

Effect of Methoxy Substituents on Wet Peroxide Oxidation of Lignin and Lignin Model Compounds: Understanding the Pathway to C₄ Dicarboxylic Acids

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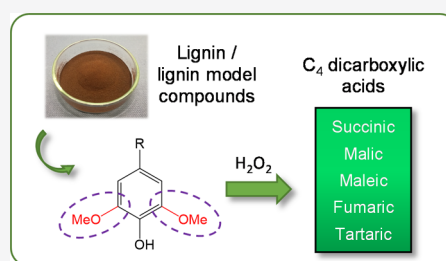
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ABSTRACT: Lignin depolymerization through peroxide oxidation produces dicarboxylic acids (DCA), especially C₄-DCA, like succinic acid. In this work, the effect of methoxy substituents on C₄-DCA production using peroxide oxidation of lignin model compounds (*p*-hydroxybenzoic acid, vanillic acid, and syringic acid) and hardwood and softwood lignin samples was studied. It was concluded that methoxy substituents increased the reactivity toward peroxide oxidation. The succinic acid yield was higher for the model compounds with fewer methoxy groups, achieving 5.8 wt % of succinic acid for *p*-hydroxybenzoic acid. For *Eucalyptus globulus* kraft lignin (hardwood lignin with guaiacyl and syringyl units), an increased reactivity was verified, and more succinic acid (3.5 wt %) was produced in a shorter time, comparatively with Indulin AT lignin (softwood lignin, with only guaiacyl units), which produced 2.7 wt %. This evidence suggests that *E. globulus* kraft lignin might be a better raw material than Indulin AT for succinic acid production by peroxide oxidation.



INTRODUCTION

A lignocellulosic biomass biorefinery has proven to be a favorable alternative to reduce the fossil fuel dependence of the chemical industry.¹ Lignin is present in all lignocellulosic biomass, at contents that vary depending on their source. Structurally, it is composed of three phenylpropane units, known as *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units.² These units can be identified in the lignin structure, respectively, as derivatives of *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol moieties. The main difference between these structures relies on the methoxy substituents located in the ortho position relative to the hydroxyl group in the phenolic ring, as shown in Figure 1a. The abundance of each monomer in the lignin is related to plant taxonomy, as shown in Table 1. The ratio between monomers is a relevant parameter because each monomer has a different chemical behavior and distinct possibilities of interlinking.³ Most of the links between monomers are alkyl- and aryl-ether linkages (60–70%), C–C linkages (~25–35%), and some ester bonds (<5%), being the most common ones the β -O-4, α -O-4, β - β , β -5, 5-5, β -1, and the 4-O-5, which lead to a complex heterogeneous structure that is difficult to isolate and depolymerize.^{4,5} Kraft lignin is obtained from kraft pulping processes, which not only modify the structure of native lignin through cleavage of α - and β -ether bonds, but also causes condensation as carbon–carbon bonds. In these processes, lignin is burnt to produce energy and recover chemicals. However, kraft lignin can also be valorized into value-added products.^{4,6}

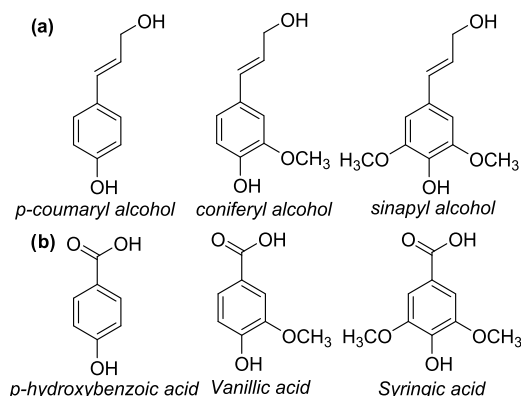


Figure 1. Structures of (a) monolignol monomers and (b) model compounds used for this work.

Lignin has been proposed as a feedstock for several products after depolymerization, which can be achieved by oxidation, reduction, pyrolysis, hydrotreatment, enzymatic hydrolysis, and many other chemical and biological treatments.^{7–10} Phenolic products, such as phenol, vanillin, syringaldehyde, and catechol, among others, have been the main focus in lignin

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Table 1. Approximate Composition (%) of Some Lignin Classes, Depending on Plant Taxonomy

phenylpropane units	guaiacylpropane (%)	syringylpropane (%)	<i>p</i> -hydroxyphenylpropane (%)
softwood lignin	95	1	4
hardwood lignin	50	50	2
grass lignin	70	25	5

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depolymerization.^{11,12} However, due to higher availability and low commercial use of lignin, the study of this renewable raw material as a feedstock for the production of a diversity of aliphatic compounds (e.g., adipic acid, succinic acid, cyclohexane), which are nowadays produced by petrochemical routes or biochemical pathways using fermentable sugars, has become of high interest.² Strong oxidative depolymerization can cause a ring-opening reaction, producing several C₁ to C₆ acids, especially dicarboxylic acids (DCA), like adipic, muconic, succinic, maleic, and oxalic acids.^{13–16} Peroxide oxidation has been considered more efficient for aromatic ring cleavage than O₂ oxidation because it avoids mass-transfer limitations. Moreover, H₂O₂ releases free radicals, which enhance lignin degradation in a shorter time under less severe conditions.^{17,18} Several of these dicarboxylic acids have shown relevance as feedstocks for polymers, cosmetics, and the food industry. They are currently under study aiming to enhance their production through chemical and biological lignin depolymerization.¹⁸ C₄-DCA (succinic, maleic, malic, fumaric, and tartaric acids) (Figure 2), the main diacids obtained in the

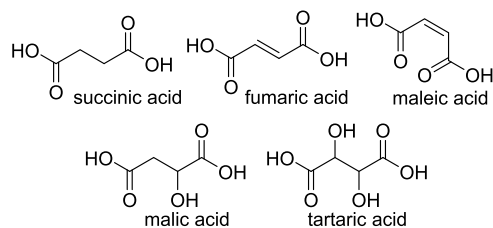


Figure 2. Structures of C₄ dicarboxylic acids (DCA).

oxidation, and oxalic acid, have great importance as renewable building blocks for the future high-value bio-based chemicals and materials.¹⁹ In particular, succinic acid has attracted special interest due to its application in the chemical industry (as a surfactant, ion chelator, etc.), food industry (acidulant, flavoring additive, and antimicrobial agent), and as an intermediate for chemical and materials production.²⁰

Initial studies on oxidation of lignin model compounds and lignin revealed the formation of C₄-DCA after the ring-opening reaction in the alkaline pulping and peroxide bleaching processes.²¹ Those studies were used to explain lignin degradation through the pulping process but were not focused on DCA production. Therefore, the quantities reported in those studies were negligible or not specified at all. More recently, different studies presented the noncatalyzed production of dicarboxylic acids from oxidation of lignin and lignin model compounds using H₂O₂. However, none of these studies focused on analyzing the impact of the model compounds' structural features on the DCA yields.^{14,22–24} A higher DCA (oxalic, malonic, and succinic acids) yield has been related to a lower ratio of aromatic to aliphatic functional groups when bagasse lignin was catalytically oxidized with H₂O₂ and sodium percarbonate or chalcopyrite.²⁵ Ma et al. (2018) reported the oxidative conversion of several biorefinery lignins to mono-

meric phenols and dicarboxylic acids (described as a mixture of C₂–C₆ acids) using chalcopyrite-catalyzed peroxide oxidation, showing that the DCA yield increased as the methoxy group content and aromatic hydroxyl groups increased.²⁶ However, this model did not discriminate C₄-DCA from other acids, especially from C₂–C₃ acids, which are degradation products of C₄-DCA formation. In fact, until now, there is no clear evidence showing the best lignin structural unit to obtain a specific dicarboxylic acid by peroxide oxidation. This can point out the most appropriate lignin for depolymerization toward a lignin-based chemical platform.

