test method.<sup>180</sup> Initially, ceramic crucibles were dried and weighed. Subsequently, 2 g of oven-dried lignin was added to each crucible (in triplicate). The samples were then subjected to a muffle furnace (Thermolyne Furnatrol) and heated to 525 °C at a rate of 5 °C/min. After 4 h, the samples were cooled to 100 °C and transferred to a desiccator. Once at room temperature, the samples were weighed, and the ash mass fraction was calculated by dividing the weight of ash by the weight of oven-dried lignin.

#### 3.2.2.2 Lignin Molecular Weight Measurement

Gel permeation chromatography (GPC) was employed to determine the number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), and polydispersity index (PDI) of the lignin samples. To ensure solubility in tetrahydrofuran (THF), each sample was subjected to acetylation.<sup>181</sup> This involved adding 1 g of lignin to a 40 mL solution consisting of a mixture of pyridine (20 mL) and acetic anhydride (20 mL), followed by stirring at room temperature for 24 h. Acetylated lignin was then precipitated using 0.1 M HCl, separated via vacuum filtration, and washed three times with a low-concentration hydrochloric acid solution (0.05 M) and deionized water. Subsequently, the acetylated sample was dried for 16 h in a vacuum oven at 40 °C.<sup>181</sup> Next, the acetylated sample was dissolved in HPLC grade THF at a concentration of 5 mg/mL, filtered using a syringe filter (PTFE, 0.45 µm), and subjected to GPC analysis. A Waters GPC system (Waters e2695 Separation Module) equipped with three 300 mm × 7.8 mm Waters columns in

series was utilized, including Styragel HR 4 THF, Styragel HR 3 THF, and Ultrastyragel THF. Calibration standards of monodisperse polystyrene (162, 370, 580, 945, 1440, 1920, 3090, 4730, 6320, 9590, 10,400, and 16,200 Da) were used. The instrument injected 25  $\mu$ L of the filtrate solution, and detection was carried out using a 2414 refractive index detector, consistently maintained at the same temperature as the columns (35 °C). Data was collected and analyzed using Empower GPC Software.

#### 3.2.2.3 Lignin Hydroxyl Content

The phenolic and aliphatic hydroxyl content of lignin samples were assessed through <sup>31</sup>P NMR, following a protocol adapted from Asgari and Argyropoulos.<sup>182</sup> In this method, a solution was prepared by combining 325  $\mu$ L of anhydrous pyridine/deuterated chloroform (in a 1.6:1 v/v ratio) with 300  $\mu$ L of anhydrous dimethylformamide (DMF). Next, 40 mg of oven-dried lignin was dissolved in this solution. To this mixture, 100  $\mu$ L of cyclohexanol (22 mg/mL concentration in anhydrous pyridine and deuterated chloroform, 1.6:1.0 v/v ratio) was added, serving as an internal standard. Additionally, 50  $\mu$ L of chromium (III) acetylacetonate solution (5.6 mg/mL concentration in a mixture of anhydrous pyridine and deuterated chloroform, 1.6:1.0 v/v ratio) was included, acting as a relaxation reagent. Finally, 100  $\mu$ L of the phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, TMDP) was added. The samples were then analyzed using an Agilent DDR2 500 MHz NMR spectrometer with 7600AS, running VnmrJ 3.2A, employing a relaxation delay of 5 s and 128 scans. Quantification of various hydroxyl groups relied on the ratio of the area under the internal standard peak relative to the integrated areas attributed to the different hydroxyl groups.

#### 3.2.2.4 Resin and Adhesive Preparation

Lignin-based resins were developed by substituting 80% of phenol with lignin samples, following a previously reported procedure with slight modifications.<sup>38</sup> The molar ratio of the phenol plus lignin to formaldehyde remained constant at 1:3 (three moles of formaldehyde per one mole of the phenolic hydroxyl group of lignin plus phenol) for all resins. Initially, a solution containing 100 g of lignin and phenol (80 g lignin and 20 g phenol) and 10% Sodium Carbonate (10 g Na<sub>2</sub>CO<sub>3</sub> when 100 g lignin and phenol were used) was prepared by dissolving them in a

minimal amount of 10% (Wt.%) NaOH in a beaker. This solution was transferred to a 1000 mL three-necked round bottom flask equipped with a thermometer, stir bar, and condenser. A dry bath stacker was used to maintain a uniform temperature. Then the temperature increased steadily from room temperature to 65 °C for over 30 min while stirring at 600 rpm using a digital hot-plate stirrer. Once the solution reached 65 °C, formaldehyde was subsequently added gradually to the phenolic solution. Then it was held at this temperature for 30 min, after which half of the original amount of 10% (Wt.%) NaOH solution was added to the flask. The temperature was then gradually increased to 90 °C and maintained for 2 h. The formulated resin was cooled to room temperature, using an ice bath, with a portion stored in a freezer to prevent further polymerization for adhesive preparation. The remaining resin was used to assess its chemical and physical properties.

The developed resins were used in formulating lignin-based adhesives, following the procedure recommended for commercial phenol-formaldehyde glue mixes in industry, as outlined by Yang et al.<sup>202</sup>, with adjustments to suit lignin-based formulations (Table 3.1). The properties of both the formulated resins and adhesives were evaluated using ASTM test methods and plywood standard test methods, following detailed descriptions provided below. These properties were tested in triplicate, except for solid content with five replicates.

Formulation Contents	Weight %
Resin	33.5
water	17
Mix for 30 seconds, at 800 rpm*	
Modal (Alder bark)	5
Extender (High protein wheat flour)	6.5
Sodium Carbonate	0.5
Mix for 5 mins, at 1500 rpm*	
Sodium Hydroxide (50% Wt.%)	3
Mix for 10 mins, at 1500 rpm*	
Resin	34.5
Mix for 2 mins, at 1500 rpm*	

Table 3.1. Step-by-step procedure for preparing lignin-based adhesive.

\*Using overhead high-speed mixture for homogenous mixing.

#### 3.2.2.5 pH and Viscosity Measurement

The pH of resins and adhesives was assessed at room temperature using a Mettler Toledo S220 digital pH meter after stirring the samples for 10 seconds at 400 rpm.<sup>38</sup> The viscosity of the formulated resins was examined using a Discovery HR-1 hybrid rheometer (TA Instruments) equipped with a 40 mm parallel plate geometry and a 1000  $\mu$ m gap, operating at 23 °C. The adhesive's viscosity was assessed at a consistent temperature of 40 °C using a Brookfield DV2T digital viscometer and employing a 40 mm stainless steel plate. The viscosity of both resins and adhesives was determined under a constant shear rate of 1000 (s<sup>-1</sup>).<sup>38</sup>

#### 3.2.2.6 Tack Measurement

Tack measurements were conducted in three replicates using a TA Instruments HR-1 rheometer, following a procedure previously outlined by Wang et al.<sup>203</sup>, with some modifications. A parallel plate configuration was utilized, with both top and bottom plates set at a constant diameter of 40 mm and made from stainless steel. After the resins were applied to the bottom plate, the experiment commenced with a compression phase (closing step), during which the top plate descended at a constant rate until reaching a predetermined gap (600  $\mu$ m); it then transitioned to an opening step, where the top plate ascended, creating a tensile force. The experiment was conducted at 25°C, with a probe velocity of 5  $\mu$ m/s.

#### 3.2.2.7 Free Formaldehyde Content

The free formaldehyde content of the formulated resins was determined using the hydroxylamine hydrochloride method, which is in accordance with the European Standard ISO 9397 test method.<sup>184</sup> When formaldehyde reacts with hydroxylamine hydrochloride, hydrochloric acid is generated. A potentiometric titration method was employed to quantify the produced hydrochloric acid. Initially, 5 g of resin was weighed and added to 100 mL of distilled water to assess the free formaldehyde content. Subsequently, the pH of the solution was adjusted to 4.0 while stirring at 350 rpm using 0.1 N HCl. Next, 20 mL of 10 wt. % hydroxylamine hydrochloride was introduced into the resin solution. After 5 min, the solution was titrated to a pH of 4.0 using 0.1 N NaOH solution. The percentage of free formaldehyde in each resin was calculated using Equation 3-1, where V represents the volume of NaOH (in liters), N denotes the

normality of NaOH, 30.03 signifies the molecular weight of formaldehyde, and w indicates the amount of resin (in grams).

