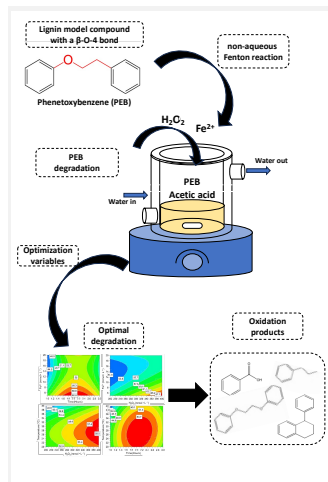


Study of Fenton Systems in Acetic Acid for the Oxidation of Bonds Between Phenylpropane Units in a Lignin Model

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Forest biomass is a replacement option for petroleum-based precursor chemicals. One of the most abundant components in biomass is lignin. Different valorization alternatives have been proposed for this natural polymer, however, most of these processes are energetically very costly. It has been described that the β -O-4 bond is the most abundant within the lignin structure, it has been described that a potential pathway to depolymerize lignin could be through the oxidation of monomeric inter-unit bonds. The Fenton reaction has been evaluated under different conditions due to its ease of implementation and good yields. In its conventional form, its oxidation capacity on lignin or model compounds cannot be evaluated due to its low solubility in water. For this reason, in the present work, an oxidation system was implemented in a non-aqueous solvent, such as acetic acid, to determine the oxidation capacity of the Fenton system on a lignin model compound with a β -O-4 bond.

Introduction

One of the main challenges of the chemical industry is finding renewable sources of energy and raw materials that can compete and eventually replace the current oil industry by producing a chemical platform based on renewable products [1]. In this sense, biomass, particularly agroforestry residues, is a great option due to their abundance and the different possibilities presented by the other components that constitute them to produce biofuels, biomaterials, and chemical bioproducts of interest [2]. One of the most abundant components in biomass is lignin. Different valorization alternatives have been proposed for this natural polymer. However, it has been found that most of these processes are very costly energetically. It has been described that the β -O-4 bond is the most abundant within the lignin structure, so oxidizing this bond could initiate the depolymerization of lignin from biomass. Advanced Oxidation Processes (AOPs), especially the Fenton reaction, have been extensively studied to oxidize various organic molecules [3]. Despite the efficacy of the Fenton reaction, its conventional form presents limitations when evaluating its oxidation capacity on lignin or model compounds due to their low solubility in water. Therefore, in the present work, an oxidation system was implemented in a non-aqueous solvent, such as acetic acid [4], to determine the oxidation capacity of the Fenton

system on a lignin model compound with a β -O-4 bond.

Material and Methods

The oxidation of phenethoxybenzene (PEB) was evaluated in a jacketed glass reactor with the aid of a thermoregulated bath to control the temperature. The reaction was carried out under stirring as a function of the variables Fe^{2+} concentration, H_2O_2 concentration, reaction time, and reactor temperature through the design of an experimental model, circumscribed face-centered model (CCF) with the MODDE 7.0 software, presenting a total of 23 experiments (Table 1). The % degradation was determined using a high-performance liquid chromatograph (HPLC, Merck Hitachi) with a mobile phase composed of acetonitrile, methanol, and water type 1 using a wavelength of 270 nm, ZORBAX Bonus-RP C-18 column (3.5 μ m, 4.6 -150 mm; Agilent Technologies) and a mobile phase flow rate of 1mL·min⁻¹. Identification of the degradation products was performed by gas chromatography coupled to mass spectrometry (GC-MS) (Agilent 7890A, MS 5975C detector) with an HP-5MS column (0.25 μ m, 30m, 0.25mm, Agilent) using the headspace solid-phase microextraction technique (HS-SPME-GC/MS) with Divinylbenzene/Carboxen/Polydimethylsiloxane fiber (DVB/CAR/PDMS).

Table 1.

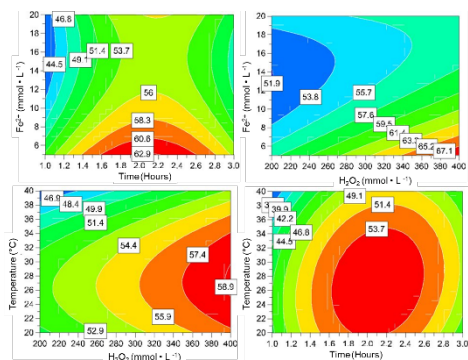
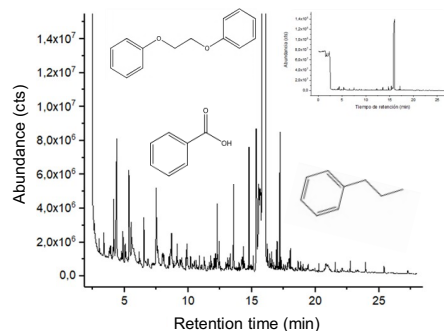
Variables	-1	0	+1
Fe ²⁺ (mmol·L ⁻¹)	5	12.5	20
H ₂ O ₂ (mmol·L ⁻¹)	200	300	400
Temperature (°C)	20	30	40
Time (Hours)	1	2	3
Response	% PEB Degradation		

Results and Discussion

The polynomial obtained from this optimization model went through a fitting process to obtain one that contains the significant variables of the system:

$$Y = 55,38(\pm 1,01) - 3,54(\pm 1,05)(Fe^{2+}) + 3,45(\pm 1,07)(H_2O_2) + 2,62(\pm 0,86)(t) - 2,41(\pm 1,01)(T) + 4,06(\pm 1,67)(Fe^{2+})(Fe^{2+}) - 9,37(\pm 1,67)(t)(t)$$

Fig 1. shows the optimization model for the degradation of PEB, where the optimal conditions for degradation were observed. The optimum point of PEB degradation was at 5 mmol · L⁻¹ of Fe²⁺, 395 mmol · L⁻¹ of H₂O₂, at a reactor temperature of 20 °C and in a reaction time of 2 hours, obtaining 67% (±10.6019, this corresponds to the 95% confidence interval) of PEB degradation. The degradation products of this reaction present an affinity to the DVB/CAR/PDMS fiber; due to this, the products in Fig 2. can be identified.

Fig 1. Response surface design for CCF model**Fig 2. Chromatogram for degradation products of PEB by HS-SPME-GC/MS with DVB/CAR/PDMS fiber.**

Conclusions

In this work it was possible to demonstrate the effectiveness of 67% of the Fenton system in a non-aqueous medium at room temperature and pressure, such as acetic acid, in the degradation of a commercial model compound of the β-O-4 bond of lignin. By identifying the products obtained from this reaction, oxidation products of different nature are obtained, mainly aromatic compounds, benzoic acid, propylbenzene, etc., as well as repolymerization to compounds of higher molar mass such as 1,2- diphenoxyethane, 1-phenyl-1,2,3,4-tetrahydronaphthalene, etc., could also be observed.

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