In the present work, the effect of the methoxy substituents in the aromatic ring was studied, with the aim of obtaining dicarboxylic acids, focused on C₄-DCA (mainly succinic, malic, fumaric, maleic, and tartaric acids), and specifically succinic acid. This effect was analyzed on *p*-hydroxybenzoic, vanillic, and syringic acids, which are lignin model compounds resembling the lignin structural monomeric units, namely, by presenting a different number of methoxy substituents in the ortho position to the phenolic OH group, as shown in Figure 1b. Moreover, this study was extended to two kraft lignins with different G/S/H ratios (a hardwood and a softwood sample).

METHODOLOGY

Materials. All chemical reagents were purchased from commercial sources and used without further purification. The following reagents were purchased from Sigma-Aldrich Co. LLC.: *p*-hydroxybenzoic acid (*p*HBA) (>99%), vanillic acid (VA) (97%), syringic acid (SA) (>95%), DL-malic acid (≥99.0%), fumaric acid (≥99.0%), maleic acid (>99%), malonic acid (>99%), oxalic acid dihydrate (≥99.0%), succinic acid (≥99.0%), acetic acid glacial (>99%), N,O-bis-(trimethylsilyl)trifluoroacetamide (≥99.0%), trimethylchlorosilane (>98%), and pyridine (>99.0%). Other reagents were purchased from different suppliers: formic acid (Chem-labs, >99%), acetonitrile (VWR, high-performance liquid chromatography (HPLC) grade), sulfuric acid (Chem-labs, 95–97% p.a.), sodium hydroxide (Merck, p.a.), and hydrogen peroxide solution (Fluka, >30% p.a.). Gases helium (ALPHAGAZ 1 He) and argon (ALPHAGAZ Ar 1) were supplied by Air Liquide.

Two lignins were used: Indulin AT, a softwood lignin, commercialized by MeadWestvaco Corporation, with a S/G/H ratio of 0:97:3.²⁷ The hardwood lignin was isolated from the black liquor obtained from a *Eucalyptus globulus* kraft pulping mill (The Navigator Company, Portugal). This lignin has a S/G/H ratio of 65:29:6.²⁸ Table 2 shows some properties of these two studied lignins.

Experimental Methods. Oxidation Procedure. Oxidation reactions were conducted in a glass-jacketed 1 dm³ Büchi autoclave (Figure 3). A Lauda E300 thermostatic bath was used to control heating, keeping the reactor at 393–413 K. All model compounds (vanillic acid [VA], syringic acid [SA], and *p*-hydroxybenzoic acid [*p*HBA]) were used at a concentration of 10 g/L and an initial pH of 7.0, adjusted with NaOH or

Table 2. Properties of the Studied Lignins

lignin	lignin isolated from kraft black liquor (hardwood) ²⁸	Indulin AT (softwood) ^{27,29}
S/G/H ratio	65:29:6	0:97:3
total lignin (wt %)	66	92.2
weight-average molecular weight (M_w) (g/mol)	10 323	4290
number-average molecular weight (M_n) (g/mol)	8768	530

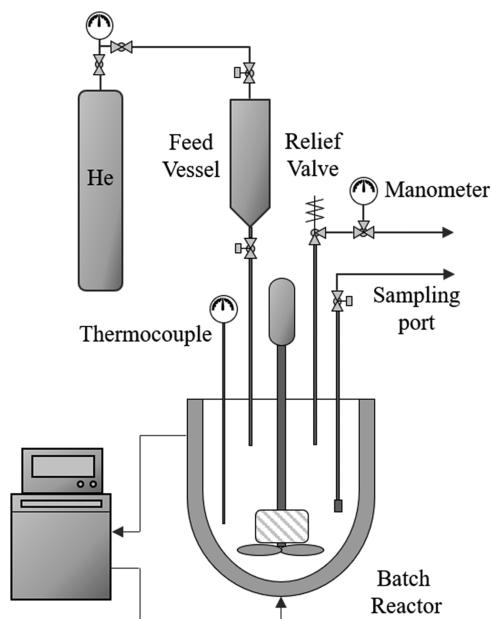
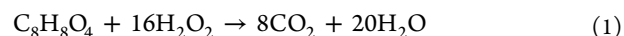


Figure 3. Scheme of the setup used for the oxidation reactions.

H_2SO_4 (1.0 mol/L), as needed. Lignin samples (10 g/L) were solubilized in a 0.1 mol/L phosphate buffer to ensure complete solubilization throughout the reaction. The solution (400 mL) was placed in a batch reactor, then closed, and pressurized with helium. Heat was applied to reach the desired temperature. A 40 mL aliquot of 30 vol % H_2O_2 was loaded into the feed vessel, which was closed and pressurized with He. When the temperature was steady, H_2O_2 was introduced into the reactor, and the reaction started. Samples were taken manually for 4 h at intervals of 10–30 min. The stirring speed was fixed at 800 rpm, and a maximum pressure of 9.0 bar was used. Signals of the thermocouple and pressure inside the reactor were registered using an acquisition board and LabVIEW software. All experiments were done in duplicate.

All of the reactions were performed using 40 mL of 30 vol % H_2O_2 (0.39 mol), which provided the molar quantities needed to achieve complete mineralization of the three used model compounds, according to eq 1 (VA, 0.023 mol, which needed 0.38 mol H_2O_2), eq 2 (*p*HBA, 0.028 mol, which needed 0.39 mol H_2O_2) and eq 3 (SA, 0.019 mol, which needed 0.34 mol H_2O_2). Even so, H_2O_2 cannot be considered as the limiting reagent because not all of the model compound molecules were mineralized but converted to low-molecular-weight compounds. The same amount of oxidant was used for lignin since preliminary tests showed that a higher amount of the oxidant caused C_4 -DCA degradation. The oxidant was added precisely when the solution was at the setpoint temperature and the system pressurized to avoid H_2O_2 degradation while heating.



Analytical Methods. Sample Preparation for Chromatographic Analysis and Lignin Quantification. Model compound oxidation samples in aqueous solution were acidified with 2 mol/L H_2SO_4 to pH \sim 2, diluted as needed, and filtered through a 0.22 μm pore-size filter. Lignin samples were acidified to pH \sim 2, then heated at 40 $^\circ\text{C}$ to coagulate the acid-insoluble lignin, followed by centrifugation at 5000 rpm for 15 min. The insoluble lignin was dried at 100 $^\circ\text{C}$ overnight to quantify the acid-insoluble lignin. The acidic supernatant was used for carboxylic acid and acid-soluble lignin quantification. Acid-soluble lignin was measured by UV spectrophotometry at 240 nm, based on a calibration curve done with the acid-soluble lignin from the original lignin. Lignin conversion was measured as the sum of the acid-insoluble and acid-soluble lignins. The pH was measured for all samples before acidification using a calibrated VWR pH110 equipment. The gaseous compounds were not quantified in this study.