% Free Formaldehyde Content = 
$$\frac{V(NaOH) \times N(NaOH) \times 30.03}{w(g)} * 100$$
 Equation 3-1

## 3.2.2.8 Alkalinity

The alkalinity of the samples was assessed following the protocol recommended by Lorenz and Christiansen.<sup>185</sup> As per their methodology, varying amounts of resin or adhesive (ranging from 2 to 10 g), depending on the anticipated quantity of NaOH in the sample, were added to 100 mL of distilled water. Subsequently, a 0.1 N hydrochloric acid solution was employed to titrate the solution to a pH of 3.5. The determination of alkalinity relies on both the volume of hydrochloric acid used and the quantity of resin or adhesive added, as indicated by Equation 3-2, where V represents the volume of HCl (in liters), N denotes the normality of HCl, 40 denotes the molecular weight of NaOH, and w indicates the amount of resin (in grams).

% Alkalinity = 
$$\frac{V(HCl) \times N(HCl) \times 40}{w(g)} * 100$$
 Equation 3-2

#### **3.2.2.9** Thermal and Thermomechanical Properties of Adhesives

The thermomechanical properties of the adhesives were evaluated using a TA Instruments dynamic mechanical analyzer (Q800) operating in dual cantilever mode under airflow conditions. The scanning procedure ranged from 50 to 175 °C, employing a fixed frequency of 1 Hz and a low heating rate of 3 °C/min to mitigate thermal lag effects. Hardwood strips (measuring 60 mm × 13 mm × 0.6 mm) were oven-dried for 1 h at 105 °C and stored in a desiccator before undergoing dynamic mechanical analysis (DMA). A thin adhesive layer was applied between the wood strips to create a sandwich specimen for each DMA test. To ensure a balanced composite design, the wood strips in the specimen were matched for grain, thickness, and weight. The bonding surfaces were lightly sanded along the grain using 220-grit sandpaper and subsequently cleaned with a paper towel prior to adhesive application. An even adhesive layer (115 g/m2) was applied to each wood strip. The specimens were assembled swiftly and enclosed in aluminum foil to maintain moisture content during analysis.

#### 3.2.2.10 Adhesion Performance

To evaluate the adhesion strength of the formulated adhesives, lap shear strength tests and wood failure percentage assessments were carried out. For the lap shear strength test, a specific amount of adhesive, 0.10 g per square inch, was uniformly spread on Douglas fir veneer samples. Subsequently, three-layer plywood samples were constructed using a digital hot press (Carver, Inc., Model 3895.4PL1000). The samples were then sectioned to create test specimens as illustrated in Figure 3.3, adhering to a standard test method (PS 1-09 Structural plywood).<sup>187</sup> The digital hot press allowed for precise control over the temperature of the press plates and the pressure applied, ensuring that the adhesive was cured under optimal conditions. These conditions were set based on industry-recommended parameters for commercial adhesives, as detailed in the following. The adhesive was applied evenly onto the veneer samples, ensuring thorough coverage. The samples were then allowed to stack for 10 min to facilitate initial penetration into the wood. Following stacking, they were subjected to cold pressing at 165 psi for 5 min. After cold pressing, a resting period of 30 min was carried out while the press plates were preheated to a temperature of 177°C. Once the desired temperature was reached, hot pressing was initiated at 177°C for a duration of 3 to 11 min under a pressure of 200 psi. Following hot pressing, a post-cure was conducted without press for a maximum of 30 seconds to finalize the bonding process. This meticulous procedure ensured optimal adhesion and bonding strength between the veneer samples. The strength of the adhesive bond was measured using an Instron 5565 Universal testing machine, which operated at a crosshead speed of 12.7 mm/min. The maximum tensile strength achieved by the adhesive was recorded. Additionally, the percentage of wood failure was visually determined for each specimen to gauge the extent of wood substrate failure at the adhesive joint.



Figure 3.3. The test specimen for measuring the adhesion strength.

# 3.3 Results and Discussion

# 3.3.1 Lignin Characterization

Table 3.2 provides an overview of the structural and chemical characteristics of commercially available K-SW and O-WS lignin samples. Previous research suggests that lignin samples with lower molecular weights exhibit superior performance in adhesion tests when integrated into lignin-based phenolic adhesives.<sup>93</sup> This advantage stems from their reduced steric hindrance and increased availability of reactive sites for formaldehyde reaction.<sup>93</sup> Moreover, lower molecular weight lignin samples allow for a more progressed condensation step during resin synthesis without gelation, thereby contributing to enhanced final adhesion strength.<sup>93</sup>

The variations in lignin properties that are identified through analysis, can influence the final adhesion strength. These variations are derived from lignin source and isolation method. O-WS lignin sample shows a lower molecular weight profile than the K-SW lignin which can enhance its reactivity with formaldehyde. Alternatively, the higher concentration of sodium in K-SW lignin is believed to facilitate the formation of a chelate ring involving alcohol, phenolic hydroxyl groups, and sodium during the condensation step. This chelate ring promotes the development of phenolic prepolymer in the resin system (Figure 3.4).<sup>4</sup>



Figure 3.4. Formation of a chelate ring involving alcohol, phenolic hydroxyl groups, and sodium during the condensation step.

Building upon this insight, which confirms the positive effect of sodium ions on facilitating the condensation step and enhancing final adhesion performance, a certain quantity of sodium ions (as sodium carbonate) was included during the resin synthesis, as earlier detailed in the resin preparation section.

The reaction between formaldehyde takes place at the vacant ortho positions adjacent to the phenolic hydroxyl group within the lignin structure. Therefore, phenolic units in lignin with more vacant ortho positions provide more active sites for the formaldehyde reaction. In preparing lignin-based phenolic resins, formaldehyde can only react with the *p*-hydroxyphenyl and guaiacyl units of lignin, which possess two and one reactive sites, respectively.<sup>96</sup>

The results from <sup>31</sup>P NMR analysis (Table 3.2) offer insights into the functional groups present in the lignin samples. According to the <sup>31</sup>P NMR analysis, O-WS lignin exhibits a higher *p*hydroxyphenyl content (0.32 mmol/g) than K-SW lignin (0.13 mmol/g). However, the guaiacyl units in K-SW lignin (1.92 mmol/g) are significantly higher than in O-WS lignin (0.74 mmol/g). Despite O-WS lignin having a higher concentration of *p*-hydroxyphenyl units with two reactive sites, the greater abundance of guaiacyl units in K-SW lignin ensures a higher availability of reactive sites for the formaldehyde reaction, suggesting an enhanced performance.

Techniques		K-SW lignin	O-WS lignin	
Ash Content (%)		0.55 ± 0.22	0.22 ± 0.08	
	₩n (Da)	1,650	1,580	
GPC Analysis	₩w (Da)	7,650	6,240	
Nesuits	PDI	4.6	4	
	Aliphatic Hydroxyl	1.71	1.82	
	Syringyl	-	0.54	
Hydroxyl Functional	Guaiacyl	1.92	0.74	
Groups of Lignin	Condensed Phenolic	1.20	0.13	
<sup>31</sup> P NMR Analysis	<i>p</i> -Hydroxyphenyl	0.13	0.32	
Result (mmol/g)	Carboxylic Acid	0.41	0.35	
	Total Phenolic	3.25	1.73	
	Total Hydroxyl Content	5.37	3.90	
	N	4,700	13,200	
	S	18,200	1,600	
	Р	100	140	
	К	200	220	
	Mg	0	40	
Elemental Analysis	Са	100	500	
Results (nnm)	Na	1,600	100	
nesures (ppm)	В	6	6	
	Zn	4	2	
	Mn	8	1	
	Fe	19	140	
	Cu	2	9	
	Al	28	30	

Table 3.2. Measured lignin properties.

## 3.3.2 Resin Characterization

In this study, the properties and performance of an industry formulated phenolic resin were evaluated as reference to ensure that the characteristics of the developed lignin-based resins comply with industry requirements. Substituting phenol with lignin in phenolic resin formulations presents several challenges. One major obstacle is that while phenol melts at 40°C, lignin requires a solvent (typically sodium hydroxide) for dissolution. Consequently, adding the solvent reduces the solid content of the final resin, resulting in higher water content in the resin system. This necessitates an increased hot curing duration to evaporate excess water, leading to additional costs for industry. Simultaneously, careful consideration is required when adjusting the catalyst concentration to minimize solvent usage, as industry guidelines often restrict the use of phenolic resins (not adhesives) with pH values exceeding 12-13 due to potential corrosivity issues. Furthermore, elevated pH and alkalinity can promote the Cannizzaro reaction of formaldehyde.<sup>141</sup> High alkalinity also detrimentally affects adhesive adhesion performance, particularly in the presence of moisture.<sup>141</sup>

Another challenge stems from lignin having fewer reactive sites than phenol (maximum of 2 available ortho sites in *p*-hydroxyphenyl compared to 3 reactive sites in phenol), resulting in lower reactivity. This not only adversely impacts the adhesion of the final adhesive but could also increases the presence of unreacted formaldehyde in the resin, which is considered carcinogenic.<sup>176</sup> Additionally, the higher molecular weight of lignin, as a naturally occurring polymer compared to phenol, not only limits its reaction with formaldehyde but also affects the condensation process, as lignin-based phenolic resins may reach the gelation point during this step.<sup>204</sup> These limitations necessitate meticulous resin synthesis and optimal utilization of materials and catalysts to mitigate synthesis constraints and ensure that the lignin-based phenolic resins possesses properties comparable to commercial PF resins.

