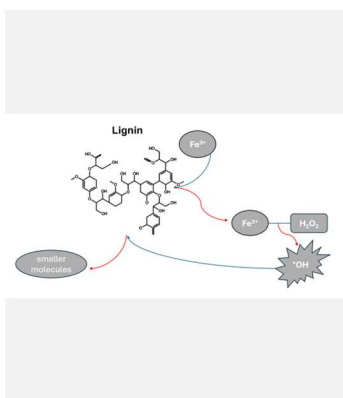# Fenton-Mediated Oxidative Depolymerization of Kraft Lignin: Understanding Reaction Mechanisms and Product Formation

C. Méndez[1,2], V.Melín[2], R.Romero[2]., D. Contreras[2] (1) Faculty of Pharmacy, University of Concepción, Concepción, Chile, cammendez@udec.cl (2) Faculty of Chemical Sciencies , University of Concepción, Concepción, Chile.

Lignin, as the second most abundant biopolymer, holds potential for replacing petroleum-derived raw materials. However, its complex structure presents challenges for valorization efforts. The Fenton-type reaction is a promising strategy for depolymerization, leveraging hydroxyl radicals and lignin's reductive capacity. This method enables selective cleavage of lignin bonds under mild conditions. Analysis of lignin's average molar mass reveals significant reduction by 50% within 50 minutes of depolymerization. Additionally, observations of lignin-Fe^{3+} complexes and subsequent reduction to Fe^{2+} establish an autocatalytic and oxidative cycle for depolymerization. Overall, the Fenton-type reaction offers an efficient route for lignin depolymerization and chemical production.

Introduction

Lignin, a polyphenolic macromolecule integral to plant cell wall structure, stands as a copious and intricate biopolymer, serving as a primary reservoir of aromatic moieties in nature[1]. However, its inherent recalcitrance poses formidable hurdles to its efficient utilization within industrial contexts[2]. Within this framework, the Fenton-type reaction has garnered attention as a promising avenue for the oxidative depolymerization of lignin. This catalytic process capitalizes on the controlled generation of hydroxyl radicals via the interaction of hydrogen peroxide with an iron catalyst under acidic milieu. By exploiting the preferential reactivity of hydroxyl radicals towards ether and carbon-carbon linkages within lignin, selective cleavage of its molecular backbone is achieved[3]. Consequently, controlled depolymerization ensues, yielding fragments of diminished molecular weight amenable to downstream valorization into high-value chemical commodities. The primary objective of this study is to optimize the Fenton-type reaction for the depolymerization of Kraft lignin within aqueous systems. This entails a comprehensive investigation involving the characterization of molecular weight distribution via Gel Permeation Chromatography (GPC) alongside an exploration of lignin's capacity to engage in complexation with Fe^{3+}, subsequently reducing it to Fe^{2+}, thereby fostering an autocatalytic and oxidative cycle conducive to lignin depolymerization.

Material and Methods

500 mg/L of Kraft lignin (Suzano, Brasil), $FeNO_3 \times 9H_2O$, H_2O_2, KSCN, Ferrozine, KF (Merck), agua tipo 1 acidificada a pH 3,00 con HNO_3.

Optimisation of the Fenton-type reaction conditions: This was done by means of a fractional factorial experimental design with two levels plus star points at a time constant of 50 minutes (which was optimised in a previous kinetic).

Table 1: Experimental Design.

Variable	High value (+1)	Low value (-1)	$-\sqrt{2}$	$+\sqrt{2}$
Fe^{3+}	0,60 mg/L	0,20 mg/L	0,11 mg/L	0,69 mg/L
H_2O_2	85 mg/L	51 mg/L	18,46 mg/L	92,03 mg/L

The design response was Mw of lignin and was measured by GPC (Waters), with refractive index detector, THF mobile phase and a flow rate of 0.5 mL/min.