Quantification by High-Performance Liquid Chromatography (HPLC). Carboxylic acids were quantified by high-performance liquid chromatography (HPLC) using a Shimadzu UFLC, equipped with a diode array detector (210 and 260 nm), refraction index detector (RI), and a Phenomenex Rezex ROA H^+ column (300 mm \times 7.8 mm) and precolumn (50 mm \times 7.8 mm). The column was operated at 50 $^\circ\text{C}$ using a gradient flow of 4 mmol/L H_2SO_4 and a solution of 15% acetonitrile in 4 mmol/L H_2SO_4 , at a flow rate of 0.5 mL/min, and an injection volume of 20 μL . Carboxylic acids were identified and quantified using calibration curves prepared with standards of each acid.

Quantified acids are expressed as C_4 -DCA (succinic, malic, maleic, fumaric, and tartaric acids), other DCA (malonic and oxalic acids), total DCA (C_4 -DCA + other DCA), and MCA (monocarboxylic acids: acetic and formic acid). Aromatic carboxylic acid (CA) is the sum of *p*HBA, VA, and SA.

Gas Chromatography-Mass Spectroscopy (GC-MS) Analysis. Qualitative analysis of the compounds produced at low concentrations was done with GC-MS to understand the degradation pathway of lignin and model compounds to C_4 -DCA. For that, a 1.0 mL of the sample (prefiltered through a 0.22 μm filter) was lyophilized in a glass tube. The solids were dissolved in 150 μL of pyridine. Then, 150 μL of BSTFA and 50 μL of TMCS were added. The mixture was mixed and placed in an oil bath at 80 $^\circ\text{C}$ for 30 min to allow complete silylation. The samples were immediately cooled in an ice bath and diluted to 1.0 mL with anhydrous acetonitrile. Derivatized samples were analyzed in a Shimadzu GC-MS-TQ8040, fitted with a Restek Rxi-5Sil MS column (30 m \times 0.25 mm \times 0.25 μm), injection port at 250 $^\circ\text{C}$, 1 μL splitless injection, and a temperature program starting at 100 $^\circ\text{C}$ (hold 2 min), ramp of 3 $^\circ\text{C}/\text{min}$ to 180 $^\circ\text{C}$, hold for 5 min, ramp of 3 $^\circ\text{C}/\text{min}$ to 200 $^\circ\text{C}$, hold for 5 min, and a final ramp of 15 $^\circ\text{C}/\text{min}$ to 250 $^\circ\text{C}$, and hold for 3 min. The mass spectrometer ion source was at 250 $^\circ\text{C}$, and the interface temperature was at 260 $^\circ\text{C}$. The resulting peaks were analyzed using the NIST library. The major components were identified by comparison with standard compounds.

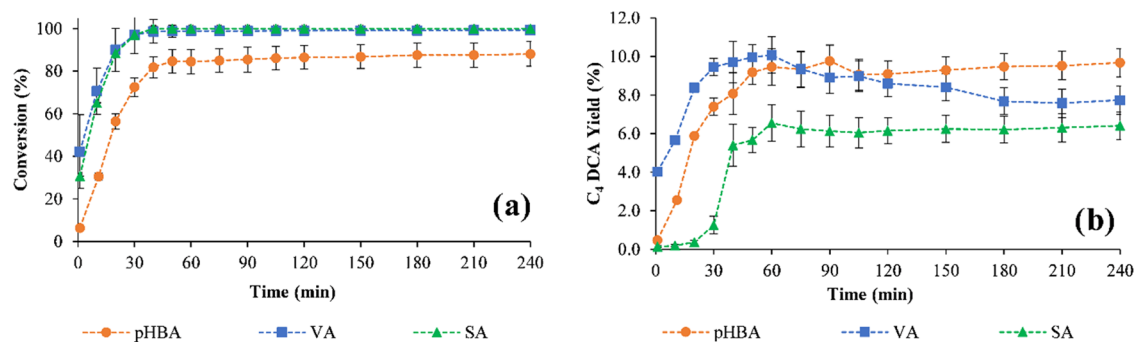


Figure 4. (a) Model compound conversion and (b) C_4 -DCA yield, at $T = 140$ °C.

Table 3. Reaction Rate Constants (k) for Model Compound Conversion, at 140 and 120 °C, Based on a Pseudo-First-Order Kinetic Equation

	<i>p</i> -hydroxybenzoic acid	vanillic acid	syringic acid
$k_{140\text{ °C}}$ (s^{-1})	$(7.2 \pm 0.3) \times 10^{-4}$	$(1.7 \pm 0.2) \times 10^{-3}$	$(1.8 \pm 0.2) \times 10^{-3}$
$k_{120\text{ °C}}$ (s^{-1})	$(3.2 \pm 0.4) \times 10^{-4}$	$(3.4 \pm 0.2) \times 10^{-4}$	$(5.1 \pm 0.2) \times 10^{-4}$

RESULTS AND DISCUSSION

Oxidation of Model Compounds: *p*-Hydroxybenzoic Acid (*p*HBA), Vanillic Acid (VA), and Syringic Acid (SA).

The model compounds presented different behaviors when oxidized using H_2O_2 at 140 °C. Figure 4 shows that both VA and SA reached a nearly full conversion at 40 min (99 and 100 wt %, respectively). However, *p*HBA reached a lower conversion, namely, 88 wt %, never being fully converted, even after 4 h of reaction (even with enough H_2O_2 to reach complete mineralization, showing that the remaining oxidant was used to oxidize the produced compounds instead of *p*HBA). Table 3 summarizes the conversion rates for each tested model compound at 140 °C, where SA and VA showed higher conversion rates, while for *p*HBA, the lowest one was observed (88 wt %). It has been reported that SA is more reactive than VA when oxidized using O_2 at an alkaline pH.^{30,31} However, when H_2O_2 at neutral pH is used, which has higher oxidizing power, no significant differences between SA and VA conversions were detected.

Lower reaction rates were found at 120 °C, as seen in Table 3. There was no significant difference between VA and *p*HBA oxidation at this temperature, while SA oxidation occurred faster, confirming its higher reactivity. Therefore, it can be concluded that *p*HBA maintained the low reactivity even at higher temperatures, while SA showed the highest reactivity.

The phenolic OH bond's strength explains most of the reactivity observed for the model compounds because it is the initial site where the compound reacts against a radical.³² After the phenolic OH bond is cleaved by accepting a radical, the radical is delocalized in the aromatic ring, which is reorganized as a quinone to be further oxidized and undergo ring-opening reactions.³² The bond-dissociation energy (BDE) for the phenolic OH bond, a parameter that measures the energy needed to cause the rupture of the bond, is affected by the presence of activating and deactivating groups in the aromatic ring, which can or cannot stabilize the radical by resonance and/or inductive effects. A compound with a lower BDE would show a higher reactivity against an oxidant because the OH bond would be cleaved easily, and the aromatic ring would be further oxidized to a quinone structure.^{32,33} As the aromatic ring becomes activated, the radical is easily dislocated in the aromatic structure, being more reactive against H_2O_2

oxidation.³⁴ The highest BDE is presented by *p*HBA (85.15 kcal/mol) when compared to VA (79.41 kcal/mol) and SA (79.42 kcal/mol),³³ because the latter two compounds have methoxy groups in the ortho position to the phenolic OH (Figure 1b), which act as electron donors, stabilizing the radical in the aromatic ring. Even though SA has two methoxy groups and VA only one, there is no significant difference between the two compounds due to the intramolecular hydrogen bond formed between the phenolic hydrogen and the methoxy oxygen in SA, stabilizing the phenolic OH bond.³³ It is expected that the real BDE for each model compound in solution is lower than the reported one because the reactions were carried out, at all moments, at a pH higher than the respective pK_{a1} (*p*HBA = 4.57, VA = 4.42, SA = 4.34).^{35,36} Over pK_{a1} , the carboxylic acid group was unprotonated, acting as a weak electron donor group by the inductive effect, thus stabilizing the radical in the aromatic ring.³⁷ In the opposite case, i.e., if the carboxylic group is protonated, it acts as a deactivating group, slightly destabilizing the radical in the aromatic ring.