Table 3.3 presents a summary of the measured properties of a commercial PF resin and lignin-based resins formulated by substituting 80% of the phenol with lignin on a weight basis (LP20F: 80% lignin/20% phenol and formaldehyde). In this investigation, a 10% (wt.%) concentration of sodium hydroxide was employed for resin synthesis. The higher catalyst concentration reduces solvent usage and increases the solid content. It also helps achieve pH and alkalinity values closer to those of commercial PF resin.

Moreover, a critical aspect of synthesizing phenolic resole resins involves preventing the side reaction of formaldehyde, known as the Cannizzaro reaction, during formaldehyde addition into the phenolic ring (addition step). In an alkaline environment, an aldehyde lacking  $\alpha$  hydrogen can undergo a disproportionation reaction, leading to the formation of alcohol and carboxylic acid.<sup>140</sup> In this study , formaldehyde was gradually introduced to the reaction mixture to

minimize the Cannizzaro reaction during the addition step. Moreover, during the condensation step, using elevated temperature in combination with a high concentration of alkaline catalyst increased the Cannizzaro reaction, which resulted in reducing the amount of free formaldehyde content of the final lignin-based resins, which was one of the major goals of this study. It is important to note that despite using a molar ratio of formaldehyde to phenolic hydroxyl groups of lignin 1:3, we still used 63-70 % less formaldehyde, on weight basis, compared to PF resin.

	Resin Properties		
Sample	Commercial PF	K-SW (LP20F)	O-WS (LP20F)
Lignin Content (%)	0	80	80
Phenol Content (%)	100	20	20
Formaldehyde (37%) Content Based on 100 g Resin	58.7	21.9	17.7
рН	12.0 ± 0.1	12.3 ± 0.1	12.2 ± 0.1
Alkalinity (%)	$5.1 \pm 0.1$	5.6 ± 0.1	$5.4 \pm 0.1$
Viscosity (MPa.s)	640 ± 10	950 ± 20	860 ± 15
Free Formaldehyde Content (%)	0.17 ± 0.02	0.36 ± 0.04	0.36 ± 0.05
Solid Content (%)	42.3 ± 0.1	32.1 ± 0.1	33.0 ± 0.1

Table 3.3. Properties of PF and lignin-containing prepolymer resins.

The tack test was utilized in this study to compare the adhesion properties of commercial PF and lignin-based resins before curing by measuring the initial adhesion strength that occurs immediately upon contact. This initial adhesion is crucial in determining the feasibility of adhesive to hold veneers or strands in place when the wood veneers are lifted to be placed in the hot press. This is particularly evident in plywood manufacturing processes, where adhesive-coated wood veneers are pre-pressed before being transferred to a hot press for final curing. A poor tack can cause the veneers to shift, preventing them from holding secure before the hot pressing step, which negatively affects the material flow and curing properties due to excessive water evaporation.<sup>193,205</sup>

Figure 3.5 presents the tack data for commercial PF and lignin-based resins. The assessment of tackiness was conducted by determining the maximum tensile force required for detachment, which is defined as the highest absolute force measured during separation. The tack value for PF resin (0.32  $\pm$  0.04 N) was significantly lower than lignin-based resins (1.83  $\pm$  0.15 N for K-SW LP20F, and 1.29  $\pm$  0.02 N for O-WS LP20F). These results confirm the advantage of using lignin, which is the natural glue in the wood to replace petrochemical phenol in wood adhesives.



Figure 3.5. Tack measurements for commercial PF, K-SW LP20, and O-WS LP20F resins.

#### 3.3.3 Adhesive Characterization

Comprehending strength development and cure kinetics in wood-adhesive composites is essential to assess the adhesive performance and efficacy of lignin-based formulations and curing processes. In this investigation, dynamic mechanical analysis (DMA) was used in triplicate for each adhesive formulation to minimize the influence of wood variations and evaluate polymer cure progress. Employing a linear heating rate, this study aimed to elucidate vitrification events and determine the curing degree at both vitrification and the endpoint of the curing process. The impact of temperature variation on the storage modulus (G') and tan  $\delta$  is illustrated in Figure 3.6A and Figure 3.6B, respectively. Figure 3.6A delineates three phases: initial thermal softening of the uncured wood-adhesive interface, adhesive curing, and subsequent thermal softening of the cured wood-adhesive system.<sup>197</sup> Once applied to the dry wood surface, the adhesive layer transitions to a semi-solid state at ambient temperature. As temperature increases, the adhesive-wood system progressively softens, decreasing in G' until reaching a minimum plateau, indicative of a competitive interaction between adhesive softening and curing. Subsequent G' elevation suggests the dominance of adhesive curing over softening, with the onset of mechanical cure described by increased storage modulus G'<sub>min</sub>.<sup>197</sup> Mechanical curing commences for the PF adhesive at 108 °C, exhibiting a faster rate than the K-SW and O-WS LP20F adhesives, which initiate curing at 118 and 117 °C, respectively.

The tan  $\delta$  peak offers valuable insights into the curing dynamics of polymeric systems. Within the tan  $\delta$  curve, this peak signifies the vitrification point, indicating when the polymer reaches its glass transition temperature.<sup>198,199</sup> Moreover, this peak corresponds to the temperature at which the mechanical curing rate reaches its maximum.<sup>200</sup> Equation 3-3 can be utilized to determine the degree of mechanical cure ( $\beta$ ) at any given time.<sup>201</sup>

$$\beta = \frac{G'(t) - G'(min)}{G'(max) - G'(min)}$$
 Equation 3-3

Where G'(t) is the storage modulus at time t.

Table 3.4 presents the degree of cure for adhesives at both the vitrification point and the endpoint of the curing process.

Sample	T at the Beginning of Mechanical Curing Point (°C)	T at the Vitrification point (°C)	Degree of cure at the Vitrification point (%)	Degree of cure at the endpoint (%)
Commercial PF	108 ± 1	119 ± 2	19 ± 2	56 ± 1
K-SW LP20F	118 ± 1	130 ± 1	25 ± 2	76 ± 3
O-WS LP20F	117 ± 3	128 ± 2	22 ± 2	76 ± 2

Table 3.4. Mechanical Degree of Cure for Commercial PF, K-SW LP20F, and O-WS LP20F adhesives.



Figure 3.6. Storage modulus (A) and tan  $\delta$  (B) plots of the commercial PF, K-SW LP20F, and O-WS LP20F adhesives.

While the difference in the mechanical curing degree between commercial and lignin-based adhesives is not notably distinct at the vitrification stage, it becomes more apparent by the end of the curing process. At this stage, the curing degrees for lignin-based adhesive were higher (76%) than PF adhesive (56%). This difference in curing degree at the end of the process for PF adhesive could be attributed to the presence of more reactive sites in phenol compared to lignin for cross-linking. In simpler terms, although PF adhesive exhibits a higher curing reaction, relatively more unreacted sites persist in the phenol's phenolic structure than lignin. DMA data further indicates that over 75% of the reactive sites in lignin-based adhesives undergo crosslinking during the curing process in this study.

Table 3.5 outlines the properties of commercial PF and lignin-based adhesives. The data indicates that the solid content of lignin-based adhesives is lower than that of commercial PF

adhesives. Although the difference in solid content between the commercial and lignin-based adhesives is smaller than the resins, it remains significant. This suggests the need for an extended curing time, as indicated by the performance data provided in the subsequent sections. In addition, although the free formaldehyde content for lignin-based adhesives is higher than that of commercial PF, it remains below 1 wt.%, which is the maximum concentration for industrial use.<sup>206</sup>

	Adhesive Propertie	S	
Sample	Commercial PF	K-SW LP20F	O-WS LP20F
рН	$13.2 \pm 0.1$	$13.5 \pm 0.1$	$13.4 \pm 0.1$
Viscosity (MPa.s)	1,650 ± 14	1,730 ± 25	1,870 ± 22
Free Formaldehyde Content (%)	0.11 ± 0.03	$0.21 \pm 0.04$	0.23 ± 0.03
Solid Content (%)	42.3 ± 0.1	35.3 ± 0.1	35.9 ± 0.1

Table 3.5. Properties of PF and lignin-containing prepolymer adhesives.

