



INFLUENCE OF LIGNIN STRUCTURE AND ISOLATION ON ITS OXIDATIVE DEPOLYMERIZATION INTO AROMATIC MONOPHENOLS

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Abstract – Oxidative depolymerization of lignin into monophenols is a promising strategy for lignin valorization. However, this reaction is strongly affected by lignin structure and reaction conditions. In this work, lignins from Pinus, Eucalyptus and Sugarcane bagasse were depolymerized. The use of in situ (native) lignin was compared with Soda lignin, demonstrating the important role of the chemical modifications introduced during the isolation process. The monophenol yield varied within the biomass, reflecting on the different reactivity toward depolymerization depending on the native structure of lignin. Native-like lignin was isolated from Sugarcane bagasse by the mild Pepper's method and submitted to oxidative depolymerization under milder conditions. Results revealed that in such conditions, α -carbonylated products are produced but increasing the oxidative potential of the reaction led to overoxidation and the decrease of monophenol yield, revealing the key role of both lignin structure and depolymerization reaction conditions to improve the monophenol yield.

Keywords: *Lignin, depolymerization, oxidation, phenol*

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Introduction

Efficient strategies for the valorization of whole lignocellulosic biomass are essential for the development of sustainable and economically viable biorefineries. While the conversion of carbohydrate fractions is well established, lignin remains an underutilized resource.¹ As a highly complex, heterogeneous aromatic polymer, lignin represents the most abundant renewable source of aromatic structures on Earth, making it a promising feedstock for the production of aromatic monomers through its depolymerization.²

However, the selective depolymerization of lignin into its monomeric units is a considerable challenge due to its complex and variable structure and the diversity of interunit linkages it presents. In addition to labile ether bonds, which are the main type of interunit linkages in native lignin, lignin contains more resistant carbon-carbon linkages that are difficult to cleave selectively. The abundance and type of these linkages, along with the monomer composition, vary with biomass origin and directly influence the polymer's reactivity.³ These structural differences directly affect the efficiency and the selectivity of lignin depolymerization processes.²

Despite this variability, characteristic patterns are observed in lignins derived from different biomass types. Lignin from softwoods, such as Pinus, is predominantly composed of G units, which are prone to condensation due to the reactive C-5 position in the aromatic ring. Hardwoods, such as Eucalyptus, typically contain both G and S units, while herbaceous feedstocks like Sugarcane bagasse exhibit a broader copolymer composition, including significant amounts of H, G, and S units, along with p-coumarate groups esterified at the γ -position of the lignin side chain.⁴

Although native lignin is already a complex polymer, its isolation from biomass can further alter its structure. Depending on the severity and type of the process, isolation can result in chemical modifications, including the cleavage of ether bonds and the formation of additional C-C linkages, leading to a more condensed and recalcitrant polymer. These changes reduce the efficiency of the catalytic depolymerization and highlight the importance of preserving the polymer's native structure when possible.²

In this study, the oxidative catalytic depolymerization of lignins derived from three distinct biomass sources was investigated. The depolymerization behavior of both native lignin (in-situ within the biomass matrix) and lignin isolated via a Soda process was compared, demonstrating that the chemical structure of the polymer strongly influences the yield and distribution of aromatic monomers. Additionally, a native-like lignin, isolated from Sugarcane bagasse through the Pepper method, was subjected to oxidative depolymerization under varying reaction conditions. The results revealed that excessive oxidation of the released monomers can decrease the yield, even when the native polymeric structure of lignin is preserved, highlighting the importance of balancing depolymerization efficiency with product stability.

Experimental

Isolation of Soda lignin

Lignin was isolated from Pinus wood, Sugarcane bagasse, and Eucalyptus wood using the Soda process. The biomass was suspended in a NaOH solution and heated to 170 °C for 1 hour. After the reaction, the slurry was filtered, and the lignin was precipitated by acidifying the filtrate to pH 2. The resulting solid was recovered by filtration, washed with water until neutral pH, and oven dried.