After 40 min of reaction, and for the three compounds, the first-order kinetic model did not fit the experimental data. At this point, a change in the pH was observed; namely, it decreased from pH 7 to 4.0–5.5 and then increased to pH 6.3–7.4 (Figure S1). These facts evidenced a change in the reactions taking place after this time. The degraded model compounds were oxidized to other compounds, namely, dicarboxylic acids, while the remaining model compounds continued to be oxidized but at a lower rate. However, after 40 min, conversion of model compounds reached more than 96% of the total conversion, i.e., the conversion registered for 240 min reaction time, confirming that the expressed kinetic constant rate explained the main behavior of the model compound conversion.

As the reaction proceeded, VA, and *p*HBA solutions turned darker due to the production of chromophoric compounds, such as quinones and condensed aromatic rings. The condensation reactions occurred in these model compounds due to the ortho available position, having two available positions in *p*HBA and just one in VA since these positions were activated for addition and condensation reactions. When SA was oxidized, an initial darker color was produced while

heating the mixture to the reaction temperature, caused by the presence of quinones produced by auto-oxidation. However, as soon as H₂O₂ was added, they were quickly degraded, and the color disappeared after a short time. As SA has no available ortho positions to the phenolic OH, no condensation reactions occurred, and no darker solutions were formed.³²

The methoxylated model compounds were oxidative demethoxylated during the first steps of oxidation, resulting in hydroxyl groups in the aromatic structure. Demethoxylation is achieved when a hydroxyl radical attacks the position where the methoxyl group is linked, retaining this radical as a hydroxyl group while the methoxyl group is released as methanol.^{38,39} This step was observed in VA and SA, where 3,4-dihydroxybenzoic acid (protocatechuic acid) was detected during the first minutes of the reaction by GC-MS analysis. This compound is more reactive than VA and SA, having a lower BDE (74.44 kcal/mol),³³ so it was oxidized faster to *o*-quinones. This compound was also found in *p*HBA oxidation, suggesting that the hydroxyl radical attacked the carbon adjacent to the OH group. It is interesting to note that 3,4,5-trihydroxybenzoic acid was not found in any oxidation, suggesting that as soon as the 3,4-dihydroxybenzoic acid was obtained it was oxidized to *o*-quinone instead of oxidizing the remaining ortho position to the trihydroxy acid.

Ring-Opening Reaction Main Products: C₄ Dicarboxylic Acids. Amongst the different compounds produced during the oxidation process, C₄-DCA were the main components in the mixture. They resulted from the aromatic ring-opening reaction, which required a strong oxidant. Figure 4.b shows how the concentration of the total C₄-DCA (which is the sum of succinic, maleic, malic, tartaric, and fumaric acids) changed through time, reaching a higher yield at 60 min for SA, at 50–60 min for VA, while for *p*HBA the highest yield was achieved at 90 min.

However, C₄-DCA were not the only acids produced. Other carboxylic acids, like formic, acetic, malonic, and oxalic acids, were identified and quantified, and their total concentration is presented conjunctly as “Other CA” in Figure 5. Most of these acids corresponded to degradation products of C₄-DCA, indicating an overoxidation. These acids increased their concentration through time, especially when *p*HBA was used as the starting compound, with the highest yield, 24.2 wt %, achieved at 75 min. VA gave rise to 17.3 wt % at 20 min, while SA to 12.9 wt % at 150 min. The remaining carbon, not

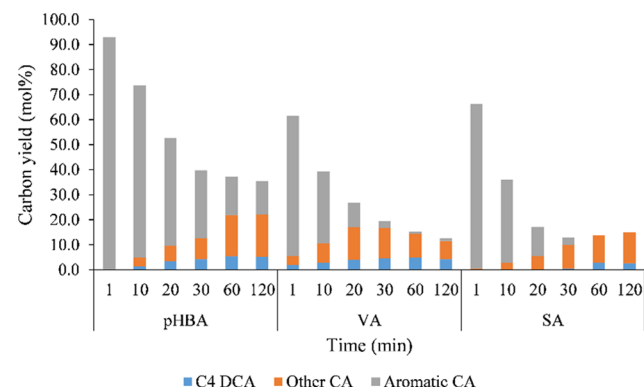


Figure 5. Carbon yield by families, based on the carbon proportion. (C₄-DCA: succinic, malic, maleic, tartaric and fumaric acids; Other CA: malonic, oxalic, acetic, and formic acids; Aromatic CA: VA, SA, *p*HBA).

quantified in this graphic representation, corresponds to gas losses (mainly CO₂) and nonquantified products in the solution.

All of the performed reactions started at neutral pH because it has been reported that many dicarboxylic acids are degraded in acidic conditions, even at lower temperatures.^{25,40} In contrast, at alkaline pH, many hydroxylated acids are obtained, which can be further oxidized to low-molecular-weight acids.⁴¹ Also, in alkaline conditions, more condensation products have been observed. The major observed C₄-DCA was succinic acid in all cases, with a lower amount of maleic acid in *p*HBA and tartaric acid in VA oxidations, as seen in Figure 6. Malic, fumaric, and tartaric acids were detected in small quantities in all cases.

In *p*HBA oxidation, the main acid obtained was succinic acid (5.4 wt %), while for maleic and fumaric acids production of up to 3.0 and 0.8 wt %, respectively, was observed. During the first 90 min, traces of malic acid were detected, the signal being very close to the limit of quantification, explaining its appearance and disappearance in several samples. After 90 min, the signal disappeared completely. Maleic acid concentration increased during the first 30 min and then decreased, being converted to other compounds, such as fumaric, malic, and succinic acids.

In VA oxidation, succinic acid was also the highest produced acid, achieving a maximum of 5.3 wt % at 60 min, then stabilizing up to 240 min. Malic acid was observed at the very first minutes, with a highest amount of 2.1 wt %, thus decreasing slowly until its disappearance after 180 min. Fumaric acid reached the highest yield (0.4 wt %) at 20 min, maintaining this percentage for the remaining time. Tartaric acid was also found at low concentrations for several minutes. The presence of tartaric and malic acids was associated with the hydroxylation of the double bond present in the maleic acid, which was the first obtained acid after the ring cleavage when *p*-quinone structures were oxidized.⁴¹ Maleic acid behavior was similar to the one observed in the *p*HBA reaction, increasing its concentration in the first 20 min, then decreasing due to conversion to other compounds.

