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Kinetics of Vanillin and Vanillic Acid Production from Pine Kraft Lignin

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Abstract: Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the main component of natural vanilla and a relevant substance in the flavoring and aromatic industries. This study presents a kinetic model to explain both vanillin and vanillic acid concentrations achieved in the alkaline oxidation of pine kraft lignin. Considering that they come from the same precursors, this approach allows an understanding of vanillin production with reaction conditions that minimize the vanillic acid pathway directly from the lignin oligomers, thus maximizing vanillin production. This study involves the effects of oxygen partial pressure, temperature, and the presence or absence of a catalyst ($CuSO_4$ and $Fe_2(SO_4)_3$ mixture) on the vanillin and vanillic acid yields. An adapted reactor (M/K Systems Inc., Williamstown, MA, USA) with a recirculation and spray liquids system was used in the experiments. The experiments were performed using one liter of a solution of NaOH 2 M and 60 g of lignin. During the lignin oxidation reaction, liquid samples were analyzed at different times (from 0 to 200 min). The oxidation products were quantified by liquid chromatography (HPLC). The catalyzed experiments presented higher maximum vanillin yields than the non-catalyzed ones (39.2–39.6% on nitrobenzene oxidation) achieved at 150 °C. A kinetic model is proposed where the kinetic parameters were estimated using Monte Carlo methods, fitting satisfactorily to the experimental results. The statistical analysis of the kinetic parameters showed that all the studied variables significantly affect the vanillin yield.

Keywords: vanillin; vanillic acid; pine kraft lignin; alkaline O_2 oxidation; kinetic model

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1. Introduction

The valorization of lignin applying the biorefinery concept has enormous potential. Currently, energy production in paper mills is the primary use of lignin to ensure the economic viability of the chemical pulp production process. Lignin can be converted into biobased products, process steam, and bioenergy, applying the biorefinery concept in chemical pulp mills. However, there is increasing interest in the valorization of lignin produced by biorefinery processes as a renewable resource of high-value-added aromatic compounds rather than being burned. Potential high-value products from lignin include carbon fibers, polymers, and various chemicals [1,2]. Kraft pulping is the dominant process in pulp production, in which most lignin and some hemicelluloses are dissolved in the alkaline liquor, constituting the black liquor burned in the recovery system. Worldwide, a minor fraction of generated kraft lignin is used to produce dispersants for dyes and pesticides [2,3]. The forest biorefinery concept application can generate a new economically and environmentally sustainable value chain in the Argentine Northeast, concerning both pine chemical pulp plants and pine sawdust biorefineries from sawmills [4].

The highly complex polymeric chemical structure of lignin and its variability make it difficult to process, limiting its use as an industrial raw material. Therefore, the most viable and currently most relevant strategy for its exploitation is obtaining low-molecular-weight phenolic compounds by depolymerization [1].

Vanilla is one of the most relevant compounds in the flavoring industry. Its main component is vanillin (4-hydroxy-3-methoxybenzaldehyde). Its properties were initially known by Aztecs, who obtained it from "Vanilla" (*Vanilla planifolia*), a tropical orchid grown in Mexico, Madagascar, Tahiti, and Indonesia, among other countries [5]. The first antecedent that proves the feasibility of obtaining vanillin from lignin dates from 1898 and consisted of oxidizing the residual liquor from sulfite pulping with air and ferric chloride. A process for producing vanillin from petroleum was patented in 1933, displacing almost totally the vanillin production from lignin at the end of the 20th century. Since 1993, Borregaard (Norway) has been the only company that produces lignin-based vanillin, using lignosulfonate as raw material [3,6].

The global vanilla and vanillin market sizes in 2020 reached 2600 and 37,300 tons, respectively. Growth expectations for 2026 are 3100 and 60,900 tons, respectively [7]. In economic terms, this market represented USD 960M in 2023, with a forecast to reach around USD 1400M in 2028, mainly driven by the growth of the Asian market [8]. The composition of the vanillin global market based on the raw material used is 12.5% derived from lignin, and less than 0.5% comes from natural sources [9]. The rest is obtained from guaiacol, a petroleum derivative, since this process has economic advantages over the other two [10]. Vanillin has a commercial value of around USD 20 kg^{-1}, without relevant changes expected in the coming years [7,8]. Also, that produced from lignin is usually USD 1–2 kg^{-1} more expensive than that made from guaiacol due to its preference by manufacturers of chocolates and perfumes (particularly in the markets of Europe and Japan) [11].

Lignin oxidation is usually carried out in strongly alkaline media, at high pressures, in the presence of oxygen and catalysts. High-value aldehydes such as vanillin, vanillic acid, and other degradation compounds of lower molecular weight are obtained as products of this oxidation [12]. Figure 1 shows a diagram of the mentioned products. The use of coniferous lignin to produce vanillin facilitates the separation of the reaction products since it is practically the only aldehyde formed, unlike in the oxidation of hardwood lignins, where syringaldehyde is present in large proportions.

