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Kinetics of Vanillin Production from Kraft Lignin Oxidation

Claire Fargues, Álvaro Mathias, and Alirio Rodrigues*

LSRE (Laboratory of Separation and Reaction Engineering), School of Engineering, University of Porto, 4099 Porto Codex, Portugal

Vanillin production from chemical oxidation of *Pinus spp.* Kraft lignin is investigated. At a temperature of 130 °C, an oxygen partial pressure of 3 bar, a total pressure of 9 bar, and a lignin concentration of 60 g/L in an alkaline medium of 2 N NaOH, a maximum vanillin yield of 10% is obtained. On the basis of experimental results in a batch reactor operated under various conditions of temperature, oxygen partial pressure, total pressure, initial lignin concentration and pH, a kinetic model is proposed to simulate vanillin production from oxidation of Kraft lignin. The reaction rate of vanillin production is, for $\text{pH} > 11.5$, $r_C = k_{\text{NC}}[\text{O}_2]^{1.75}[\text{L}] - k_{\text{CI}}[\text{O}_2][\text{C}]$ and, for $\text{pH} < 11.5$, $r_C = k_{\text{NC}}[\text{O}_2]^{1.75}[\text{L}] - A(\text{pH})[\text{C}]^2$. An attempt to predict pH variation during the reaction is also made. The overall flowsheet of the process is briefly addressed, and the recovery of vanillin by adsorption is discussed.

Introduction

The use of lignin as a source of chemical products has been extensively studied. The various methods used to destroy this polymer (hydrolysis, pyrolysis, oxidation) lead to phenolic compounds of low molecular weight of great interest, which are produced with low yields. However, high yields, mainly of vanillin and syringaldehyde, can be obtained by mild oxidation of lignin in an alkaline medium (Dardelet et al., 1985).

Any lignin-containing substance can be used as a raw material, but pulp and paper industries are the main source of pure lignin; its quality depends on the type of plant or wood. Softwood, hardwood, and grass lignins differ with respect to the proportion of building units like guaiacyl, syringyl, and (*p*-hydroxyphenyl)propane (Bist et al., 1982; Ayres and Loike, 1990). In the case of gymnosperms, essentially formed from guaiacyl units, the main aldehyde produced is vanillin (Higuchi, 1980; Adachi, 1992). The Kraft pulping process of wood delignification accounts for $\frac{2}{3}$ of the production of lignin (30 million tons of Kraft lignin/year), and the remaining comes from the sulfite process (Marshall and Vincent, 1978). The Kraft process is an alkaline method for cooking wood which uses a mixture of sodium hydroxide and sodium sulfite. The lignin thus obtained can be considered as a tridimensional polyphenolate polymer (Kundrot and Tillman, 1990), whereas the sulfite delignification leads to lignosulfonic acid compounds.

Most of the studies of production of vanillin or syringaldehyde were carried out with lignin from waste sulfite liquors. It has been known since the 1920s that lignin heated under reflux conditions for long time, in the presence of active alkali, produces a maximum yield of vanillin (Van Ness, 1983); pressure, temperature, and time of reaction influence the yield and the nature of phenolic compounds obtained. However, chemical hydrolysis is not enough to obtain good production yields (Sandborn et al., 1936), and oxidation is needed.

The most generally used and economical source for oxidation has been oxygen from atmospheric air. Some authors agree that the oxygen partial pressure should not be too high, in order to avoid a further degradation of the aldehydes produced, leading to a mixture of small acids (formic, acetic, lactic, or oxalic acids). For the same reason, the reaction should not last too long (not

more than 2 h) (Marshall and Sankey, 1950, 1951; Bryan, 1954; Craig and Logan, 1962a). Furthermore, according to Bryan (1954), oxygen in the early stages of the reaction is necessary to break the lignin polymer into smaller molecular fragments, but thereafter oxygen pressure should be rapidly decreased. The optimal oxygen partial pressure for the production of vanillin was found to be around 1 bar, under temperature in the range of 170–200 °C (Marshall and Sankey, 1950, 1951; Fisher and Marshall, 1951a,b; Fisher and Sankey, 1951; Bryan, 1954; Craig and Logan, 1962a,b).

Another important process parameter is the type of active alkali. In all cases, the pH should stay higher than 12 during the reaction. Bryan (1954) found that sodium hydroxide gave better results than potassium hydroxide. According to Marshall and Sankey (1950, 1951), a minimum concentration around 2 N NaOH is required. Lime was also used associated to Na_2CO_3 (Fisher and Marshall, 1951a,b; Fisher and Sankey, 1951; Craig and Logan, 1962a,b), at the optimized concentration of 1 M.

The variation of the total pressure from 5 to 14 bar does not affect the production yields (Marshall and Sankey, 1950, 1951).

