

Studies on electrolytic mediator system (EMS) oxidation of lignin model compounds

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Summary

In summary, the studies focused on various aspects of electrochemical oxidation of lignin-related compounds using different mediators and solvent systems. Solubility tests helped identify suitable solvents for the electrochemical experiments, with CH₃CN/H₂O (7:3) demonstrating favorable redox stability for the mediators. CV measurements revealed the influence of solvents on the electrochemical properties, while the choice of mediator impacted the reaction selectivity. Mediators such as PZH, NHPI, and ABTS showed promise in mediating the oxidation of specific lignin linkages. Fe(bpy)₃ was found to be an effective mediator for lignin dimer and polymer oxidation, with cleavage and carbonylation reactions observed. TEMPO-mediated electro-oxidation under alkaline conditions exhibited high efficiency in oxidizing both dimer and polymer model compounds. Notably, TEMPO facilitated C α -C β bond cleavage, yielding monomers with specific end-units. However, further investigations are needed to understand certain observations and optimize reaction conditions. These findings contribute to a deeper understanding of lignin EMS and offer potential applications for lignin modification and biomass processing.

The primary findings of this study are as follows:

Significant conversions were observed in the phenolic model compounds containing β -O-4 and β -5 linkages upon direct electro-oxidation at 0.8 V, while only partial changes were noted in the non-phenolic model compounds. However, the direct electro-oxidation of G-DHP did not yield satisfactory outcomes compared to the dimer model compounds. The intricate and bulky structure of G-DHP restricts the interaction between the electrode's active sites and the internal architecture of the macromolecule, leading to minimal oxidation. These findings highlight that the bulk electrolysis conditions established in this study are not suitable for the direct electrolysis of lignin polymers.

Electro-oxidation of lignin dimer models 1b-3b and the lignin polymer model G-DHP was conducted with three mediators (PZH, NHPI, ABTS). The mediators demonstrated effective facilitation of the electro-oxidation reactions, displaying distinct reaction selectivity. PZH exhibited preferential oxidation of β -O-4 and β - β linkages, NHPI favored β -O-4 linkages, and ABTS preferred β -O-4 and β - β linkages. The degradation of major lignin linkages involved partial C α -C β cleavage along with C α - and/or C γ -oxidations. Furthermore, the mediators facilitated the conversion of coniferyl alcohol end-units, with NHPI and ABTS likely mediating C α -C β cleavage through hydrogen atom transfer (HAT) and electron transfer (ET) mechanisms, respectively. Overall, PZH, NHPI, and ABTS show

promise as mediators for efficient lignin modification and degradation, contributing to improved biomass processing and lignin valorization. Further investigation is necessary to understand the mechanisms underlying the degradation of major lignin linkages and to optimize EMS conditions for higher lignin conversions with reduced mediator usage. Additionally, evaluating the recyclability and toxicity of the mediators is crucial for practical implementation of lignin EMS in biorefineries.

LA was tested as an alternative mediator in EMS oxidation, replacing MLS biomimetic oxidation. In LA-mediated electro-oxidations of lignin dimer model compounds 1a-3a and 1b-3b at 0.8 V, efficient conversion was observed except for compounds 3a (phenolic β - β compound) and 2b (non-phenolic β -5 compound). However, LA's role as a mediator had mostly negative effects due to significant direct electro-oxidation contributions. When LA was used solely as the mediator, moderate electro-oxidations of G-DHP occurred at 0.8 V and 1.8 V. The conversion of G-DHP increased with O_2 -sparging, but the results were similar to direct electro-oxidations without LA in the presence of O_2 . Combination use of LA with $Fe(bpy)_3$ or PCA showed some effectiveness in G-DHP conversion. Conversely, when LA was combined with HBT, efficient electro-oxidation of G-DHP took place, and the yield of residue LA/HBT-0.6 was the lowest. This suggests that HBT acted as a co-oxidant, facilitating the efficient generation of LA radicals. However, O_2 -sparging had a negative effect on the electro-oxidation. Overall, EMS oxidation using LA/HBT was identified as a promising biomimetic method.

The transition-metal complexes $Mn(acac)_2$, $Mn(bpy)_3$, $Fe(acac)_2$, and $Fe(bpy)_3$ were tested as mediators in lignin EMS. After screening experiments using the lignin monomer model compound 1G, $Fe(bpy)_3$ was chosen as the transition-metal mediator for the electrolysis of lignin dimer model 3G and polymer model G-DHP. In $Fe(bpy)_3$ -mediated electrooxidations of the lignin dimer model 3G, efficient $C\alpha$ - $C\beta$ cleavage and $C\alpha$ -carbonylation occurred in 0.1 M $LiClO_4/70\%$ - CH_3CN/H_2O , while $C\alpha$ -carbonylation was dominant in the 10%-dioxane/0.1 M acetate buffer (pH 4) system. $Fe(bpy)_3$ -mediated electro-oxidations of the lignin polymer model G-DHP also proceeded effectively via $C\alpha$ - $C\beta$ cleavage and $C\alpha$ -carbonylation in 0.1 M $LiClO_4/70\%$ - CH_3CN/H_2O , with enhanced lignin oxidations observed upon addition of 2,6-lutidine as a base. However, $Fe(bpy)_3$ -mediated electro-oxidations of G-DHP were inefficient in 10%-dioxane/0.1 M acetate buffer (pH 4), regardless of the presence of 2,6-lutidine under the given conditions. Overall, $Fe(bpy)_3$ shows promise as a mediator for lignin EMS, facilitating lignin modification and degradation to improve biomass processing and lignin valorization efficiencies. Future studies should focus on elucidating the detailed mechanisms of lignin degradation, particularly by identifying specific low-molecular-weight lignin fragments released during lignin EMS.