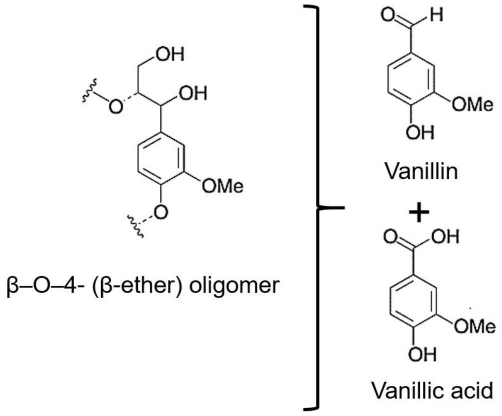
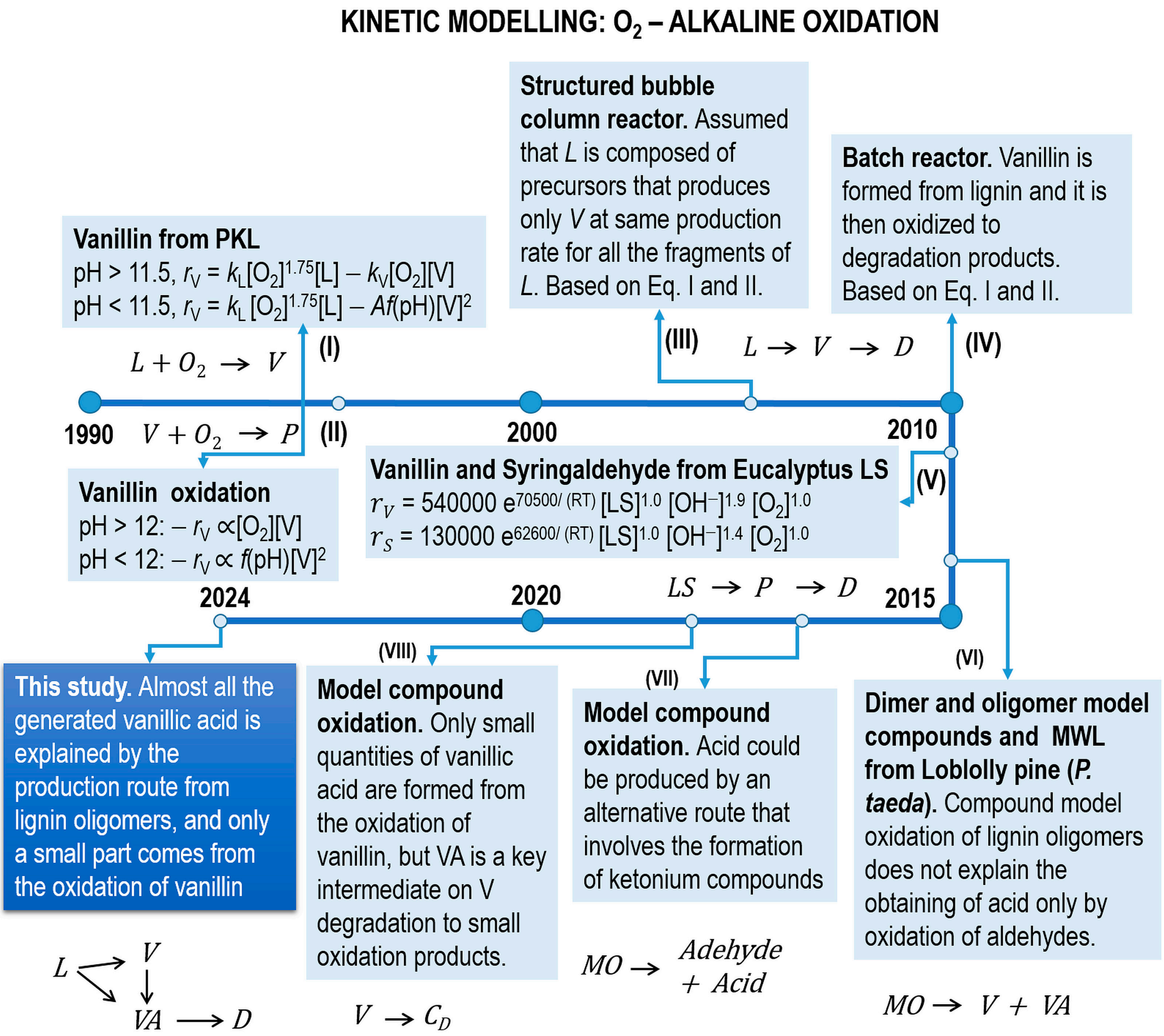


Figure 1. A diagram of the oxidation of β–O–4- (β-ether) oligomers from lignin and the obtained products [12].

The kinetics of the vanillin conversion reaction from lignin depends on several factors, such as the reaction conditions, the catalysts, and the lignin composition. Generally, it involves lignin depolymerization to produce vanillin as one of the products. The kinetics of these reactions can be described by mathematical models that consider the reaction rate and the reactant and product concentrations over time. The kinetics of the lignin conversion to vanillin and vanillic acid can be complex due to its chemical structure nature and the formation of intermediate products.

Previous kinetic models do not consider vanillic acid production or contemplate it only as a degradation product of vanillin [12–19]. In contrast, new studies indicate that only small quantities of vanillic acid are formed from the oxidation of vanillin [19]. Additionally, analogous behaviors were observed for model compounds of aldehyde and acid, which does not explain the obtaining of acid only by aldehyde oxidation [12]. Rinesch et al., using model compounds, explained the acid produced by an alternative route that involves the formation of ketonium compounds [18]. A similar study using Eucalyptus lignosulfonate showed analogous results [17]. Since the large amounts obtained of vanillic acid could not be explained by previous models, an alternative one is proposed, including its obtainment from lignin oligomers. Recent studies have shown this possibility from lignin model compounds; however, the previously proposed kinetic models did not contemplate this option. Figure 2 [13–16,20] summarizes the previously proposed kinetic models and the studies that allowed the proposed model presented here.



KINETIC MODELLING: O_2 – ALKALINE OXIDATION

Vanillin from PKL
pH > 11.5, $r_V = k_L[O_2]^{1.75}[L] - k_V[O_2][V]$
pH < 11.5, $r_V = k_L[O_2]^{1.75}[L] - Af(pH)[V]^2$

Vanillin oxidation
pH > 12: $-r_V \propto [O_2][V]$
pH < 12: $-r_V \propto f(pH)[V]^2$

Structured bubble column reactor. Assumed that *L* is composed of precursors that produces only *V* at same production rate for all the fragments of *L*. Based on Eq. I and II.

Batch reactor. Vanillin is formed from lignin and it is then oxidized to degradation products. Based on Eq. I and II.

Vanillin and Syringaldehyde from Eucalyptus LS
$r_V = 540000\ e^{70500/(RT)}\ [LS]^{1.0}\ [OH^-]^{1.9}\ [O_2]^{1.0}$
$r_S = 130000\ e^{62600/(RT)}\ [LS]^{1.0}\ [OH^-]^{1.4}\ [O_2]^{1.0}$

This study. Almost all the generated vanillic acid is explained by the production route from lignin oligomers, and only a small part comes from the oxidation of vanillin

Model compound oxidation. Only small quantities of vanillic acid are formed from the oxidation of vanillin, but VA is a key intermediate on V degradation to small oxidation products.