Results and Discussion

"The results of all responses are summarized in surface plots (Figure 1), where it is observed that the minimum Mw is found at concentrations of 0.44 mg/L Fe^{3+} and 68 mg/L H_2O_2, yielding a value of 1662 Da. Considering the initial Mw value of lignin, which is 3000 Da, the Fenton-type reaction was successfully optimized, achieving a 55.4% decrease in Mw. This reduction indicates that lignin

underwent fragmentation or cleavage of its molecular chains due to the action of oxidizing agents, particularly hydroxyl radicals, resulting in the formation of smaller molecules.
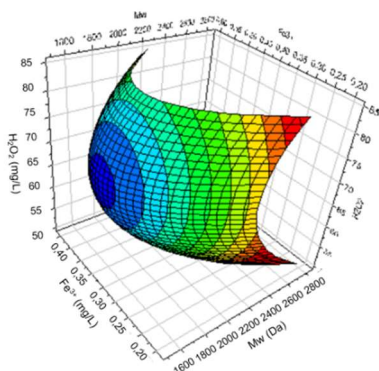
Figure 1. Response Surface for CCC Design.

The analysis of the distribution of molar masses of lignin before (black line) and after (red line) depolymerization clearly shows a shift to the left, indicating a decrease in the size of Mw molecules. Furthermore, the mass dispersion decreased from 3.27 to 2.52, suggesting that after depolymerization, lignin exhibits a narrower and more uniform distribution in terms of molecular mass.

It has been observed that during the depolymerization process, lignin forms complexes with Fe^{3+}, reducing it to Fe^{2+}, thereby allowing the latter to exist in the system and promoting the formation of hydroxyl radicals. These radicals are responsible for breaking the lignin chains. This phenomenon is reflected in Figure 2, where an aqueous system involving lignin and a $[FeSCN]^{+2}$ complex is depicted. In this figure, the concentration of the $[FeSCN]^{+2}$ complex decreases over time, indicating that lignin sequesters Fe^{3+} from SCN^- (black squares) and subsequently reduces it to Fe^{2+}, thereby increasing its concentration (red circles) in the system. This is evidenced by the formation of the Fe^{2+} complex with ferrozine.
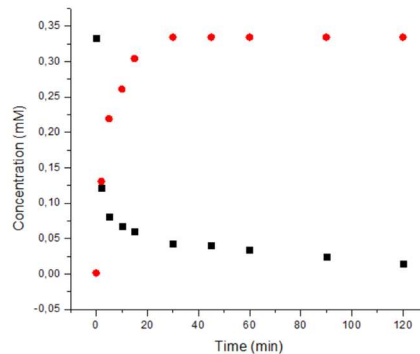
Figure 2. Kinetics of the chelating (black squares) and reducing (red circles, Fe^{2+} production) capacity of lignin towards Fe^{3+}.

Conclusions

The Fenton-like reaction, carried out under mild conditions and in aqueous systems, has been shown to be effective in the depolymerisation of Kraft lignin, achieving a 55.4% reduction in its weight-average molecular mass. The optimum conditions for this depolymerisation were determined using a composite centre design (CCC), which established ideal concentrations of 0.44 mg/L for Fe^{3+} and 68 mg/L for H_2O_2, with a maximum reaction time of 50 minutes. It has been observed that Kraft lignin exhibits chelating and reducing capacity towards Fe^{3+}, suggesting the formation of complexes between lignin and iron. Analysis of the depolymerisation mechanism reveals that lignin initially reduces Fe^{3+} to Fe2+, leading to the generation of hydroxyl radicals ($\cdot$OH) in the presence of H_2O_2. These radicals are responsible for breaking bonds in the lignin structure, resulting in the formation of smaller molecules. These findings support the feasibility and efficiency of the Fenton-type reaction as a promising strategy for the controlled depolymerisation of Kraft lignin, with potential implications for the valorisation of lignocellulosic biomass and the production of high value-added chemicals.

References

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