In SA oxidation, succinic acid was practically the only C₄-DCA present in the mixture, with the highest amount of 3.8 wt %. For several minutes, small quantities of maleic (0.4 wt %) and fumaric (0.1 wt %) acids were observed, but these compounds disappeared after 60 min of reaction. No hydroxylated acids were quantified during the analyzed reaction time.

GC-MS analysis allowed identifying more compounds (presented in Table S1 and their chemical structures in Figure S2). Among them, different carboxylic acids were found, most of them precursors (e.g., isocitric, *cis*-aconitic, and 2,5-furandicarboxylic acids) or derivatives from the already quantified DCA (e.g., itaconic, tartronic, glycolic, and glyceric acids). The presence of these compounds was directly related to the oxidized model compounds, and therefore correlated to the original structure. With this data, it was possible to establish the oxidation pathway for each model compound and, consequently, to study the effect of the methoxy substituents in the aromatic structure toward the production of C₄-DCA.

Figure 7 shows the oxidation pathway for *p*HBA, which was identified after a detailed analysis of the data included in Table S1. Since the hydroxyl group in *p*HBA activated the aromatic ring, the first step in the oxidation was the hydroxylation in the ortho position, forming 3,4-dihydroxybenzoic acid, as con-

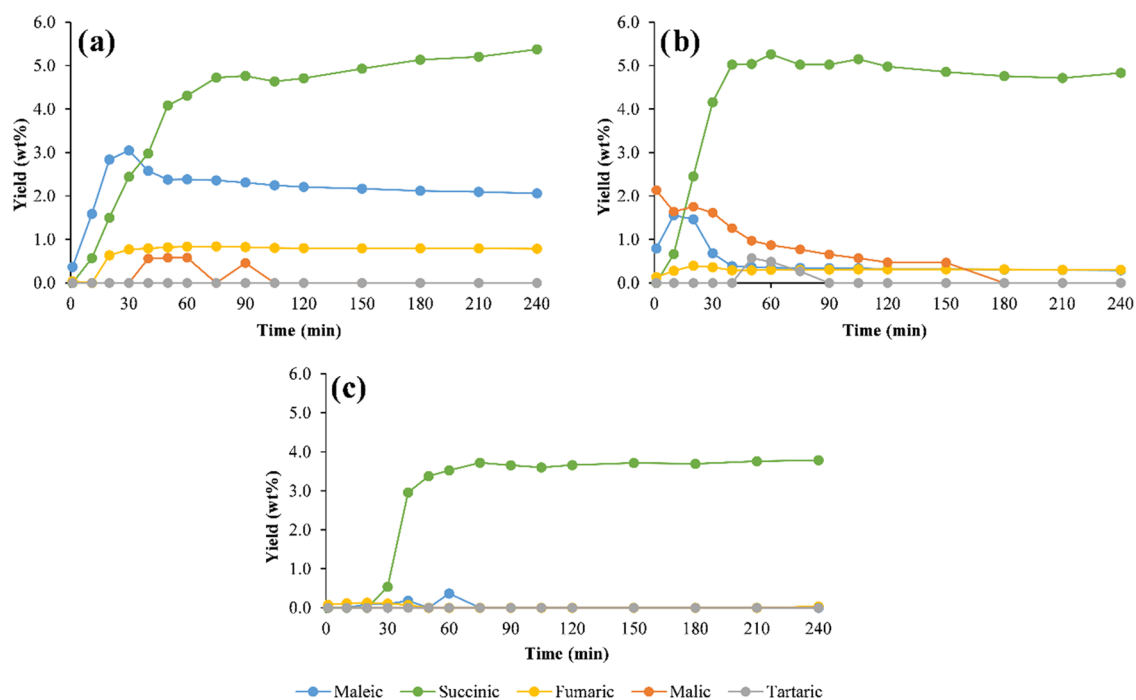


Figure 6. C₄-DCA yield for model compound oxidation: (a) pHBA, (b) VA, and (c) SA, at 140 °C.

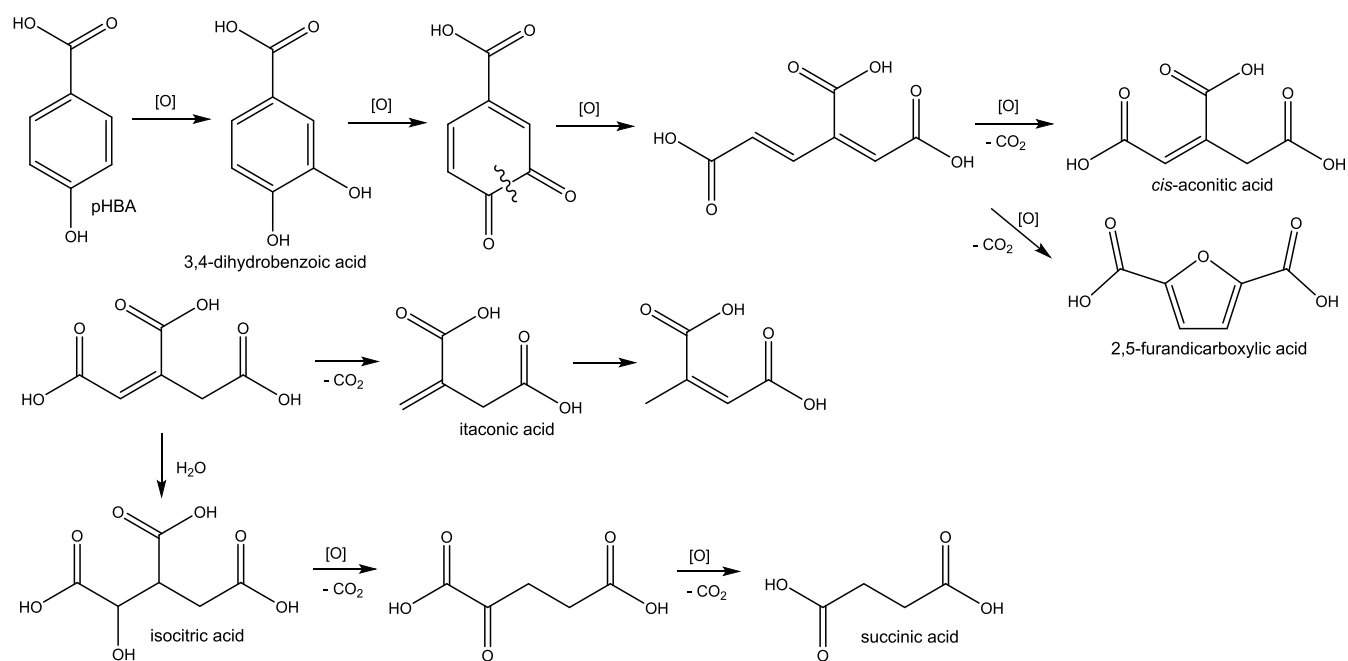


Figure 7. Proposed pathway for *p*-hydroxybenzoic acid oxidation to achieve succinic and itaconic acids.