In this study, adhesion strength and percent wood failure in dry and wet conditions were evaluated to ensure that the performance of the formulated lignin-based adhesives is comparable to that of commercial PF adhesives and meets the criteria set by plywood associations. The curing conditions for the three-layer plywood samples were also ensured to be identical in terms of curing temperature and pressure so that the formulations could be scaled up for industry-scale applications. The hot curing time was extended as needed to meet 85% of wood failure in wet conditions, which is the minimum requirement set for phenolic wood adhesives for exterior applications.<sup>187</sup>

Table 3.6 and Figure 3.7 illustrate the adhesion characteristics of both commercial and lignin-based adhesives across various hot curing durations. The dry and wet adhesion strengths for commercial PF adhesive stand at 1.8 and 1.2 MPa, respectively, comparable to K-SW adhesive (1.5 and 0.9 MPa) and O-WS LP20F adhesive (2.0 and 1.3 MPa). Notably, commercial PF adhesives demonstrated 100% wood failure in both dry and wet conditions, while K-SW and O-WS LP20F adhesives achieves the minimum acceptable wet wood failure percentage of 85% after 5 and 7 min of hot curing, respectively. Even with just 3 min of hot curing, all commercial and lignin-based

adhesives exhibited satisfactory performance in dry conditions, making them suitable for interior grade plywood. However, for exterior use, where robustness in wet conditions is essential, commercial PF adhesive outperformed others after 3 min of hot curing. This advantage is attributed to the lower solid content of lignin-based adhesives, necessitating prolonged hot curing durations, and their possession of fewer reactive sites for crosslinking, especially in the para position, resulting in less crosslinking crucial for acceptable wet performance.

Table 3.6. Percent wood failure in dry and wet environment for commercial PF and lignin-based formulation under various hot curing times.

Adhesive Performance							
Sample	Commercial PF	K-SW LP20F O-WS LP20F		OF			
Hot Curing time (min)	3	3	5	7	3	5	7
Dry Wood Failure (%)	100	100	100	100	85	100	100
Wet Wood Failure (%)	100	80	90	100	60	70	90



Figure 3.7. Adhesion strength in dry and wet environment for commercial PF and lignin-based formulation under various hot curing times.



Figure 3.8. Wood failure (A) and adhesive failure (B) in wet environment.

# Chapter 4 has been submitted as a journal paper in "Green Chemistry" journal

#### CHAPTER 4:

# A Fundamental Study of Lignin Reactions with Formaldehyde and Glyoxal 4.1 Introduction

Adhesives have played a pivotal role in enhancing the efficient utilization of wood resources.<sup>1</sup> A wood adhesive can interact with the wood's surface through physical and/or chemical bonding. This interaction effectively transfers stresses between bonded components, ensuring the adhesive creates strong bonds with wood without detachment or rupture.<sup>2</sup> The rising demand for wood-based composites has driven research to develop advanced adhesives. Formaldehyde-based adhesives, categorized as thermosetting polymers, have significantly contributed to the advancement and utilization of various wood-based products.<sup>207</sup> The widespread use of these adhesives in the wood industry can be attributed to their ability to create enduring and robust bonds with wood.<sup>4</sup>

Phenol-formaldehyde polymers, developed in the early 20th century, are among the earliest synthetic polymers.<sup>7,46</sup> Their widespread use in laminations and composites is due to their exceptional durability, resulting from strong adhesion to wood, robust polymer strength, and chemical stability.<sup>24</sup> PF adhesives meet most wood bonding needs when cost and hot curing time are not primary concerns.<sup>5,6</sup> These adhesives are synthesized by reacting phenol with formaldehyde or a formaldehyde precursor under specific conditions, resulting in a resin that can further polymerize during the setting phase. There are two primary categories of pre-polymers: novolacs produced under acidic conditions, with a formaldehyde/phenol (F/P) ratio below 1, and resole resins, produced under basic conditions with F/P ratios above 1.<sup>208</sup> In wood adhesive applications, resole resins are preferred due to their solubility, excellent wood penetration, and ability to delay curing until activated by heat, allowing ample time for assembly.<sup>5</sup>

Resole resins are produced using alkali hydroxides, a F/P ratio of 1-3, and a pH between 7-13. In basic conditions, formaldehyde adds to phenol quickly, but hydroxymethyl derivatives transform into oligomers slowly. This allows higher formaldehyde concentrations without forming the final polymer until sufficient heat is applied during press time.<sup>5,6</sup>

Although resole resins are widely used for their durability and excellent water resistance properties, concerns are raised due to the toxicity of phenol and formaldehyde and the fact that both are derived from petrochemicals.<sup>209,210</sup> Addressing these challenges can be achieved by replacing the raw materials with renewable alternatives. In our previous study<sup>38</sup>, we used two bio-based raw materials with lower toxicity than phenol and formaldehyde and developed a fully bio-based adhesive using lignin and glyoxal. This study focuses on investigating the reactions of lignin with formaldehyde and glyoxal in liquid and solid cured resins.

Lignin is the most abundant natural aromatic biopolymer, polymerized and synthesized from three hydroxycinnamyl alcohol monomers: *p*-coumaryl alcohol (H), coniferyl alcohol (G), and sinapyl alcohol (S).<sup>211–214</sup> This results in a disordered, three-dimensional polymer network coexisting with various polysaccharides within the secondary plant cell wall.<sup>215–219</sup> Lignin composition varies among plant species, tissues, and cell type.<sup>220–223</sup> Ecological factors like tree age, climate, nutrients, and sunlight influence this diversity.<sup>44,45</sup> Hardwood lignin mainly contains G and S units, with few H units. Softwood lignin is primarily G units with fewer H units.<sup>220,224</sup> Annual crops have similar levels of G and S units and a higher proportion of H units than softwoods and hardwoods.<sup>220,225,226</sup>

Glyoxal, a non-toxic aldehyde with two neighboring aldehyde groups, is recognized for its non-volatility and biodegradability, making it a promising formaldehyde substitute in phenolic adhesives.<sup>38</sup> Glyoxal is known to have much lower toxicity compared to formaldehyde.<sup>51</sup> Formaldehyde is classified as a carcinogen, mutagen, and reprotoxic substance by the European Chemicals Agency (ECHA) and has an LD<sub>50</sub> value ranging from 500 to 800 mg/kg<sup>176</sup>, significantly lower than glyoxal, which has an LD<sub>50</sub> between 2960 and 8979 mg/kg.<sup>177</sup> Glyoxal is typically found in a 40 wt.% aqueous solution and naturally exists in many foods.<sup>51,76,127</sup> It acts as a cross-linker or precursor in paper, textiles, and leather applications.<sup>51,76,127</sup> Glyoxal's water solubility allows it to equilibrate between mono- and di-hydrated states and form dimers and small oligomers through reversible condensation, depending on concentration.<sup>51</sup>

While lignin and glyoxal may initially seem similar active functional groups to phenol and formaldehyde, they have significant differences. Lignin is solid, requiring a solvent for dissolution,

and has lower reactivity due to its complex structure and significantly fewer reactive sites than phenol. In addition, glyoxal is less reactive and more prone to side reactions than formaldehyde.<sup>38</sup> These differences significantly impact resin synthesis and properties.<sup>38</sup> Therefore, a comprehensive structural investigation of the resulting resins using advanced analytical techniques is essential to better understand the reaction of lignin with glyoxal, compared with the reaction of lignin with formaldehyde.