Oxidation by air associated with the use of catalysts such as CuSO_4 was also studied, but the vanillin yield was not improved significantly (Marshall and Sankey, 1950, 1951). Better yields are obtained when nitrobenzene is the oxidant concerning the production of phenolic aldehydes but the nitro products of the reaction must be separated afterward which does not allow industrial application. Very often the nitrobenzene oxidation of lignin is used to obtain the maximum conversion value of the lignin under study.

In all cases of lignin oxidation in the batch reactor described above, the concentrations of vanillin produced are in the range of 1–8 g/L (Fisher and Marshall, 1951a,b; Craig and Logan, 1962a,b) or around 10% relatively to the initial concentration of lignin (Marshall and Sankey, 1950, 1951). However, no kinetic study was undertaken as far as we know. In two cases attempts of modeling were done, considering a first-order reaction rate of vanillin production with respect to the lignin concentration (Nadezhdin and Robertson, 1990; Adachi et al., 1992); however, the influence of oxygen partial pressure was not discussed.

A research program on the production of vanillin from lignin was started in our laboratory some years ago. The

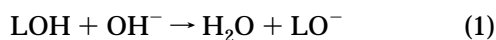
* To whom correspondence should be addressed.

oxidation of *Pinus spp.* lignin (Westvaco Co.) in an alkaline solution (sodium hydroxide) was carried out with commercial oxygen. An optimal production was found for an oxygen partial pressure of 2.8 bar, under a temperature of 133 °C for a lignin concentration of 60 g/L, dissolved in 2 N NaOH. The reaction time corresponding to the maximum of vanillin yield (10.8%) is 35 min. In that case, only vanillin was detected. It was also checked that no vanillin production occurred during the heating phase (Mathias and Rodrigues, 1995). The kinetics of vanillin degradation was also investigated; a model was developed to account for this degradation rate at various pH (Fargues et al., 1995).

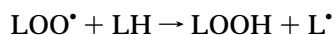
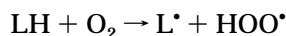
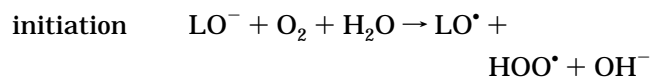
The objectives of this work are (i) to analyze the effect of process parameters (temperature, partial pressure of oxygen, lignin concentration) on the yield of vanillin production from Kraft lignin by oxidation, (ii) to develop a kinetic model for the complete process of lignin oxidation to vanillin, and (iii) to briefly discuss the overall process including vanillin recovery.

Kinetic Model for Lignin Oxidation

Oxidation of lignin consists of a depolymerization of the molecule; in an alkaline medium of sodium hydroxide the hydroxyl anions solubilize the lignin (LOH) according to:



The polyphenolate anion LO^- would react with the oxygen as follows (Dardelet et al., 1985):



The radical LOO^\bullet will further suffer several types of reactions, leading mainly to vanillin or syringaldehyde.

It was previously shown that the vanillin produced could be further destroyed by oxidation (Marshall and Sankey, 1950, 1951; Fisher and Marshall, 1951a,b; Fisher and Sankey, 1951; Mathias, 1993), and a theoretical model was built to account for this oxidation in alkaline conditions ($\text{pH} > 12$) as well as when the pH decreases until 6 (Fargues et al., 1995). The transition between the two mechanisms would be in the range of pH 11–12.

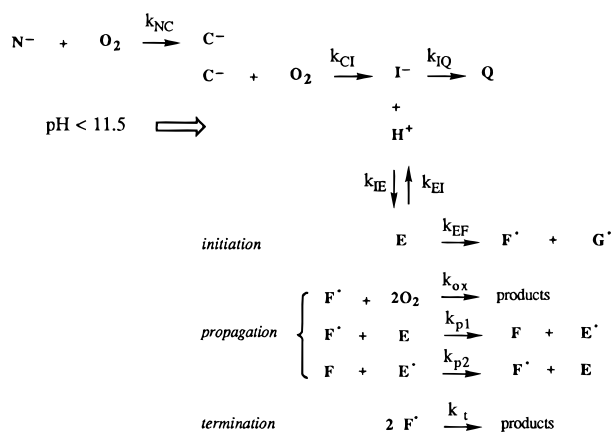
If N^- is a fragment of lignin which can lead to the production of vanillin, the reaction scheme for vanillin production from lignin and oxidation of the vanillin in an alkaline medium can then be written as in Scheme 1.

The rate of production of the vanillin could then be expressed as:

$$r_C = k_{\text{NC}} [\text{O}_2]^m [\text{L}]^n \quad (3)$$

The orders m and n with respect to oxygen and lignin concentrations come from the sketch of reactions 2 and

Scheme 1



more reactions on the radical species LOO^\bullet . It would be very hazardous to try to determine them theoretically.