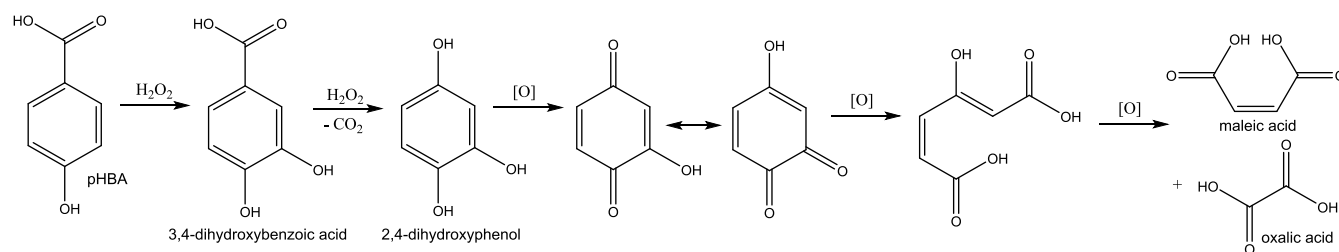


Figure 8. Proposed pathway for *p*-hydroxybenzoic acid oxidation to achieve maleic and oxalic acids.

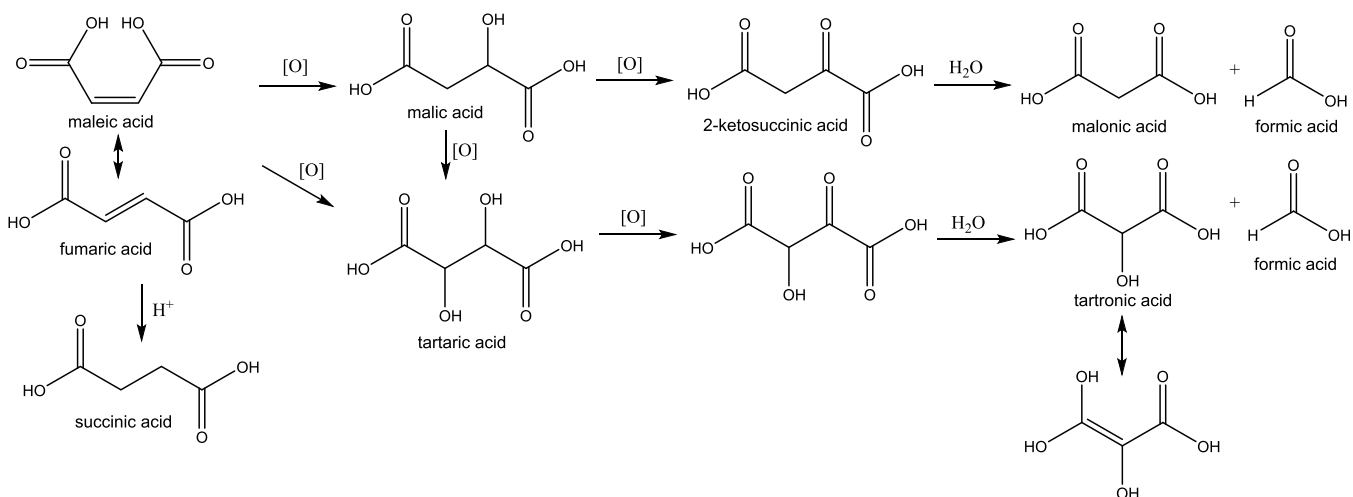


Figure 9. Proposed pathway for maleic acid conversion.

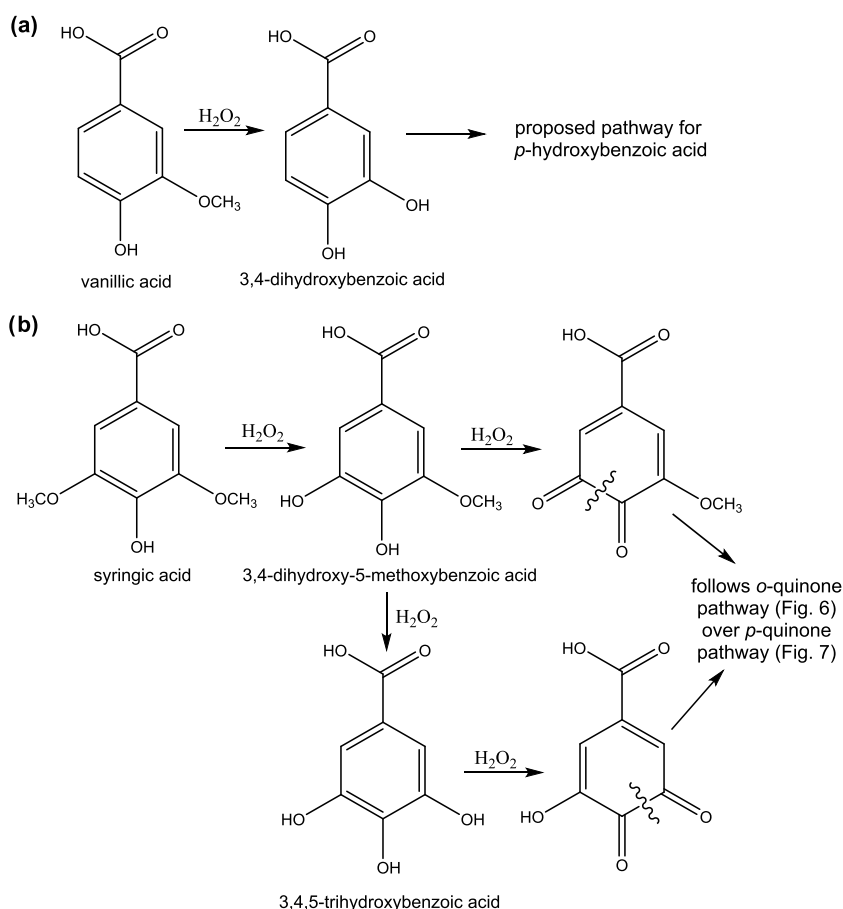


Figure 10. Proposed pathways for (a) vanillic acid and (b) syringic acid.

firming by Kang et al.⁴² Later, the hydroxyl groups were oxidized to a *o*-benzoquinone structure, which underwent a ring-opening reaction, to obtain a muconic acid derivative.^{13,22} After decarboxylation, several 6-carbon dicarboxylic acids were obtained, like *cis*-aconitic acid or 2,5-furandicarboxylic acid. These compounds were very reactive, and the *cis*-aconitic acid was decarboxylated to itaconic acid or converted to isocitric acid, being oxidized and decarboxylated to succinic acid. Most of these compounds showed a high response in GC-MS, confirming their presence along the reaction course.

*p*HBA can also react through a *p*-benzoquinone structure, as detailed in Figure 8. To form the *p*-benzoquinone structure, it must be first oxidized to 3,4-dihydroxybenzoic acid and then decarboxylated to 2,4-dihydroxyphenol, which could then be oxidized to a *p*-benzoquinone derivative. Later, this structure underwent a ring-opening reaction and a rearrangement to obtain maleic and oxalic acids as the main products.