The synthesis of alkali-catalyzed resole PF resin involves a two-stage reaction. Initially, phenolate/enolate intermediates form, creating resonance-stabilized ions with high negative charge density at the 2-, 4-, and 6-positions of phenol. Subsequently, methylol formation occurs through the nucleophilic attack of the anion on the formaldehyde carbonyl. In the second stage, increased temperature causes resoles to condense, forming methylene bridges through a quinone methide intermediate.<sup>192</sup>

A key difference between lignin and phenol in producing phenolic adhesives is lignin's side chain at the para position of the phenolic hydroxyl group, hindering methylol or methylene bridge formation. This prevents reactions at the para position, which is usually more reactive than the ortho sites.<sup>4</sup> Furthermore, the replacement of formaldehyde with glyoxal brings changes in the resulting compounds. During the methylolation process, formaldehyde is introduced into an alkaline lignin solution, leading to three distinct reactions, as depicted in Figure 4.1. The primary reaction involves the Lederer–Manasse reaction, where hydroxymethyl groups (–CH<sub>2</sub>OH) become part of the C5 position of the aromatic rings in lignin.<sup>138</sup> However, concurrent side reactions may take place, such as Cannizzaro reaction in which two formaldehyde molecules react together, resulting in the formation of formic acid and methanol. Another side reaction, known as the Tollens reaction, replaces lignin's side chains with aliphatic methylol groups.<sup>51</sup> Glyoxalation involves introducing glyoxal into lignin's ortho positions, glyoxal's Cannizzaro reaction, and substituting glyoxal at lignin's side chains.<sup>51,139</sup>



Figure 4.1. Reactions occurring during methylolation (left) and glyoxalation (right) of Lignin. (a) Linder-Manasse reaction, (b) Self-Cannizzaro reaction, (c) Tollen's reaction.<sup>51</sup>

A crucial element in the synthesis of phenolic resole resins involves the prevention of aldehyde side reactions, with a particular focus on avoiding the Cannizzaro reaction. Aldehydes that lack an alpha hydrogen tend to undergo a disproportionation reaction in an alkaline setting, forming alcohol and carboxylic acid compounds.<sup>140</sup> Glyoxal, with its two neighboring carbonyl groups, readily undergoes an intramolecular Cannizzaro reaction in an alkaline solution, as depicted in Figure 4.2b.<sup>51</sup> This reaction can occur even under relatively mild alkaline conditions, leading to the production of glycolic acid.<sup>51</sup> Since glyoxal can undergo the Cannizzaro reaction within a single molecule without the need for two aldehyde molecules, the potential for glyoxal's side reaction exceeds that of formaldehyde. Additionally, the proximity of the two carbonyl groups with partial positive charges makes glyoxal more susceptible to this side reaction.<sup>38</sup> The production of glycolic acid leads to a decline in the resin's pH level.<sup>38</sup> If the resin's alkalinity is not properly controlled, this pH decrease can interfere with the electrophilic substitution reactions between lignin and glyoxal during the synthesis of phenolic resole resin. Conversely, excessive alkalinity can adversely affect the adhesive's adhesion performance, especially when exposed to moisture. Therefore, it becomes crucial to control the pH of the reaction media to achieve optimal properties.<sup>141</sup>





Despite extensive research aimed at elucidating the reaction mechanism of lignin with formaldehyde and glyoxal, particularly formaldehyde, there is a gap in the systematic investigation into the reactions of lignin and its monomers with formaldehyde and glyoxal, especially post-curing (solid resin).

This study aimed to investigate the reaction mechanisms of commercial kraft softwood lignin with formaldehyde and glyoxal to determine the potential formation of methylene and glyoxylene linkages during the reaction. For this purpose, phenol-formaldehyde and phenolglyoxal resins were synthesized, and phenol was substituted with commercial lignin. Formaldehyde and glyoxal resins were also prepared using H and G lignin monomers as intermediate models between phenol and lignin to provide insights into lignin's behavior. The analysis was planned for all three monomers. However, due to the very low solubility of syringyl (S) monomers, even at high solvent concentrations, the study focused on H and G monomers. Liquid and solid-state NMR, along with Fourier-transform infrared (FT-IR), were employed to examine the reactions of phenol, H and G lignin monomers, and commercial K-SW lignin with <sup>13</sup>Cformaldehyde and glyoxal in resole resins. As the majority of methylene and glyoxylene linkages were formed after curing and due to the low solubility of cured resins in organic solvents, solidstate NMR was used to address this challenge.

# 4.2 Materials and Methods

#### 4.2.1 Materials

Ingevity generously supplied the kraft softwood (K-SW) lignin (Indulin-AT) sample. Glyoxal (40 wt.% in water), <sup>13</sup>C-formaldehyde, standard formaldehyde (37 wt.% in water), and all additional reagents were procured from Sigma-Aldrich and Fisher Scientific, Inc., and utilized without further modification.

## 4.2.2 Methods

#### 4.2.2.1 Ash Content of Lignin

The ash content of lignin was assessed following the TAPPI-T 211 om-93 test method.<sup>180</sup> Ceramic crucibles were dried and weighed. Then two grams of oven-dried lignin were added to each crucible (in triplicate). The samples were heated in a muffle furnace to 525 °C at a rate of 5 °C/min. After 4 hours, the samples were cooled to 100 °C and transferred to a desiccator. Once at room temperature, the samples were weighed, and the ash mass fraction was calculated by dividing the weight of the ash by the weight of the oven-dried lignin.

#### 4.2.2.2 Lignin Molecular Weight Measurement

The number average molecular weight (M<sub>n</sub>), weight average molecular weight (M<sub>w</sub>), and polydispersity index (PDI) of the lignin sample were determined using gel permeation chromatography (GPC). To ensure solubility in tetrahydrofuran (THF), lignin samples were acetylated.<sup>182</sup> This process involved adding 1 g of lignin to a 40 mL mixture of pyridine (20 mL) and acetic anhydride (20 mL), and stirring at room temperature for 24 hours. The acetylated lignin was precipitated with 0.1 M HCl, separated by vacuum filtration, and washed three times with 0.05 M HCl and deionized water. The sample was then dried in a vacuum oven at 40 °C for 16 hours.<sup>182</sup> The acetylated sample was dissolved in HPLC grade THF (5 mg/mL), filtered through

a PTFE syringe filter (0.45  $\mu$ m), and analyzed by GPC. The GPC system (Waters e2695 Separation Module) was equipped with Styragel HR 4 THF, Styragel HR 3 THF, and Ultrastyragel THF columns. Calibration standards of monodisperse polystyrene (162-16,200 Da) were used. The instrument injected 25  $\mu$ L of the filtrate, and detection was performed with a 2414 refractive index detector at 35 °C. Data were analyzed using Empower GPC Software.

#### 4.2.2.3 Lignin Hydroxyl Content

The determination of the phenolic and aliphatic hydroxyl content in K-SW lignin involved using <sup>31</sup>P NMR, following the method outlined by Asgari and Argyropoulos<sup>182</sup> with some modifications. A solution was prepared by combining 325 µL of anhydrous pyridine/deuterated chloroform (1.6:1 v/v) and 300 µL of anhydrous dimethylformamide (DMF). Subsequently, 40 mg of oven-dried lignin was dissolved in the solution. To this mixture, 100 µL of cyclohexanol (22 mg/mL in anhydrous pyridine and deuterated chloroform at a ratio of 1.6:1.0 v/v) was added, followed by the addition of 50 µL of chromium (III) acetylacetonate solution (5.6 mg/mL concentration in the mixture of 1.6:1.0 v/v anhydrous pyridine and deuterated chloroform). Cyclohexanol served as the internal standard, and chromium (III) acetylacetonate functioned as a relaxation reagent. Finally, 100 µL of the phosphitylating reagent (2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane or TMDP) was introduced to the mixture. The samples were analyzed using an Agilent DDR2 500 MHz NMR spectrometer with 7600AS, running VnmrJ 3.2A, a relaxation delay of 5 s, and 128 scans. Various hydroxyl groups were calculated based on the ratio of the area under the internal standard peak to the integrated areas corresponding to different hydroxyl groups.

#### 4.2.2.4 Solution NMR Spectroscopy

<sup>13</sup>C NMR and <sup>1</sup>H–<sup>13</sup>C-gradient heteronuclear single-quantum coherence (HSQC) spectra were recorded at room temperature on a 600 MHz Bruker NMR spectrometer equipped with a 5 mm iProbe. For the NMR experiments, 100 mg of the sample (based on the dry weight of the resin or raw materials) was dissolved in 600 microliters of deuterated dimethyl sulfoxide (d-DMSO), followed by the addition of 2.5 mg of chromium (III) acetylacetonate as the relaxation

agent. In the <sup>13</sup>C NMR test, 100 microliters of a standard solution (1,3,5 trioxane in d-DMSO at 100 mg/mL) were also added.