The rate of oxidation of vanillin is (Fargues et al., 1995):

$$\text{for } \text{pH} > 11.5 \quad -r_C = k_{\text{CI}} [\text{O}_2] [\text{C}] \quad (4)$$

$$\text{for } \text{pH} < 11.5 \quad -r_C = A f(\text{pH}) [\text{C}]^2 \quad (5)$$

with

$$f(\text{pH}) = \left(\frac{B[\text{H}^+]}{1 + B[\text{H}^+]} \right)^2$$

The kinetic model to be developed in order to describe lignin oxidation in batch reactors will be based on the following assumptions:

(a) The experimental kinetic study was entirely based on the concentration of vanillin produced as a function of time, as it was not possible to measure the concentration of lignin nor other products of the oxidation (Mathias, 1993).

(b) The concentration of dissolved oxygen in the solution was calculated from a correlation (see the Experimental Section).

(c) The lignin is composed of precursors (or nuclei N) that will create only vanillin. The maximum conversion obtained by nitrobenzene oxidation gives us a useful molecular weight for the nucleus N of the lignin of *Pinus spp.* of 1141 (Mathias, 1993).

(d) The reaction of lignin oxidation into vanillin is irreversible.

(e) The production rate of the vanillin is the same for all the fragments of the lignin.

(f) The reactor is perfectly mixed.

(g) There is no mass-transfer limitation from the gas to liquid phase.

We have now to determine experimentally the orders of vanillin production rate with respect to oxygen and lignin concentrations, as well as the dependency of the constant k_{NC} with temperature.

Experimental Section

Lignin of *Pinus spp.* (Westvaco Co.) is used for this study. In most cases it is dissolved at a concentration of 60 g/L in 500 mL of a solution of 2 N NaOH. The oxygen contained in that solution is partly expelled during the dissolution of the lignin carried out at a

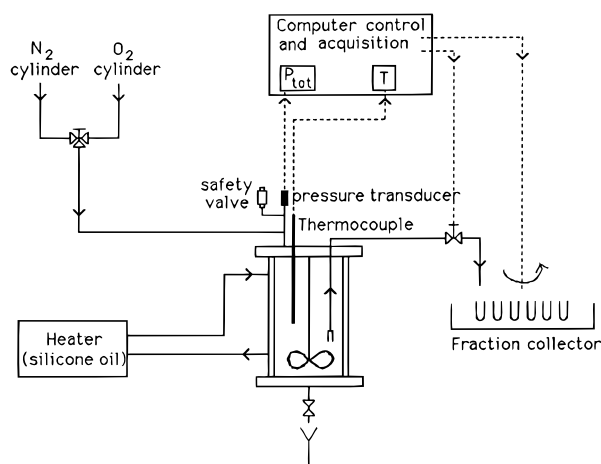


Figure 1. Experimental setup for kinetic studies of vanillin production from Kraft lignin oxidation.

temperature of $\approx 70^\circ\text{C}$ and by bubbling nitrogen in the solution before its introduction in the reactor.

All experiments of lignin oxidation are performed in a laboratory autoclave reactor BEP 280, type II with 1 L capacity, manufactured by Buchi AG (Switzerland). A sketch of the experimental setup is shown in Figure 1. It is heated by circulation of a silicone oil, from a thermostatic bath. The rotation speed of the stirrer is about 1150 rpm. The temperature inside the autoclave is measured by a "K" thermocouple (nickel–chromium/nickel–aluminum), and the total pressure is measured with a pressure transducer. Their electromotive forces are acquired by the data acquisition system. Fractions are collected for further analysis. These operations as well as the rotation of the collector are controlled by the computer IBM PS2/55.

A typical run is now described. The cold lignin solution (500 mL) is introduced in the reactor, and the heating-up program then starts under a slight nitrogen pressure. When the solution reaches the desired temperature, nitrogen is added in most cases until 5 bars. Time zero corresponds to the admission of oxygen until a total pressure of 9 bars. The duration of a run is around 2 h. The total pressure in the reactor is kept at 9 bars by continuous addition of oxygen along the time of its consumption. Initial nitrogen pressure and vapor pressure are known and are corrected with the increase in the gas phase due to the collection of fractions, as well as with the changes in temperature that may happen during the experimental run. With the measurement of the total pressure along the time of the experiment, the partial pressure of oxygen can then be calculated. It is further used to determine the dissolved oxygen concentration in the solution. The correlation used has been proposed by Mathias (1993):

$$[\text{O}_2] = \left(3.559 - 6.659 \times 10^{-3}T - 5.606P_{\text{O}_2} + 1.594 \times 10^{-5}P_{\text{O}_2}^2 + 1.498 \times 10^3 \frac{P_{\text{O}_2}}{T} \right) (10^{-0.144I})(10^{-3}) \text{ mol/L}$$

where $[\text{O}_2]$ is the dissolved oxygen concentration (mol/L), T is the absolute temperature (K), P_{O_2} is the oxygen partial pressure (bar), and I is the ionic strength of the solvent (mol/L).