Model compound oxidation. Acid could be produced by an alternative route that involves the formation of ketonium compounds

Dimer and oligomer model compounds and MWL from Loblolly pine (*P. taeda*). Compound model oxidation of lignin oligomers does not explain the obtaining of acid only by oxidation of aldehydes.

Figure 2. Previous studies on kinetic modeling of O_2 alkaline oxidation. PKP: *Pinus* kraft lignin; ELS: Eucalypt lignosulfonate; P: oxidation products, aromatic aldehydes (vanillin and syringaldehyde); *D*: degradation products; MO: β–O–4- (β-ether) oligomer; *L*: lignin; *V*: vanillin; *VA*: vanillic acid; C_D: mall acids, alcohols, and other monophenols, even dimers; MWL: milled wood lignin, *r*: reaction rate; k_L, k_V, and A: kinetic model constants. (I) Fargues et al., 1996 (a) [13]; (II) Fargues et al., 1996 (b) [14]; (III) Sridhar et al., 2005 [15]; (IV) Araújo et al., 2010 [16]; (V) Santos et al., 2011 [17]; (VI) Azarpira et al., 2014 [12]; (VII) Rinesch et al., 2017 [18]; (VIII) Zhu et al., 2018 [19].

The complex and heterogeneous chemical structure of lignin, such as the effects of different parameters on yield and selectivity, makes it difficult to fully understand the reaction mechanism of converting lignin to vanillin. One challenge is to explain the large quantities of vanillic acid obtained under the strongly oxidative conditions usually used. Understanding vanillic acid production could also optimize the pathway that favors obtaining aldehyde over acid since these products could come from the same precursors. This study aims to explain both vanillin and vanillic acid concentrations and the effect that temperature, partial pressure of oxygen, and the catalyst have on these concentrations.

2. Materials and Methods

2.1. Raw Material

Black liquor from the pine kraft pulping (*Pinus elliottii* and *P. taeda* mixture, kraft liner mill, Misiones, Argentina) was used as a lignin source. The solid content of this liquor was 28.7%. The procedure for lignin recovery from pine kraft black liquor, operational conditions, and characterization are shown in Figure 3. Lignin was precipitated from black liquor by acidification with 30% H_2SO_4 to pH 2 in a stirred glass reactor (4 L) at 80 °C. Precipitated lignin was filtered using a metal screen (200 mesh) and vacuum, and the remainder of the lignin in liquor was recovered by filtering with a cloth felt. Both fractions were mixed and dried at room temperature. The precipitated lignin was stored in a hermetically sealed container.

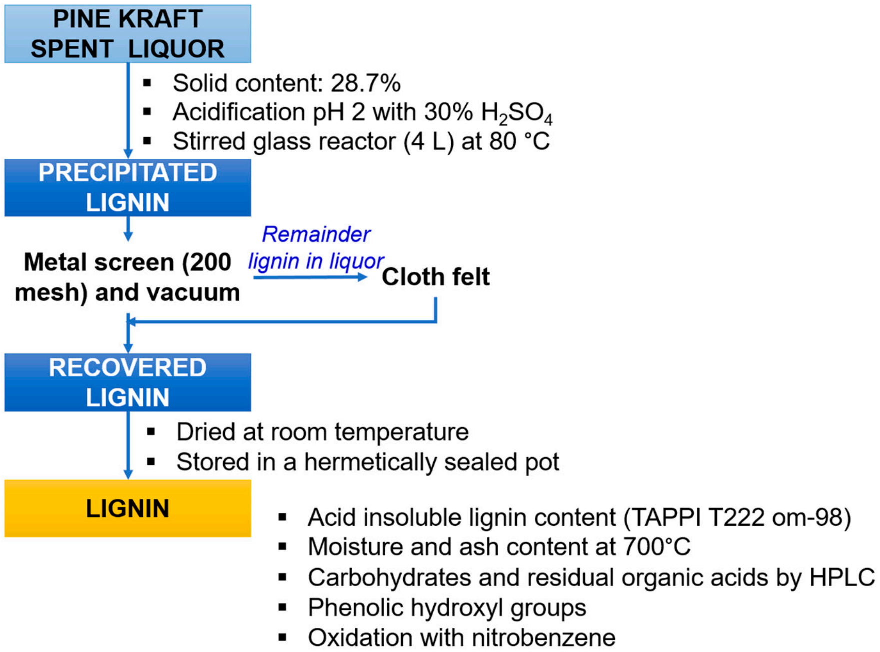


Figure 3. Procedure and conditions for lignin recovery and characterization.

The acid-insoluble lignin content (Klason lignin) was determined by TAPPI T222 om-98. Lignin was characterized by moisture and ash content at 700 °C, carbohydrates, and residual organic acids by liquid chromatography (Waters Alliance HPLC, Milford, MA, USA) with refractive index and diode array detectors. The phenolic hydroxyl group content was determined by UV spectroscopy (Shimadzu, Kyoto, Japan) from the absorption difference of phenolic units in neutral and alkaline solutions at 300 and 360 nm [21]. The unconjugated phenolic structures (I and III) are identified with a maxima absorbance at 300 nm and 350–360 nm, whereas the conjugated structures (II and IV) are at 350–370 nm. The change in the sample molar absorptivity ($\Delta\varepsilon$) was compared with model compounds (I, II, III, and IV). In addition, oxidation with nitrobenzene was performed according to the procedure described in the literature [22] to determine the maximum yield in vanillin conversion from this lignin [23].