#### 4.2.2.5 Solid-State NMR

Cured resins were packed into Magic-Angle Spinning (MAS) rotors for measurements on 400 MHz (9.4 Tesla) Bruker Avance Neo spectrometer using a 3.2 mm HCN MAS probe. All experiments were collected under 15 kHz MAS at 298 K unless otherwise stated. <sup>13</sup>C chemical shifts were referenced to the tetramethyl silane (TMS) scale and externally referenced to the methyl C<sub> $\delta$ </sub> of a model peptide N-formyl-Met-Leu-Phe-OH (MLF) at 14.0 ppm. The radiofrequency field strengths were 83.3 kHz for <sup>1</sup>H decoupling, 62.5 kHz for <sup>1</sup>H cross-polarization (CP) contact pulse, and 50–62.5 kHz for <sup>13</sup>C. The analysis and plotting of NMR data were conducted using TopSpin, Microsoft Excel, OriginPro, and Adobe Illustrator.

#### 4.2.2.6 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR was employed to record the spectrum of each oven-dried raw material or cured sample. A Perkin Elmer Spectrum II was utilized in attenuated total reflectance (ATR) mode, covering a wavenumber range of 4000-400 cm<sup>-1</sup>, with a resolution set at 4 cm<sup>-1</sup>, and a total of 64 scans.

#### 4.2.2.7 Resin Preparation

The formulation of lignin-based resins followed a slightly modified procedure as outlined by Siahkamari et al.<sup>38</sup> The consistent molar ratio of total phenolic content to formaldehyde or glyoxal was maintained at 1:2, signifying two moles of aldehyde per one mole of the phenolic hydroxyl group in lignin, lignin monomers, or phenol, across all resin variations. Initially, 0.5 g of phenolic material (including Phenol, lignin monomers, or lignin) was dissolved in 2 mL of 1 M NaOH (or 2 M NaOH for glyoxal). The temperature was then set at 65 °C using a water bath, lasting for 60 min with continuous stirring at 600 rpm using a digital hot-plate stirrer. Subsequently, 1 M NaOH solution (or 1 mL of 2 M NaOH for glyoxal) was added to the vial, followed by an increase in temperature to 90 °C, maintained for 2 hours. The resulting resin was then cooled to room temperature and stored in a freezer to prevent further polymerization.

# 4.3 Results and Discussion

# 4.3.1 Lignin Characterization

Table 4.1 summarizes the chemical characteristics of commercially available K-SW lignin. Data from <sup>31</sup>P NMR analysis is essential for determining the total phenolic hydroxyl content of lignin. The <sup>31</sup>P NMR method is employed following the reactions of hydroxyl groups in lignin, which provides a precise way to quantify different hydroxyl groups by using phosphorus-containing reagents.<sup>182</sup> This information calculates the amount of formaldehyde or glyoxal needed to achieve a 2:1 molar ratio with lignin, based on its phenolic OH content. Formaldehyde (or glyoxal) reacts at the ortho positions adjacent to the phenolic hydroxyl group in lignin. Phenolic units with more vacant ortho positions offer more active sites for this reaction. In this case, the aldehyde reacts with *p*-hydroxyphenyl and guaiacyl units, which have two and one reactive sites, respectively.<sup>96</sup> According to <sup>31</sup>P NMR analysis, K-SW lignin contains 0.27 mmol/g of *p*-hydroxyphenyl and 1.76 mmol/g of guaiacyl units, making it suitable for reactions with formaldehyde and glyoxal.

Tecl	K-SW lignin		
Ash Content (%)		4.34 ± 0.22	
	Мี <sub>п</sub> (Da)	1,900	
GPC Analysis Results	М <sub>w</sub> (Da)	6,230	
	PDI	3.3	
	Aliphatic Hydroxyl	1.98	
	Syringyl	-	
	Guaiacyl	1.76	
of Lignin	Condensed Phenolic	1.24	
<sup>31</sup> P NMR Analysis Result	<i>p</i> -Hydroxyphenyl	0.27	
(mmol/g)	Carboxylic Acid	0.39	
	Total Phenolic	5.25	
	Total Hydroxyl Content	5.64	

Table 4.1. Measured ligh	iin proj	perties.
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## 4.3.2 Characterization of Formaldehyde Resins

In the synthesis of resole resin, methylolphenols are formed through the Lederer–Manasse reaction (Figure 4.3a), which involves aromatic hydroxylation, attaching a -CH<sub>2</sub>OH group to a phenolic ring.<sup>227</sup> These methylolphenols can self-condense, creating binuclear or polynuclear oligomers by forming methylene bridges between aromatic rings. When phenol reacts with *o*-methylolphenols (I), it primarily forms ortho-ortho (III) intermediates, while *p*-methylolphenols produce ortho-para (IV) and para-para (V) dimers (Figure 4.3b and c). These reactions increase molecular weight, leading to branching and crosslinking in thermosetting resins. To avoid solidification, the reaction is halted by cooling, yielding resole resin with low polymerization. This intermediate remains soluble in alkaline conditions and needs heating to complete curing.<sup>228</sup>



Figure 4.3. Reaction of Phenol with formaldehyde. Ortho and para-Methylolphenols formation (I and II) (a), Ortho-ortho methylene linkage formation (III) (b), ortho-para and para-para methylene linkage formation (IV and V) (c). Here, linkages coming from formaldehyde are represented in red color, and labeled carbons are brown circles.

In resole resin synthesis, the condensation step is the rate-limiting step, so the reaction rate is initially slow for further oligomer reactions. However, at elevated temperatures (>100°C), hydroxymethylphenols (compound VI) react with unreacted phenols to continue polymerization, as shown in Figure 4.4a.<sup>229</sup> Alternative pathways include combining two hydroxymethyl groups
to form a dibenzyl ether linkage (Ar-CH<sub>2</sub>-O-CH<sub>2</sub>-Ar), depicted in Figure 4.4b (VIII). Phenolic hydroxyl groups can also form Ar-O-CH<sub>2</sub>-Ar ethers with hydroxymethyl groups (Figure 4.4c) (IX). Additionally, methylene linkages can react with formaldehyde to yield bis(hydroxymethyl)phenol (X), as shown in Figure 4.4d. Formic acid, a principal product of the self-Cannizzaro reaction, can react with hydroxymethyl and phenolic hydroxyl groups to produce formate esters XI and XII, as illustrated in Figure 4.4e.



Figure 4.4. Different condensation reactions of PF resin. (a) Formation of tetramer (VII) from dimer (VII); (b) Formation of dibenzyl ether through two CH<sub>2</sub>OH (VIII); (c) Formation of phenyl benzyl ether (IX); (d) Reaction of methylene linkage with formaldehyde forms compound X; (e) Formation of formate esters.

The PF resin, synthesized using <sup>13</sup>C-formaldehyde, was analyzed using <sup>13</sup>C-NMR experiments to confirm the successful incorporation of formaldehyde into the phenolic ring and the development of desirable linkages. <sup>13</sup>C-formaldehyde was utilized in the synthesis because <sup>13</sup>C is a naturally less abundant isotope (about 1.1% of carbon). Using <sup>13</sup>C-labeled formaldehyde increases the sensitivity and detection capability of the NMR experiment for the carbon atoms in formaldehyde. Additionally, <sup>13</sup>C-labeling allows precise tracking of the formaldehyde carbon throughout the chemical reactions, providing detailed insights into reaction mechanisms and product formation.<sup>230</sup>

In Figure 4.5a, the presence of CH<sub>2</sub>OH groups was identified by peaks ranging from 61-64 ppm, referenced by TMS.<sup>231</sup> At temperatures below 100°C, minimal methylene linkages were formed, shown around 34 ppm in the liquid PF resin spectra. Conversely, the crosslinked PF resin,

which was obtained after curing for 30 minutes at 130 °C, exhibited significantly increased methylene linkages (Figure 4.5b). Additional peaks at 155 ppm and 170 ppm correspond to phenolic carbon 1 and carbonyl carbon, respectively.<sup>80,232</sup> The carbonyl peak is attributed to the self-Cannizzaro reaction of formaldehyde (Figure 4.7d).<sup>232</sup> Furthermore, the formation of the directly bonded proton with the carbon is revealed by HSQC experiments. Particularly the aliphatic -CH<sub>2</sub>- protons have completely different chemical shifts from aromatic protons. In Figure 4.8, the <sup>1</sup>H peak at 3.7 ppm correlates with methylene linkages at 35 ppm, while methylol (CH<sub>2</sub>OH) protons appear around 4.5 ppm.<sup>233</sup> Additionally, proton peaks at approximately 5-8 ppm are associated with aromatic carbons.



Figure 4.5. Comparison of liquid <sup>13</sup>C NMR spectra of liquid PF resin with the <sup>13</sup>C-CP MAS spectra of cured PF resin (CH<sub>2</sub>OH at 63.2 ppm and methylene linkage at 34.7 ppm) (a) Dimer fragment of the polymeric cured PF resin which consist of both CH<sub>2</sub>OH group and methylene linkage. (b) (Conversion of CH<sub>2</sub>OH to CH<sub>2</sub> is identified by blue circles).