Due to the double bond in maleic acid, this compound could be later oxidized to other compounds, such as malic acid and tartaric acid, as shown in Figure 9. These acids could be further

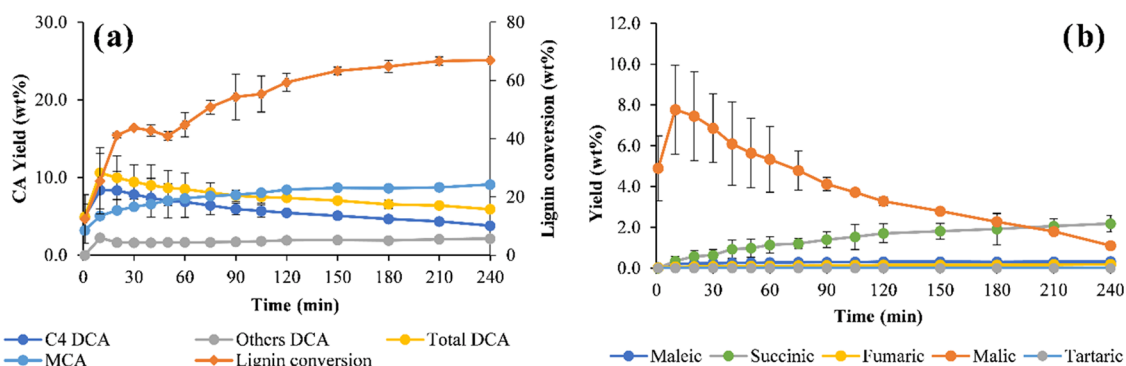


Figure 11. Indulin AT lignin oxidation with H_2O_2 , at $140\text{ }^\circ\text{C}$; (a) CA yield (C_4 -dicarboxylic acids [DCA], other DCA, and monocarboxylic acids [MCA]) and lignin conversion; (b) C_4 -DCA yield.

degraded to low-molecular-weight compounds, such as malonic acid, tartronic acid, 2,3,3-trihydroxy-2-propenoic acid, and formic acid.

The proposed pathway has been established for *p*-hydroxybenzoic acid oxidation, but it can also explain vanillic and syringic acid oxidation. However, some changes should be mentioned to elucidate the observed differences in the produced compounds and their respective yields due to the presence of methoxy substituents.

Vanillic acid has a methoxy group in the ortho position to the OH group. However, one of the first steps in the oxidation was the demethoxylation, as suggested by several authors,^{38,39,43} forming 3,4-dihydroxybenzoic acid, as shown in Figure 10a. This compound was the starting point of the oxidation in the pathway shown in Figure 7 for *p*HBA, therefore avoiding the aromatic ring's hydroxylation step. Both VA and *p*HBA followed the same reaction pathway, expecting to obtain the same products, especially for C_4 -DCA, as confirmed by the results presented in Figure 6 and Table S1. The main difference lay in the obtained yield for C_4 -DCA, which was higher for VA oxidation, and derived from the higher reactivity of the aromatic ring due to the presence of the methoxy group as an activating group, as explained before.

SA oxidation behaved slightly differently, having as the main product succinic acid accompanied by lower amounts of other C_4 -DCA. The small traces of maleic and fumaric acids were explained because when the molecule was demethoxylated, it formed 3,4,5-trihydroxybenzoic acid or 3,4-dihydroxy-5-methoxybenzoic acid, compounds that were easily oxidized to *o*-quinone derivatives (Figure 10b). Decarboxylation had been reported in the first steps for SA oxidation³⁹ but their products were not observed in the present study. The possibility of the reaction through the *o*-quinone pathway (Figure 7) is higher than through the *p*-quinone pathway (Figure 8) because various *o*-quinone derived structures were produced, leading to a higher yield of succinic acid and a lower amount of maleic and fumaric acids. The absence of maleic and fumaric acids explained the nonappearance of malic and malonic acids, which were obtained from hydroxylation and further decarboxylation of fumaric/maleic acids, as shown in Figure 9. A similar behavior concerning the low yield of maleic and fumaric acids was observed by Sun et al.⁴³ when lignin model compounds were oxidized with H_2O_2 using UV radiation. Also, SA oxidation generated propane-1,2,3-tricarboxylic acid (Table S1), which was more stable than *cis*-aconitic acid due to the lack of an unsaturated bond,

avoiding the production of succinic acid at yields as high as the ones observed for VA and *p*HBA oxidation.

Summarizing, it can be concluded that syringic acid oxidation mainly produced succinic acid at a higher selectivity. However, vanillic acid produced succinic acid at a yield higher (5.3 wt %) than syringic acid oxidation (3.8 wt %). The oxidation of *p*HBA gave rise to the highest succinic acid yield (up to 5.7 wt % after 4 h), but mixed with other acids at higher concentrations, with the disadvantage of needing several hours to achieve a competitive yield, when compared to the faster reaction undergone by VA and SA. Regarding other C_4 -DCA, only VA produced malic acid at significant yields, while *p*HBA produced unsaturated C_4 -DCA.

Oxidation of Hardwood and Softwood Lignin. Lignin was oxidized to evaluate the behavior observed with model compounds using real samples. For that reason, two lignins with different proportions of structural units, one from softwood and another from hardwood were chosen. Both lignins are derived from the kraft pulping process, hence avoiding any difference associated with the pulping process. Indulin AT, chosen as the softwood lignin, is commercialized by MeadWestvaco Corporation, having a S/G/H ratio of 0.97:3.²⁷ The hardwood lignin was isolated from a black liquor obtained from a *E. globulus* kraft pulping mill (The Navigator Company, Portugal), presenting a S/G/H ratio of 65:29:6.²⁸ The two lignins were chosen to represent kraft hardwood and softwood lignins. Since it was not possible to find hardwood and softwood lignins from the same provider, thus guaranteeing the application of the same process, this option was considered adequate to conduct the present study. Both lignins were solubilized in a 0.1 mol/L phosphate buffer to ensure that the lignin was at a pH around 7 during the oxidation process, avoiding precipitation in an acidic environment. However, this buffer caused a partial degradation of peroxide inside the reactor, therefore lowering its oxidation potential.

Figure 11 summarizes the results obtained for Indulin AT (softwood lignin) conversion after 4 h, which was 68%. The amount of monocarboxylic acids (obtained from lignin degradation into C_4 -DCA) increased up to 14 wt % after 4 h. Malic and succinic acids were the main DCA obtained; the malic acid yield was high at the starting of the reaction (8.0 wt % at 10 min), but then decreased to 1.0 wt % after 4 h, while the succinic acid yield increased slowly, reaching a maximum of 2.5 wt % at the end of the reaction (240 min). Small quantities of maleic and fumaric acids were also observed but at yields lower than 0.30 wt %.

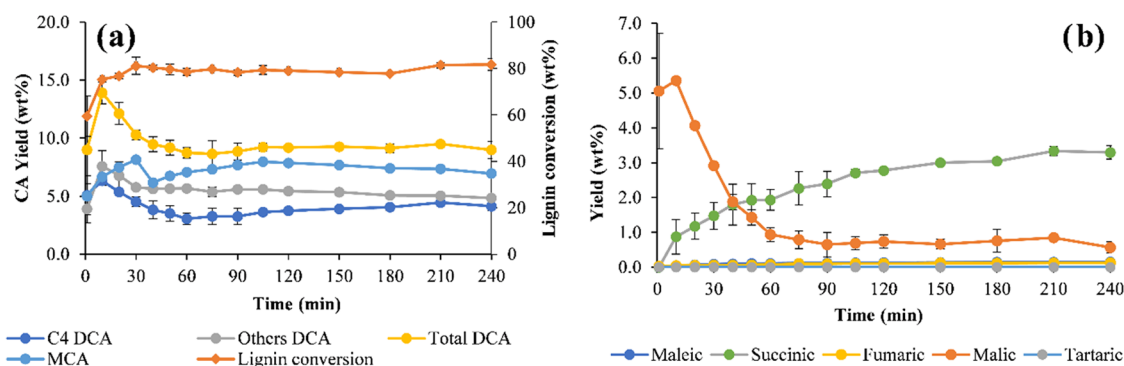


Figure 12. Hardwood lignin oxidation with H_2O_2 , at $140\text{ }^\circ\text{C}$; (a) CA yield (C_4 -dicarboxylic acids [DCA], other DCA, and monocarboxylic acids [MCA]) and lignin conversion; (b) C_4 -DCA yield.