2.2. Alkaline O_2 Oxidation

The lignin oxidation assays were carried out following factorial design 23 to determine the effect of oxygen partial pressure (P_{O_2}), which was 2 and 4 kg cm^{-2}; temperature (T) (130–150 °C); and the presence of a catalyst (with–without) on the amount of vanillin and vanillic acid produced. The reaction time was varied between 0 and 200 min. In all the assays, 60 g of dry lignin and free of ash was dissolved in a liter of a 2 M NaOH solution. The dissolved oxygen concentration in an aqueous solution of sodium hydroxide was estimated according to the model proposed by Mathias [24], considering the temperature and pressure of the alkaline oxidation. The dissolved oxygen concentration (C_{O_2}) for working conditions is summarized in Table 1.

Table 1. Dissolved oxygen concentration for working conditions.

T (°C)	130		150	
P_{O_2} (kg cm^{-2})	2	4	2	4
C_{O_2} (mmol L^{-1})	1.18	1.91	1.20	2.01

$P_{O_2}C_{O_2}$ The catalyzed assays were performed with 2.21 g of Cu^{2+} and 0.19 g of Fe^{3+} per 100 g of lignin, using $CuSO_4{\cdot}5H_2O$ and $Fe_2(SO_4)_3$, respectively. The experiments were carried out in an adapted laboratory pulp digester of M/K Systems Inc. (7 L) with recirculation, liquid spraying, a gas (O_2) injection system, and a refrigerated sample collector (Figure 4).

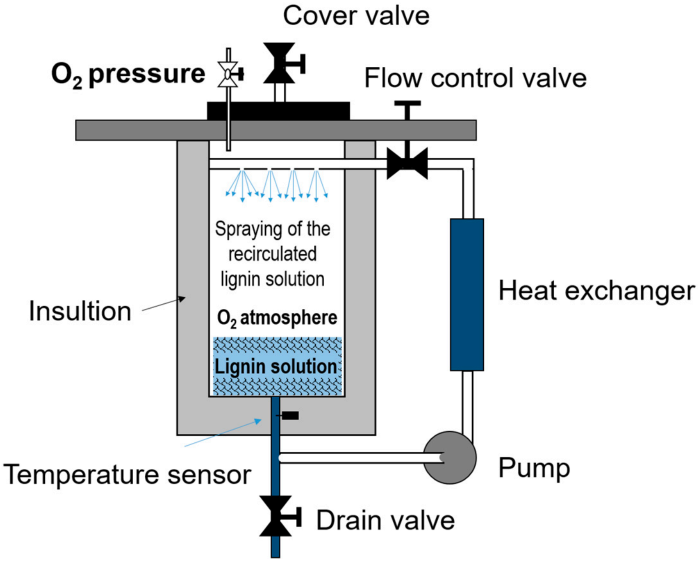


Figure 4. The scheme of the digester with a recirculation and liquid spraying system.

The alkaline solution was charged to the reactor, which was programmed to reach the desired temperature in 20 min. Then, the gas valve was opened to purge the air in the reactor until the pressure gauge matched the steam pressure corresponding to the working temperature (130 or 150 °C).

The oxygen was injected (time = 0), maintaining the pressure at the desired value. During the reaction, liquid samples were taken at different times (between 0 and 200 min) for the analysis.

Vanillin and vanillic acid were quantified by liquid chromatography (HPLC) using an Aminex HPX-87H column with a diode array detector. Calibration with vanilla and vanillic acid external standards was used to quantify these compounds in the samples. The samples were acidified to pH 2 with H_2SO_4 and centrifuged, and the supernatant was filtered through a nylon membrane with 0.2 µm of pore size. The chromatographic conditions were mobile phase H_2SO_4 4 mM/CH_3CN: 90/10, flow rate: 0.6 mL min^{-1}, column temperature: 55 °C.

2.3. Kinetic Model and Data Analysis

The kinetic model was developed supposing that (i) lignin is composed of a potentially oxidizable fraction (*L*) to vanillin (*V*) and vanillic acid (*VA*), and subsequently to other degradation compounds (*D*), and a non-oxidable fraction by this pathway; (ii) *L* is determined by nitrobenzene oxidation; (iii) *L* is related to the oxidized fraction (*V*, *VA*, and *D*) by a "reactive fraction" α (0 < α < 1); (iv) vanillic acid is also obtained by vanillin oxidation; (v) degradation products (*D*) derive from vanillic acid. These assumptions, in particular (i), were implemented to explain the large amounts of vanillic acid obtained, not justified by previous models. The model proposed for the reactions involved in vanillin and vanillic acid production from pine kraft lignin by alkaline oxidation is shown in Figure 5.

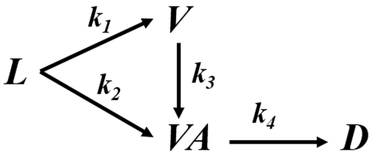


Figure 5. Reaction pathway by alkaline O_2 oxidation. *L*: oligomers from lignin potentially oxidizable to vanillin (*V*), vanillic acid (*VA*), and degradation products (*D*).

The model for alkaline oxidation assumes that vanillin and vanillic acid are formed directly from the lignin oligomers [12,18]. Furthermore, vanillin is degraded to vanillic acid, which generates degradation compounds. Based on these assumptions, a pseudo-first-order kinetic model concerning *L*, *V*, *VA*, and *D* is suggested, proposing Equations (1)–(4). The kinetic constants of the equations were deduced by experiments at different temperatures and oxygen partial pressures and a catalyst presence or absence by a numerical integration using the fourth-order Runge–Kutta method. The parameters k_1 to k_4 and α were obtained by minimizing the difference of squares between the experimental values and those obtained by the model.

$$d[C_L]/dt = -(k_1 + k_2)([C_L] - (1-\alpha)[C_{L_o}]) \tag{1}$$

$$d[C_V]/dt = k_1([C_L] - (1-\alpha)[C_{L_o}]) - k_3[C_V] \tag{2}$$

$$d[C_{VA}]/dt = k_2([C_L] - (1-\alpha)[C_{L_o}]) + k_3[C_V] - k_4[C_{VA}] \tag{3}$$

$$d[C_D]/dt = k_4[C_{VA}] \tag{4}$$

C_L is *L* concentration at time = t min; C_{L_o} is *L* concentration at time = 0 min; and C_V, C_{VA}, and C_D are the vanillin, vanillic acid, and degradation compound concentrations, respectively. The concentrations are expressed as C_V in mmol of vanillin per liter, and C_L, C_{L_o}, C_{VA}, and C_D in mmol equivalents to vanillin per liter.