Isolation of native like lignin

To obtain a native like lignin isolated from Sugarcane bagasse, the Pepper method, a selective and milder extraction technique was employed. The ethanol extracted biomass was treated with a dioxane/2 N HCl solution (9:1 v/v) under reflux at approximately 95 °C. Following the reaction, the mixture was filtered, and the filtrate was neutralized with sodium bicarbonate. A concentrated solution (~150 mL) was obtained by the evaporation of part of the solvent under reduced pressure. This was then slowly added to 2 L of water to precipitate the native like lignin. The suspension was centrifuged, and the recovered lignin was oven dried at 45 °C.

Oxidative depolymerization of lignins

Oxidative depolymerization was performed by solubilizing 4.5 g of lignin in 20 mL of 2 M NaOH. For the depolymerization of native (in-situ) lignin, 20 g of untreated biomass was used instead. CuO (0.45 g) was added as a heterogeneous catalyst. The reaction mixture was sealed in a reactor, pressurized with synthetic air to 20 bar at room temperature, and then heated to 180 °C. Reactions were carried out for 3 hours. After cooling, the solid residue, rich in cellulose in the case of native lignin, was separated by filtration. The liquid phase was acidified to pH 2 and extracted with ethyl acetate to recover the aromatic monomers, which were quantified by GC-FID. For the depolymerization of native-like lignin, similar conditions were used, except that smaller reaction scales were employed, the reaction time was reduced to 1 hour and the initial pressure of synthetic air was varied.

Results and Discussion

The monophenol yields obtained from the oxidative depolymerization of in-situ lignin varied depending on the biomass source, as shown in Fig. 1. These differences reflect the distinct lignin compositions of each biomass. Eucalyptus yielded higher amounts of S- and G-derived monophenols; Sugarcane bagasse produced appreciable amounts of products derived from all three major lignin units (H, G, and S); while Pinus primarily yielded G-derived monophenols. The nature of the lignin polymer also helps explain the differences in overall monophenol yield among the three biomasses. G units, which possess a free C-5 position on the aromatic ring, are more susceptible to condensation reactions than S units. Therefore, the lower yield of monophenols observed for Pinus may be attributed to the high G-unit content of its lignin, which increases its tendency to undergo condensation in alkaline solution. In contrast, both Eucalyptus and Sugarcane

bagasse exhibited higher monophenol yields, with Eucalyptus achieving the highest total yield.

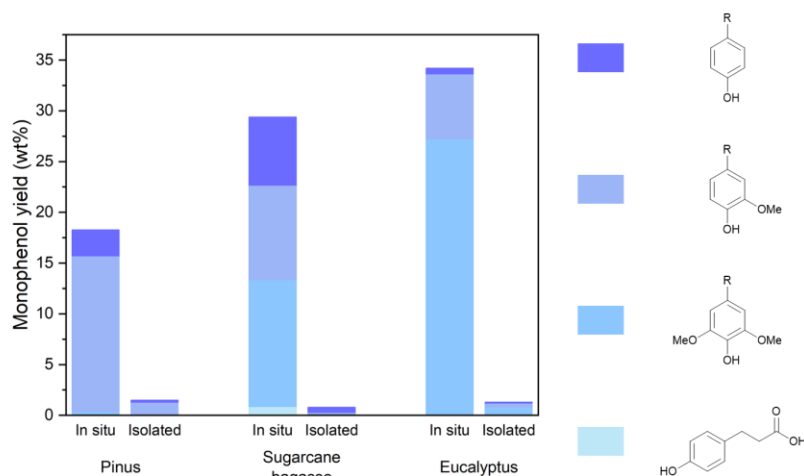


Figure 1 – Monophenol yields from the oxidative depolymerization of *in situ* and Soda lignins from different biomass.