When the 1D solution <sup>13</sup>C-NMR spectra was compared with the <sup>13</sup>C-CP MAS spectra, a significant change after curing was observed. A decrease in intensity at 64 ppm and an increase at 34 ppm indicated the crucial role of curing in resin synthesis. The dominance of the band around 34 ppm suggested that most methylol groups participated in condensation to form methylene linkages.

Before delving into commercial lignin, the reaction of lignin monomers with formaldehyde was studied using both liquid and solid-state NMR techniques (Figure 4.6). The reaction of H-monomer and G-monomer with formaldehyde resulted in adducts similar to PF resin which

indicated CH<sub>2</sub>OH, methylene linkages, ether, and formate ester formation. Peaks at approximately 63 ppm and 34 ppm indicated CH<sub>2</sub>OH and CH<sub>2</sub> linkages, respectively.<sup>80,231,233</sup> For further verifications, HSQC spectra of HF and GF resins were acquired (Figure 8 b and c).



Figure 4.6. Comparison between the liquid NMR of liquid formaldehyde resins with solid state NMR of cured formaldehyde resins. NMR spectra of HF liquid resin (blue) and cured HF resin (purple) (Chemical shifts of CH<sub>2</sub>OH and methylene linkage are respectively 63.3 ppm and 34.3 ppm) (a); Dimer form of cured HF resin(b); NMR spectra of GF liquid resin (pink) and cured GF resin (brown) (Chemical shifts of CH<sub>2</sub>OH and methylene linkage are respectively 62.9 ppm and 34.5 ppm) (c); Dimer form of cured GF resin (d).(Methylene linkages in dimers are represented in dark blue color with yellow circle representing <sup>13</sup>C labeled formaldehyde carbon).

The analysis of PF resin, along with the structural similarities observed in HF and GF resins, suggests that similar linkage information applies to lignin-formaldehyde (LF) resin (Figure 4.7a). The limited availability of reactive sites in commercial lignin, compared to lignin monomers, significantly reduces the possibility of reactions.<sup>24</sup> In a liquid medium, the predominant reaction pathway is the self-Cannizzaro reaction of formaldehyde, producing peaks at 172 ppm (carbonyl) and 50 ppm (CH<sub>3</sub>OH).<sup>80,232</sup> The self-Cannizzaro reaction, depicted in Figure 4.7d, involves one unit oxidized to form formic acid (172 ppm) and another reduced to form a CH<sub>3</sub>OH group (50 ppm) (detailed mechanism depicted in Figure 4.2a).<sup>232</sup> However, after curing, <sup>13</sup>C-CP MAS analysis of cured LF resin shows a significant increase in peaks at 64.7 ppm to that at 64.7 ppm reveals an approximately sixfold increase in methylene linkage formation after curing (Figure 4.7c). The peak around 172 ppm indicates the potential formation of formate ester with CH<sub>2</sub>OH groups.<sup>234</sup>



Figure 4.7. Comparison between <sup>13</sup>C NMR spectra of lignin with the liquid LF resin, which shows self-Cannizaro reaction of formaldehyde that form formic acid (172 ppm) and methanol (50 ppm) (a); Comparison of liquid NMR of liquid LF resin (green) with <sup>13</sup>C-CP MAS NMR spectra of cured LF resin (orange) (CH<sub>2</sub>OH at 64.7 ppm and methylene linkage at 34.5 ppm) (missing of methanol peak at 50 ppm) (b); Table of relative intensity study of Figure (b) with respect to CH<sub>2</sub>OH band (as it is the primary product of addition reaction) (c); Self-Cannizaro reaction of formaldehyde which for formic acid (172 ppm) and methanol (50 ppm), which ultimately form methyl formate(d).



Figure 4.8. HSQC spectra of formaldehyde resins. PF resin with  $C_{aro}$ ,  $CH_2OH$  and  $CH_2$  peaks(a). HF resin(b) and GF resin (c) have similar peaks. LF resin has two major peaks of formate ester and CH<sub>3</sub>OH, along with CH<sub>2</sub>OH (d).

### 4.3.3 Characterization of Glyoxal Resins

In the reaction between lignin and glyoxal, various condensates can be produced. Therefore, simple phenol was used as a model compound to identify possible reactions and products before investigating lignin monomers and commercially available K-SW lignin. When phenol reacts with glyoxal in an alkaline environment, it initially forms compound XIV (depicted in Figure 4.9b) through the addition step.<sup>51,235</sup> This addition occurs at the ortho or para positions, with -CH(OH)-CHO being added to either position. For simplicity, compound XIV is illustrated as an ortho-substituted intermediate. This ortho-substituted compound then undergoes a further Cannizzaro reaction with another glyoxal unit, yielding compound XV and oxidized glyoxal (XVI) (Figure 4.9b).<sup>51,235</sup> Following glyoxalation, further condensation by unreacted phenolic units leads to the formation of compound XVII (Figure 4.9c).<sup>51,235</sup>

In contrast to formaldehyde, glyoxal can undergo a self-Cannizzaro reaction to produce glycolic acid (Figure 4.9a). Even under mild basic conditions, glyoxal readily converts into glycolic acid.<sup>38</sup> This transformation influences the structure of Phenol-glyoxal (PG) resin, similar to what was reported previously by Ramires et al.<sup>236,237</sup> through <sup>31</sup>P, <sup>1</sup>H, and <sup>13</sup>C NMR techniques. They detected residual glycolic acid and glycolic ester derivatives in PG resin samples. Their findings showed that the glycolic enol ester derivative (XXI) (depicted in Figure 4.9d) forms through the

esterification of residual glycolic acid with the enolate structure of compound XX, created via keto-enol tautomerism. Additionally, the glycolic enol ester is stabilized through hydrogen bonding, resulting in a six-membered ring, as illustrated in Figure 4.9d.



Figure 4.9. Reaction of phenol and glyoxal. Self-Cannizaro reaction of glyoxal forms glycolic acid (XI) (a); Ortho substitution of phenol forms -CH(OH)-CHO (XII) and -CH(OH)-CH2OH (XIII) (b). Also oxidized form of glyoxal (XIV); Formation of dibenzyl derivative with CHCH<sub>2</sub>OH (XV) (c); Formation of compound XVIII and compound XIX (enol ester) (d). Compound XIX is stabilized by hydrogen bonding.

The reaction between lignin and glyoxal is more complex than that of LF resin. Functional groups potentially associated with condensates are evident in the <sup>13</sup>C CP-MAS NMR spectra of glyoxylated lignin. In Figure 4.10a, the CH<sub>2</sub>OH group in PG resin is indicated by a peak at approximately 61.9 ppm<sup>132,235,238</sup>, with an additional band around 73.2 ppm, signifying the presence of the CHOH group.<sup>130</sup> Furthermore, a notable band between 180-190 ppm is linked to the formation of a quinone-stabilized structure and glyoxylate, which results from the self-Cannizzaro reaction of glyoxal in a basic environment.<sup>236</sup>



Figure 4.10. Comparison of liquid <sup>13</sup>C NMR spectra of liquid PG resin with the <sup>13</sup>C-CP MAS spectra of cured PG resin (CH<sub>2</sub>OH at 61.9 ppm and methylene linkage at 34.9 ppm) (a), Dimer fragment of the polymeric cured PG resin which consist of both CH<sub>2</sub>OH group and methylene linkage(b).