Oxygen partial pressure was kept constant, so its concentration was not considered. However, its effect and that of all the other variables were evaluated by an analysis of variance with a confidence level of 95%, using STATGRAPHICS Centurion 18. All of the analysis was accomplished until two hours of reaction, considering that some tests were carried out only during that time. The samples were taken at 0, 10, 20, 30, 45, 60, 80, 100, and 120 min.

3. Results and Discussion

3.1. Raw Material

The lignin precipitation yield was 38.8% concerning the solid content in the liquor. The results of the characterization of the precipitated lignin were as follows: 90.4% total lignin (Klason lignin), 4.6% inorganic, 1.4% organic acids, and 1.0% carbohydrates. The ashes are slightly higher, and the carbohydrates are lower than the Indulin commercial lignin [25]. It did not present monomeric sugars as impurities.

The results of the quantification of phenolic hydroxyls expressed as grams of phenolic hydroxyls per 100 g of dry lignin were as follows:

- I: 2.79; II: 0.39; III: 1.29; IV: 0.05
- Non-conjugated phenolic structures (I + III): 3.18
- Conjugated phenolic structures (II + IV): 0.44
- Total amount of phenolic hydroxyl groups (I + II + III + IV): 4.52

Phenolic OH is slightly lower than Indulin and pine kraft lignin from Plymouth Mill of Domtar [26,27]. These lignin characteristics reflect severe pulping conditions [28] and a consequent low reactivity.

The analytical oxidation with nitrobenzene reached a yield of vanillin and vanillic acid of 4.10% and 0.49%, respectively, both calculated on the Klason lignin of the sample. These values are low compared to those of pine kraft lignin from Plymouth Mill of Domtar (15.6% and 4.7%), Indulin (15.0% and 3.9%), and *Pinus taeda* milled wood lignins (41.7% and 4.1%) [27].

In the analyzed region, the final pH ranged between 14.0 and 13.4, which means that vanillin production and degradation rates are directly proportional to the concentration of lignin and vanillin, respectively [13].

3.2. Alkaline O_2 Oxidation

The liquor samples were taken at different times during the alkaline O_2 oxidation reaction for each condition to determine their effect on the vanillin and vanillic acid concentrations. Figure 6 shows this evolution for each condition.

The evolution of vanillin and vanillic acid concentrations in mild conditions is shown in Figure 6a. During the first 120 min, vanillin and vanillic acid concentrations behave similarly in the catalyzed and uncatalyzed reactions. A different behavior occurs in the most severe condition (Figure 6d), where the vanillin concentration showed a fast decrease after 45 min in the uncatalyzed reaction, decreasing more slowly and only after 60 min in the catalyzed experiences. The different behaviors found between the mildest and the most severe conditions coincide with those described by Wu and Heitz [27], who observed that Fe^{3+} has almost no effect on the former but does on the latter, possibly due to the activation energy necessary to form the intermediary that intervenes in the reaction.

The effect of Cu^{2+} and Fe^{3+} ions on vanillin and vanillic acid concentrations shown in Figure 6b is notable. For the uncatalyzed experience, the concentration of vanillin increases only up to 45 min of reaction and then decreases quickly. However, this concentration grows to 100 min for the catalyzed reaction, showing a flat maximum, with little difference between 80 and 120 min. Vanillic acid decreases more significantly in the uncatalyzed experience, but the behavior in both assays is similar from the start of the reaction to 80 min.

Figure 6c shows that the catalyzed and non-catalyzed reactions behave similarly during the first hour. Then, the vanillin concentration stops growing significantly for the uncatalyzed experience, peaking at 100 min of reaction and then decreasing. However, for the catalyzed experience, the vanillin concentration continues to grow steadily.

It is evident that when working at low partial pressures of oxygen, the concentration of vanillin grows linearly, at least during the first hour (Figure 6a,c). On the other hand, the experiences with a higher partial pressure of oxygen (Figure 6b,d) present steeper initial slopes than the previous ones, with higher degradation rates, especially for non-catalyzed tests.

Note that although the differences are minimal, the catalyzed curves present steeper initial slopes in all experiments than the non-catalyzed ones. These results coincide with the literature since Cu^{2+} could favor the free radical oxidation pathway, increasing between 3 and 10% compared to non-catalyzed reactions, where the ionic pathway is predominant [29].