Figure 12 illustrates that *E. globulus* kraft lignin (hardwood lignin) oxidation reached a total conversion of 83% after 30 min, then remained practically constant. C_4 -DCA were also produced in the first minutes, while the monocarboxylic acids' yield increased, but only slightly when compared to softwood lignin. The main DCA obtained were also malic and succinic acids. Malic acid showed the same behavior as the one observed for Indulin AT lignin, i.e., achieving a high yield at the starting of the reaction (5.3 wt % at 10 min) but then decreasing quickly to 0.5 wt % after 4 h. Succinic acid yield increased, reaching a maximum of 3.2 wt %. Small quantities of maleic and fumaric acids were detected but at yields lower than 0.13 wt %.

The presence of malic acid during the first minutes of the reaction was associated with the high content of guaiacyl units in both lignins, which result was similar to the one observed for VA oxidation. In this case, softwood lignin was composed mainly of guaiacyl units and therefore produced more malic acid than hardwood lignin, which has a S/G ratio of 65:29. However, the higher yield of malic acid observed during the reaction starting phase in both lignins, comparatively with VA oxidation, could be caused by the solution's slightly different pH conditions. When lignins were oxidized, the buffer kept the pH around 6.5–7.0 during the overall reaction avoiding lignin precipitation. In contrast, in the model compound oxidation, which was done without a buffer, the medium was quickly acidified and then back to neutral pH (Figure S1). When the reaction took place at a higher pH, there was a higher chance to obtain hydroxylated compounds in the peroxide oxidation, as previously reported.⁴¹ During the first minutes of model compound oxidation, the acidic pH could prevent malic acid formation at high yields, converting any produced malic acid to succinic acid. Even though malic acid was obtained at high yields during the first minutes of lignin oxidation, it was quickly converted to succinic acid or degraded to low-molecular-weight compounds due to the slightly acidic environment.

E. globulus kraft lignin gave rise to the highest conversion in the first 30 min, while Indulin AT needed more than 210 min to reach the highest conversion, but without attaining the level achieved for hardwood lignin. It has been reported that hardwood lignins are more reactive toward peroxide oxidation when compared to softwood lignins due to structural differences.^{14,26} Since the hardwood lignin had a higher S/G ratio, it became more reactive against peroxide oxidation due to the high content of S units, which was also observed in SA comparatively to VA.

VA showed a higher succinic acid yield than SA oxidation, so softwood lignin was expected to result in a higher succinic acid yield, based only on the lower S/G ratio (due to higher content on guaiacyl units). However, due to S groups' higher reactivity, hardwood lignin (with a higher S/G ratio) had a higher reactivity and was degraded easily. This fact helped open the lignin structure, making more lignin fractions available for further oxidation toward DCA and presenting a slightly better succinic acid yield, as observed in Figure 12. It was also noticed that *E. globulus* kraft lignin oxidation produced succinic acid faster than Indulin AT lignin, while malic acid was also degraded faster. In several studies, lignin peroxide oxidation using lignins with a high S/G ratio showed a higher yield for dicarboxylic acids than lignins based on guaiacyl moieties (softwood lignins), especially under an acidic pH.^{16,23,26,44} Ma et al.²⁶ reported that a higher amount of methoxy groups in lignin had a positive effect on the total dicarboxylic acid yield (quantified in their work as C_2 – C_6 DCA, and not only C_4 -DCA), while the presence of these groups had a negative influence on lignin depolymerization to monomeric phenolic compounds. Although methoxy groups apparently hindered lignin depolymerization to phenolic compounds, they activated the aromatic ring creating electron-rich areas that competed with the alkyl side chains between aromatic lignin monomeric units, enhancing ring-opening reactions. Hardwood lignin showed a higher yield of the total DCA, as seen in Figures 11a and 12a. Therefore, this work's findings corroborated the model proposed by Ma et al. for DCA production, even though this model was not entirely focused on C_4 -DCA. Still, DCA yields changed through time, especially with softwood lignin (due to malic acid degradation), which was not considered in their model. They evaluated a specific point of the reaction time and not the variations along time giving rise to DCA production and degradation.

In conclusion, the *E. globulus* kraft lignin seems to be a better lignin than Indulin AT to obtain succinic acid by peroxide oxidation. It was degraded faster than Indulin AT lignin, produced malic acid, and other acids at lower yields, and gave rise to succinic acid at higher yields through a faster reaction. This finding confirmed that lignins with a higher S/G ratio could be better for peroxide oxidation and ring-opening reactions toward C_4 -DCA, especially succinic acid. However, it should be noted that a more detailed analysis should include the different bonding structures of lignin, which vary from biomass to biomass and the used pulping techniques. Namely, lignins with high condensation degrees have been reported as very stable toward oxidation. Future studies must be

conducted to increase and optimize C₄-DCA yields, taking into account the type and origin of lignin, the reactor design, and presence of catalysts. Moreover, the profit exploitation of lignin must consider a cascade of products in its value chain, for which C₄-DCAs can contribute.

CONCLUSIONS

This study demonstrated that *p*-hydroxybenzoic acid, vanillic acid, and syringic acid peroxide oxidation produced C₄ dicarboxylic acids (succinic, malic, fumaric, maleic, and tartaric acids) at different contents, yields, and kinetics, which was justified by the different amounts of methoxy groups present in the aromatic structure. SA had the higher reactivity toward oxidation, while *p*HBA had the lower one due to the activation effect of the methoxy groups in the aromatic ring. The observed succinic acid yield followed the relation *p*HBA > VA > SA but needed longer times for *p*HBA to reach a competitive yield. VA and *p*HBA produced other C₄-DCA besides succinic acid, SA oxidation being much more selective toward succinic acid.

When two lignins with different S/G/H ratios were oxidized, the softwood lignin (Indulin AT) produced a lower amount of succinic acid than a hardwood lignin (lignin obtained from *E. globulus* black liquor). Moreover, the hardwood lignin reacted faster than the softwood lignin due to the higher reactivity observed in syringyl units. Both lignins produced malic acid at an initially high yield, then converted to other compounds during the reaction time. Summarizing, it can be concluded that lignins richer in syringyl groups have a higher reactivity toward peroxide oxidation reactions. They are converted faster, producing succinic acid at higher yields, justified by the activation effect of methoxy groups in aromatic rings.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.iecr.0c05085>.

Additional graphics of the pH behavior during model compound oxidation (Figure S1); chemical structures of the compounds detected by GC-MS analysis for *p*HBA, VA, and SA oxidation with H₂O₂ at 140 °C (Figure S2); a table with the compounds identified by GC-MS for *p*HBA, VA, and SA oxidation at 140 °C (Table S1) (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All authors contributed equally.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CA	carboxylic acids
DCA	dicarboxylic acids
HPLC	high-performance liquid chromatography
GC-MS	gas chromatography-mass spectroscopy
MCA	monocarboxylic acids
<i>p</i> HBA	<i>p</i> -hydroxybenzoic acid
VA	vanillic acid
SA	syringic acid

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