A comparison between in-situ lignin and Soda-isolated lignin revealed a clear reduction in monophenol yield after isolation. Two main factors may account for this trend. First, the chemical modifications introduced during alkaline isolation result in a more recalcitrant polymer, less prone to depolymerization and selective cleavage.² Second, isolated lignin, being readily soluble in alkaline medium, has increased contact with the catalyst. While this facilitates oxidative depolymerization into monophenols, it also promotes overoxidation to aliphatic acids and other degradation products, reducing the monophenol yield, as the aromatic monomers produced are unstable in the presence of oxygen.⁵

To address both the chemical modifications introduced during lignin isolation and the overoxidation typically observed in oxidative treatments, lignin was isolated from Sugarcane bagasse using the Pepper method, a mild isolation process that can preserve some of native lignin structures.⁶ This native-like lignin was then subjected to oxidative depolymerization under varied reaction conditions, including shorter reaction times and different synthetic air pressures, consequently varying the partial pressure of oxygen, a key factor influencing lignin oxidation, even in the presence of a catalyst. The resulting monophenol yields are presented in Fig. 2. Some of the following results have been previously published elsewhere.⁶

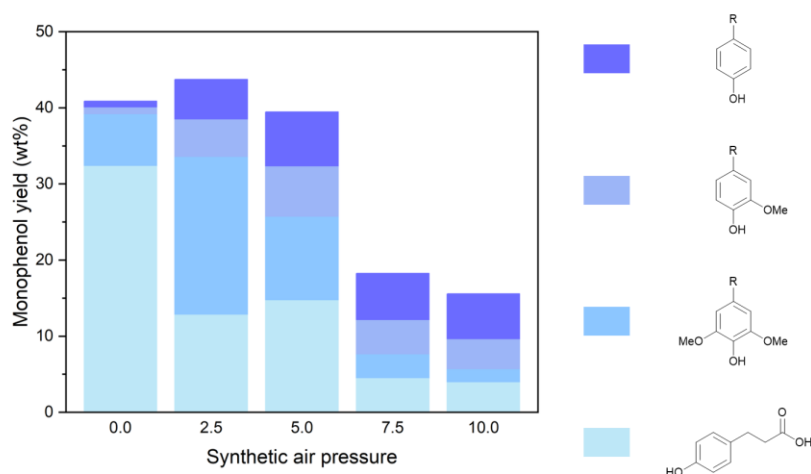


Figure 2 – Monophenol yields from the oxidative depolymerization of native like lignin isolated from Sugarcane bagasse.

Interestingly, a high monophenol yield was obtained in the absence of synthetic air, with *p*-coumaric acid identified as the main product. *p*-Coumaric acid originates from the base-catalyzed hydrolysis of ester bonds in lignin, instead of its oxidative depolymerization. As the pressure of synthetic air increased, the yield of *p*-coumaric acid decreased, likely due to its further oxidation into other products.⁷ Simultaneously, the yield of α -carbonylated compounds, which are the main products of oxidative depolymerization of lignin, initially increased, reaching a maximum at 2.5 bar. Beyond this point, their yields declined, indicating instability and overoxidation of the initially formed products under more oxidative conditions.

These findings suggest that when using isolated lignin, reaction conditions must be carefully tuned to enable partial oxidation, sufficient to generate α -carbonylated monophenols, but mild enough to prevent their overoxidation and degradation, which reduces the yields.

Conclusions

Results showed here demonstrated that the monophenol yields from the oxidative catalytic depolymerization is highly dependent on the structure and composition of lignin as well as the reaction conditions. Varying the biomass showed that S-type lignins from Eucalyptus is more susceptible to depolymerization and the comparison between the isolated and the native lignins demonstrated that the modification introduced during lignin isolation suppress the depolymerization process, suggesting that the native structure of *in situ* lignin is more propitious for the production of monophenols. Furthermore, controlling the severity of the oxidative depolymerization reaction is a key factor for the monophenol yields, as it should allow the formation of α -carbonylated products but prevent its degradation.

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