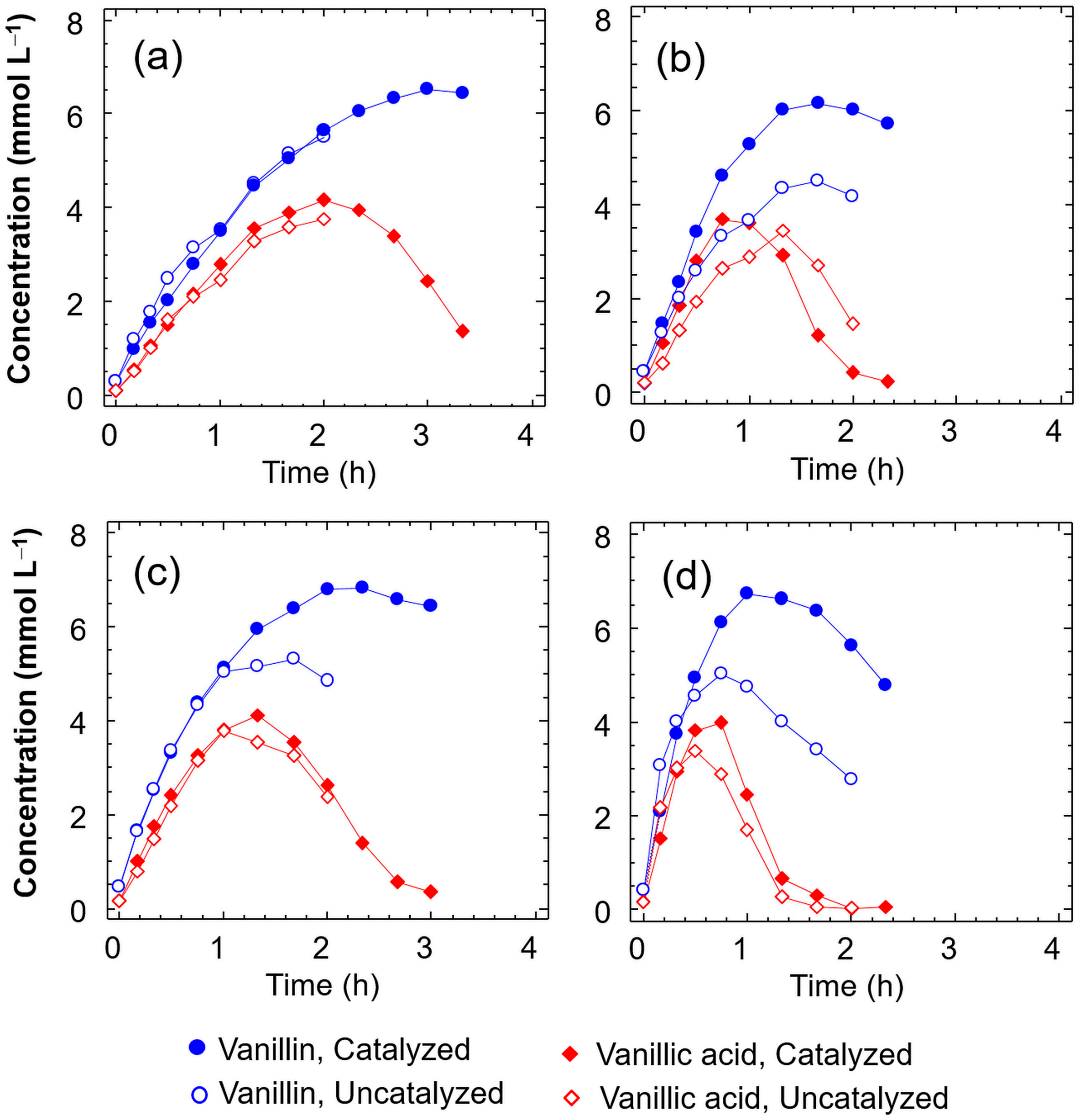


Figure 6. Evolution of vanillin and vanillic acid concentrations. Conditions: Temperature (°C)/oxygen partial pressure (kg cm^{-2}): (**a**) 130/2; (**b**) 130/4; (**c**) 150/2; (**d**) 150/4.

The maximum obtaining of vanillin and vanillic acid is considered to be generated in the oxidation of lignin with nitrobenzene. The maximum vanillin yields reached in each experiment, referred to as the percentage of vanillin and vanillic acid calculated on nitrobenzene oxidation (on NBO), are shown in Figure 7. The best experiences were those catalyzed at 150 °C, with very similar yields for the cases of 2 and 4 kg cm^{-2} of the oxygen partial pressure (6.80 and 6.74 mmol L^{-1}, respectively, which represent 39.6 and 39.2% on NBO). In the first case, the reaction time necessary to reach the maximum is more than twice the second. The maximum yields achieved in the catalyzed experiments were the highest in all cases. At high oxygen partial pressures (4 kg cm^{-2}) and low temperatures (130 °C), the maximum vanillin yield achieved compared to the other conditions decreases, both with and without a catalyst. These yields are lower than those achieved by Fargues et al. [13] under similar conditions (85% on NBO), and the differences are probably due to the initial characteristics of the lignin.