In HG resin (Figure 4.11a and b), the peak at 62.2 ppm corresponds to CH<sub>2</sub>OH,<sup>132,235,238</sup> and an additional band at 71.5 ppm indicates the presence of CHOH groups.<sup>130</sup> The range of peaks from 62-72 ppm is attributed to CH<sub>2</sub>OH and CHOH groups due to structural complexities. After curing, there is a significant increase in peaks at 71.5 ppm (CHOH) and 32.4 ppm (CH<sub>2</sub>), suggesting further progress toward condensation reaction.<sup>235</sup> In the HSQC of HG resin (Figure 4.12b), a <sup>1</sup>H peak around 3.8 ppm correlates with <sup>13</sup>C peaks between 60-70 ppm, representing CH<sub>2</sub>OH and CHOH groups.<sup>236</sup> Furthermore, the 8.3 ppm peak correlates with 178 ppm, indicating the presence of glyoxylate.<sup>236</sup>

In the cured GG resin (Figure 4.11 c and d), a broad band around 37.2 ppm confirms the formation of CH<sub>2</sub> linkages, while the band at approximately 71.6 ppm indicates CHOH groups.<sup>235</sup> The hindered ortho positions, evidenced by the sharp OCH<sub>3</sub> band at 54.1 ppm in the 1D CP-MAS spectra (Figure 4.11c), result in a lower rate of condensation in GG resin.<sup>239–241</sup> Additionally, the peak at 182.2 ppm signifies the carbonyl carbon of quinone formed before glyoxalation. Another band around 175-177 ppm suggests glyoxylate ester formation in both cured HG and GG resin.<sup>236</sup> Moreover, the significant increase in the intensity of the peaks at 71.6 ppm and 32-35 ppm indicates condensation and CH<sub>2</sub> linkage formation, along with CHOH groups.<sup>235</sup> The HSQC spectra of GG resin (Figure 4.12c) exhibit a peak at 3.8 ppm, which signify the presence of CH<sub>2</sub>OH which has a <sup>13</sup>C chemical shift near about 63 ppm.<sup>236</sup>

The broad peak spanning 171-184 ppm indicates glyoxal and lignin oxidation, potentially leading to various linkages (Figure 4.11 b, d, and f). The <sup>13</sup>C CP-MAS spectra of cured LG resin (Figure 4.11e) appears broader due to the complex linkages formed by the reaction of lignin with glyoxal. After curing, CH<sub>2</sub> linkage formation results in a band in the 30-40 ppm region, while a band around 62-75 ppm depicts CHOH and CH<sub>2</sub>OH groups.<sup>235</sup> Similar to GG resin, LG resin shows a distinct OCH<sub>3</sub> peak at approximately 55 ppm.<sup>131,242</sup>



Figure 4.11. Comparison of the liquid NMR of liquid glyoxal resin with the solid NMR of cured glyoxal resin (In cured resin there are distinct band of CH<sub>2</sub>OH (60-72 ppm), CHOH and ethers (70-72 ppm), methylene linkages (30-40 ppm), quinone and glyoxylate (170-190 ppm))
Overlapped spectra of HG liquid and cured resin(a); Dimer fragment of cured HG resin(b); Overlapped spectra of GG liquid and cured resin(c); Dimer fragment of cured GG resin(d); Overlapped spectra of LG liquid and cured resin(e); Dimer fragment of cured LG resin (f).



Figure 4.12. HSQC spectra of glyoxal resins. PG resin with -CHO, C<sub>aro</sub> and CH<sub>2</sub>OH peaks (a), HG resin (b) and GG resin (c) have similar peaks of -CHO, Caro and CH<sub>2</sub>OH.

#### 4.3.4 Fourier-Transform Infrared Analysis of Resins

Fourier-transform infrared spectroscopy is particularly valuable for detecting changes in specific functional groups and monitoring chemical reactions in various materials.<sup>243</sup>

For PF resin (Figure 4.13b), after curing, the O-H stretches become broad (3500-2700 cm<sup>-1</sup>), contrasting with the sharper O-H stretch around 3300-3250 cm<sup>-1</sup> observed in pure phenol (Figure 4.13a). The broadening in the O-H stretch region indicates increased hydroxyl group incorporation, potentially from unreacted CH<sub>2</sub>OH groups, suggesting both intramolecular and intermolecular interactions.<sup>244</sup> A sharp peak increase in the 1150-1050 cm<sup>-1</sup> region suggests the incorporation of aliphatic C-O stretches. Additionally, significant changes in the 750-730 cm<sup>-1</sup> range represents aromatic C-H bending, which reduces after the formation of methylene linkages as aromatic C-H bonds are substituted by methylene groups.<sup>244</sup>

The IR spectra of PG resin (Figure 4.13c) are quite similar to that of PF resin. Due to glyoxalation, more OH groups are introduced into the cured resins, resulting in a much broader O-H stretch region than in PF resin. The aromatic C-H bending (750-730 cm<sup>-1</sup>) in PG resin

decreases significantly due to the association of CH(OH)CH<sub>2</sub>OH and CHCH<sub>2</sub>OH linkages.<sup>135,136,245,246</sup>

Similar changes were observed for the reaction of various lignin monomers with formaldehyde. However, LF resin (Figure 4.14b) exhibits a notable increase in the 1120 cm<sup>-1</sup> peak, indicating the formation of C-O bonds. This bond formation may arise from the incorporation of CH<sub>2</sub>OH or ether groups.<sup>244</sup> The presence of methylene linkages is evidenced by the alkane C-H stretch in the 3000-2700 cm<sup>-1</sup> region. A decrease in peaks within the 860-680 cm<sup>-1</sup> range also suggests substitution reactions leading to CH<sub>2</sub>OH or methylene linkages.<sup>244</sup> Additionally, the cured LG resin (Figure 4.14c) displays FT-IR spectra similar to those of LF cured resin.



Figure 4.13. FT-IR spectra of Phenol (contain sharp O-H stretch) (phenol structure in green color) (a); FT-IR spectra of PF cured resin (orange). O-H stretch becomes broad due to presence of intra and inter-molecular bonding and incorporation of CH<sub>2</sub>OH. In corporation of aliphatic O-H bending and C-O stretch at 145-1310 cm<sup>-1</sup> (red circle and red arrow) and 1150-1050 cm<sup>-1</sup> respectively. Decrease in C-H bending in the fingerprint region (750-730 cm<sup>-1</sup>) (PF dimer in blue color) (b); FT-IR spectra of PG cured resin (yellow). (red box usually shows the changes in the regions) (c).



Figure 4.14. FT-IR spectra of commercial lignin which contains broad O-H stretching (green spectra)(a); (b) FT-IR spectra of LF cured resin which contain sharp C-O stretch at 1120 cm-1 and significant changes in O-H and fingerprint region (orange spectra) (Dimerization in LF resin in blue) (b); FT-IR spectra of LG cured resin which contain sharp C-O stretch at 1120 cm-1 and significant changes in O-H and fingerprint region (yellow spectra) (Dimerization in LG resin in orange) (c).

#### CHAPTER 5:

#### **Conclusions and Future Recommendations**

## 5.1 Conclusions

This research explored the development of bio-based wood adhesives by replacing petroleum-based phenol and formaldehyde with lignin and glyoxal, aiming to address environmental and health concerns with acceptable adhesive performance based on industry standards. Lignin, a renewable polyphenolic feedstock, was studied for its ability to replace petroleum-based phenol in adhesive formulations. On the other hand, glyoxal, a greener crosslinker, was investigated as a sustainable alternative to formaldehyde, offering reduced toxicity and environmental impact. Adhesives formulated with lignin and glyoxal demonstrated excellent performance for interior wood panel applications, eliminating formaldehyde emissions and significantly lowering toxicity. However, the lower reactivity of glyoxal compared to formaldehyde, resulting in reduced water resistance, remains a challenge for outdoor applications. This emphasizes the need for further improvements in resin formulations to enhance performance in more demanding environments. Additionally, lignin-based phenolic adhesives were developed by replacing 80–100% of phenol with commercially available lignin samples, with a focus on reducing formaldehyde consumption and enhancing curing efficiency through the use of sodium carbonate. This approach provided a practical solution to reduce hot curing time, allowing the adhesives to meet industrial standards for interior and exterior-grade plywood. The adhesives achieved high adhesion performance in both dry and wet conditions with minimal curing time adjustments while reducing formaldehyde consumption by at least 63%. Structural analysis in this study confirmed the effective integration of lignin and glyoxal into adhesive systems, forming methylene and glyoxylene linkages essential for optimal performance. This work provides a strong foundation for reducing the environmental impact of the wood composites industry, addressing both toxicity and sustainability concerns while opening new pathways for the production and use of renewable feedstocks.

# 5.2 Future Recommendation

This study focused on developing lignin-based phenolic resins using unmodified lignins and glyoxal as sustainable alternatives to petroleum-based phenol and formaldehyde. To optimize these resins for exterior-grade plywood adhesives, several recommendations are proposed:

One potential avenue for improvement is to explore more efficient catalysts that could reduce the hot curing time when phenol is partially replaced with commercial lignin samples. Additionally, investigating unmodified commercial lignin samples with higher reactivity towards aldehydes may enhance the overall reactivity of the resin system, making it more suitable for industrial applications.

Furthermore, simulating hot curing conditions using thermal analysis techniques, such as Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA), could provide valuable insights into the curing behaviors of these resins. Another important aspect to examine is the use of alternative lignin solvents with lower reactivity towards glyoxal, beyond sodium hydroxide, to minimize undesirable side reactions and improve the overall performance of the resins.

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