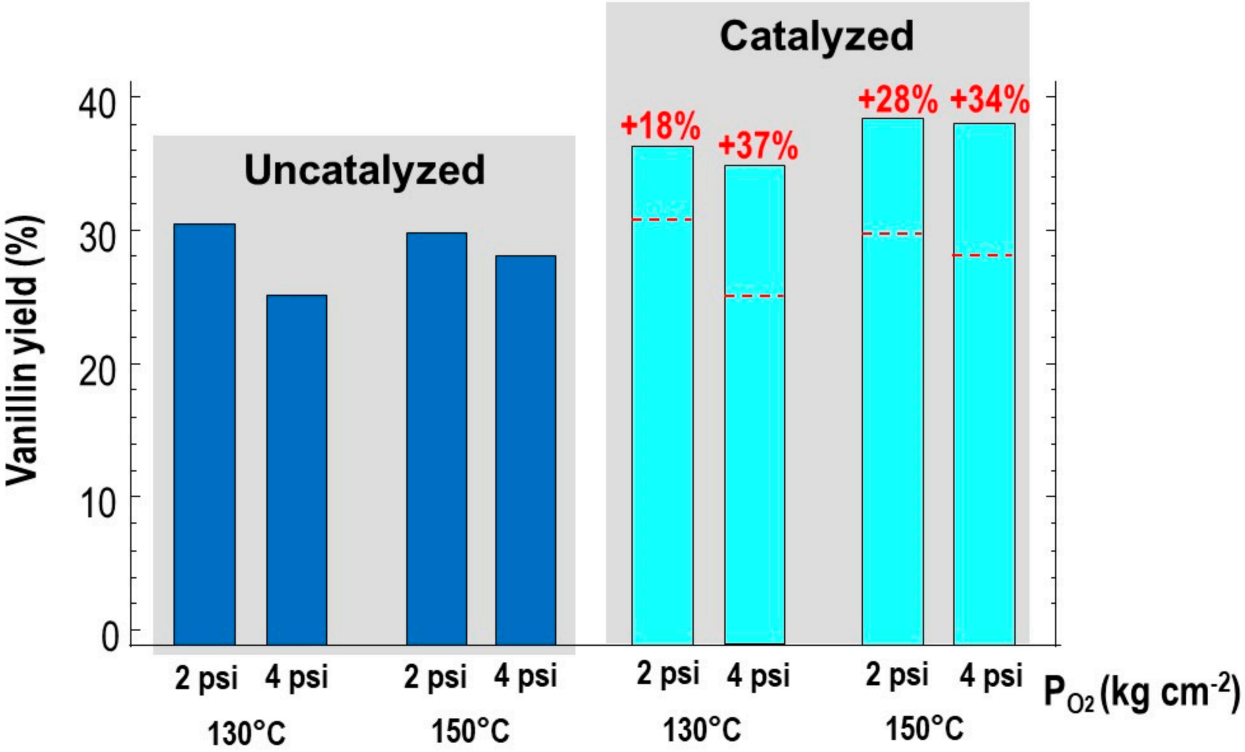


Figure 7. Maximum vanillin yield reached in each alkaline O_2 oxidation reaction. The increases are calculated based on a similar condition but without the catalyst.

The vanillin amount obtained in these reaction conditions for alkaline O_2 oxidation is less than that by other authors [11,20,24]. A possible cause is the low reactivity of lignin due to a high degree of condensation. The aromatic units that undergo condensation reactions have C-C bonds with other similar groups, which are usually irreversible due to their stability [30]. Therefore, once formed, the availability of units suitable to produce vanillin highly decreased. Additionally, O_2 oxidation produces more than twice as much vanillic acid than nitrobenzene oxidation (about 1.20% vs. 0.49%, respectively), reducing the availability of guayacil groups for vanillin production. Once the vanillic acid is formed, it is impossible to obtain vanillin from that molecule because of the strongly oxidizing medium.

When adding the maximum molar amounts of vanillin and vanillic acid obtained by oxygen oxidation for the experiences catalyzed at 150 °C, the yield is 65%, which is relatively high compared with those achieved in the analytical trial with nitrobenzene, considering that other degradation products there were not quantified. Therefore, the only way to increase the vanillin yield in experiments using oxygen would be to find conditions that decrease the vanillic acid production, increasing the proportion of the aldehyde over the acid.

3.3. Kinetic Model and Data Analysis

The experimentally obtained vanillin and vanillic acid concentrations were used to model the concentrations of lignin, vanillin, vanillic acid, and degradation products under different conditions of alkaline O_2 oxidation. The sum of the differences of squares varied between 0.10 and 4.59 (mmol L^{-1})^2. This value is calculated on the nine concentrations of vanillin and vanillic acid, so the data fit is satisfactory. Figures 8 and 9 show the evolution of species concentrations (*V* and *VA*).

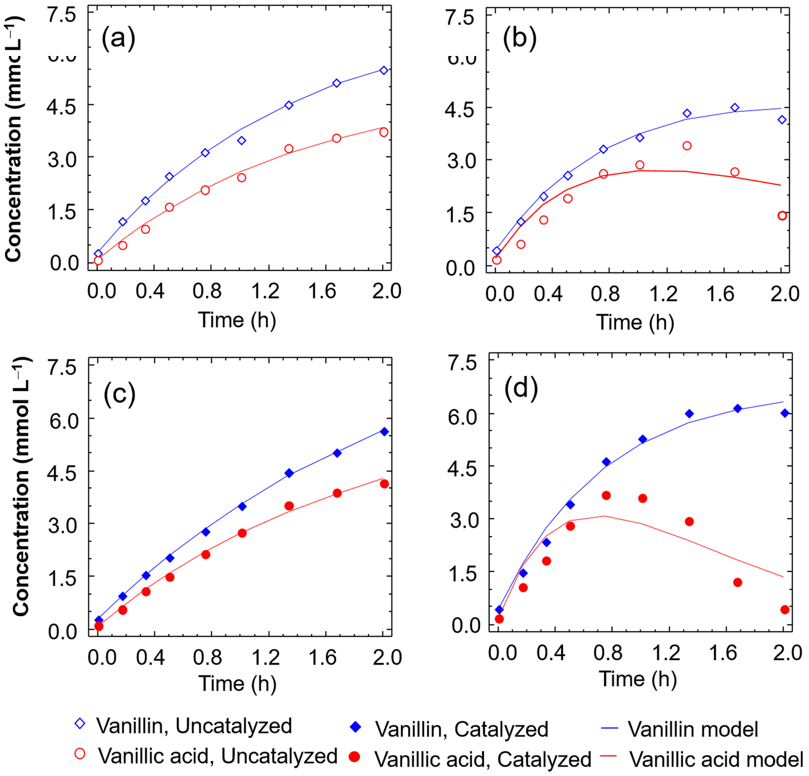


Figure 8. The evolution of the species concentration, both in the laboratory experiences and in the model. Conditions: Temperature of 130 °C. Oxygen partial pressure: (**a**,**b**) 2 kg cm^{-2}; (**c**,**d**) 4 kg cm^{-2}; (**a**,**c**) Uncatalyzed; (**b**,**d**) Catalyzed.

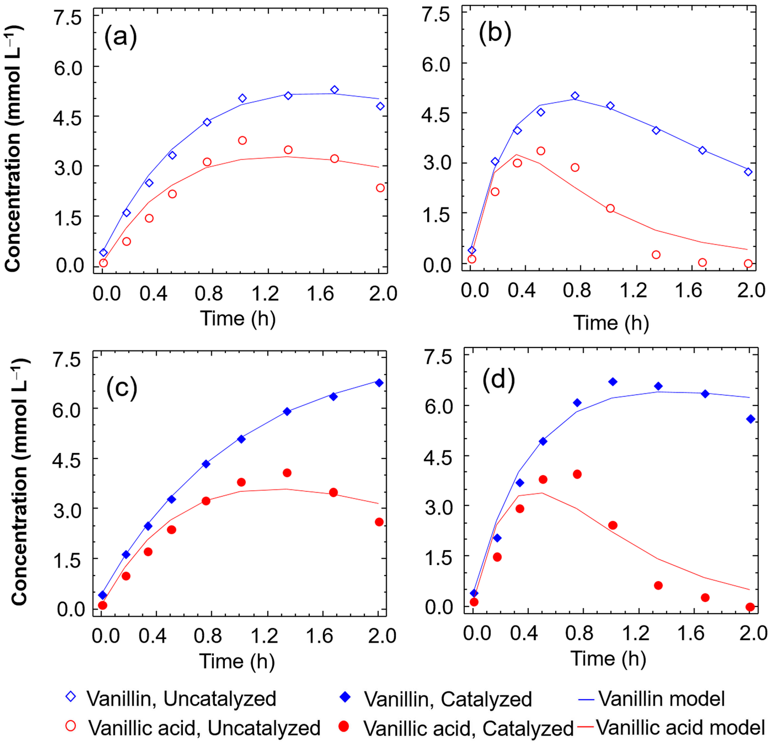


Figure 9. The evolution of the species concentration, both in the laboratory experiences and in the model. Conditions: Temperature of 150 °C. Oxygen partial pressure: (**a**,**b**) 2 kg cm^{-2}; (**c**,**d**) 4 kg cm^{-2}; (**a**,**c**) Uncatalyzed; (**b**,**d**) Catalyzed.

To understand the effect of the oxygen partial pressure, temperature, and presence of the catalyst, the parameters that allow the model adjustment (k_1 to k_4 and α) were studied through the analysis of variance.

The reactive fraction under the studied conditions (α) varies between 0.6333 and 1.000 but does not show statistically significant effects of the variables ($p > 0.05$). Table 2 shows the value of each parameter that allows the model adjustment.

Table 2. Parameter values in the fitted model.

T	**130 °C**				**150 °C**			
P_{O_2}	**2 kg cm^{-2}**		**4 kg cm^{-2}**		**2 kg cm^{-2}**		**4 kg cm^{-2}**	
Catalyst	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**	**Yes**	**No**
α	1.000	0.724	0.882	0.633	0.901	1.000	0.908	0.968
k_1	0.277	0.471	0.660	0.625	0.565	0.605	1.155	1.350
k_2	0.233	0.327	0.894	0.670	0.588	0.488	1.507	1.873
k_3	0.000	0.011	0.000	0.095	0.000	0.395	0.066	0.534
k_4	0.065	0.000	1.466	0.786	0.614	1.256	2.233	3.842

Temperature, oxygen partial pressure, and their interaction significantly affect lignin conversion, both for vanillin (k_1) and vanillic acid (k_2), which is expected since more severe conditions increase the reaction rate; however, the presence of the catalyst has no significative effect.

In the vanillin conversion to vanillic acid (k_3), the partial pressure of oxygen has no statistical effect ($p = 0.4986$). After excluding this variable from the analysis, the temperature and catalyst present a positive ($p = 0.0073$) and negative ($p = 0.0053$) effect, respectively. In addition, the catalyst cancels the effect of the temperature, which is reflected in a statistically significant interaction ($p = 0.0127$). Other authors have also reported this "protective effect" [29].

The effect of the variables on the degradation of vanillic acid (k_4) is similar to that observed on the oxidizable fraction of lignin (k_1 and k_2). However, there is no statistically significant pressure–temperature interaction in this case.

Under the studied conditions, k_2 is higher than k_3, with average values of 0.822 and 0.138, respectively. It indicates that almost all of the vanillic acid generated is explained by the production route from lignin oligomers, with only a small part coming from the vanillin oxidation. These results justify the incorporation of this pathway in the kinetic study and coincide with the conclusions of Zhu et al. [19], who only detected traces of vanillic acid in the vanillin oxidation in an alkaline medium. However, the authors recognize vanillic acid as a crucial intermediate for degradation to lower-molecular-weight products, among which acetic acid stands out.

Developing efficient processes for converting lignin to valued products is critical in biorefinery research. Even if there are studies about the kinetics of lignin oxidation in an alkaline medium, some aspects related to the selectivity of lignin oxidation to aromatic aldehydes need to be better understood. A relevant result of this kinetic study is that almost all of the vanillic acid generated is explained by the production route from lignin oligomers, and only a small part comes from the oxidation of vanillin. For this reason, it is necessary to disfavor this reaction pathway to improve vanillin yields, probably by using more selective catalysts.

Cu^{2+} salts improve lignin oxidation in high-alkaline conditions and inhibit vanillin conversion to vanillic acid, nullifying the effect of temperature. Monsanto's original patent for obtaining vanillin from lignin (1950) already cites the optional use of Cu (II) salts. Other catalysts tested by other authors (Co and Ce salts) are more expensive options. Extensive studies about the catalytic oxidation of lignin can be found in the literature [31–34]. The activity order of transition metal cations informed by Li et al. is Co > Cr > Fe > Ni > Mn ≫ Cu [33].

4. Conclusions

This work proposes a kinetic model to explain the vanillin and vanillic acid concentrations reached in the alkaline oxidation of lignin precipitated from black liquor from pine kraft pulping.

The catalyzed experiments presented higher maximum vanillin yields compared to the non-catalyzed ones. Furthermore, after reaching the maximums, the decrease in the concentration of vanillin occurs more slowly in the former. The maximum vanillin yields varied between 1.81 and 1.83% on Klason lignin (39.2% and 39.6% on nitrobenzene oxidation, respectively), achieved using a catalyzed process at 150 °C and for the tests at 4 and 2 kg cm^{-2} of the partial pressure of oxygen, respectively. Compared to other authors, the relatively low yields could be due to a high degree of condensation of the used lignin.

The proposed kinetic model satisfactorily adjusts to the experimental data, varying the kinetic constants (k_1–k_4) and the reactive fraction under the assay conditions, α. A relevant result of this kinetic study is that almost all the generated vanillic acid is explained by the production route from lignin oligomers, and only a small part comes from the oxidation of vanillin. For this reason, it is necessary to disfavor this reaction pathway to improve vanillin yields, probably by using more selective catalysts. Also, the catalyst inhibits vanillin conversion to vanillic acid, nullifying the effect of temperature.

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