Vanillin concentration is measured by gas chromatography, as described by Hartley (1971), after pretreatment of the samples. These are first acidified by

Table 1. Yield of Vanillin Production from Oxidation of *Pinus spp.* Lignin, for Different Temperatures, Oxygen Partial Pressures, and Lignin Concentrations^a

run	temp ^b (°C)	oxygen partial pressure ^b (bar)	lignin concn (g/L)	reaction time (min)	vanillin yield (%)
1	110	3.5	60	60	8.3
2	125	3.0	60	60	8.3
3	133	2.8	60	35	10.8
4	154	4.0	60	30	7.8
5	130	1.2	60	70	8.3
6	135	5.0	60	20	8.3
7	128	3.0	30	40	6.7
8	125	4.0	30	45	9.0
9	120	2.5	120	50	6.3

^a Other conditions: NaOH = 2 N, $P_{\text{tot}} \approx 9.7$ bar. ^b Average values during the run time.

addition of concentrated hydrochloric acid, which leads to the precipitation of high molecular weight components (including lignin). The precipitated solids are separated by centrifugation during 15 min at 5000 rpm. The vanillin is extracted from the supernatant with diethyl ether. A 2.5 μL portion of the organic phase is directly injected in the gas chromatograph for analysis. The conditions of the gas chromatograph are as follows: injection temperature, 230°C ; oven temperature, 220°C ; flow rate of nitrogen carrier through the column (CQ Diatomite with 10% CDMS, Phase Separations, U.K.), 60 mL/min. Calibrated solutions of 1 and 2 g/L of vanillin are used for the calculation of the samples' concentrations and are treated like the samples. They are prepared in a solution of 2 N NaOH containing lignin at the initial concentration used in each experiment (30, 60, or 120 g/L). We effectively noticed that the results of the analysis of the calibrated solutions changed with the concentration of lignin they contain. This is probably due to a coprecipitation of part of the vanillin during the acidification step of the samples (Craig and Logan, 1962b). The determinations are carried out carefully and the preparation of the initial samples duplicated in some cases.

The pH of the collected samples is measured, after cooling, with a pH-meter CRISON type 2002 equipped with a combined electrode and calibrated in the alkaline range.

Results and Discussion

Yields of Vanillin Production. Influence of Process Parameters. Table 1 shows the influence of temperature, oxygen partial pressure, and lignin concentration on the vanillin yield, calculated relative to the initial lignin concentration. Yields are in the range of 7–10%, in agreement with values found by other authors (Marshall and Sankey, 1950, 1951; Fisher and Marshall, 1951a,b; Fisher and Sankey, 1951; Craig and Logan, 1962a,b), even a little higher. We also confirm the optimal conditions found by Mathias and Rodrigues (1994) for a temperature around 130°C , oxygen partial pressure around 3 bar, and lignin concentration of 60 g/L, prepared in a solution of 2 N NaOH. In these conditions, the vanillin yield of 10.8% is 85% of the maximal recovery of vanillin found for this type of lignin (*Pinus spp.*) by nitrobenzene oxidation, which was of 13% (Mathias, 1993). Further increases of oxygen partial pressure (runs 2, 3, 5, and 6) as well as temperature (runs 1–4) do not improve the production, since vanillin is then more oxidized. A reaction time of 40 min is enough to reach the maximum vanillin concentration.

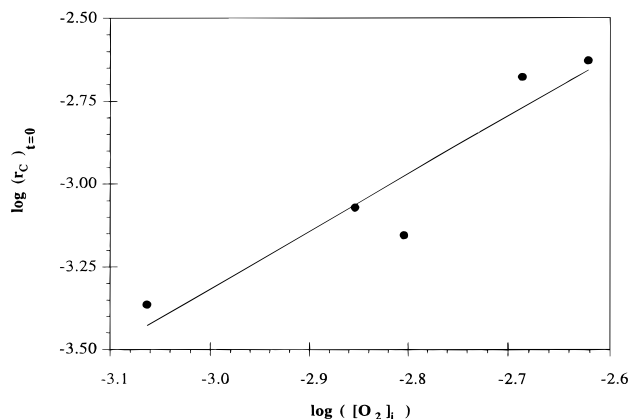


Figure 2. Initial rate of lignin oxidation versus dissolved oxygen concentration: determination of the reaction order with respect to oxygen. Experimental points correspond to runs 2, 3, 5, 6, and 10.

The effect of lignin concentration was analyzed in runs 2, 3, and 7–9. It can be seen that a lignin concentration of 120 g/L does not lead to a higher production yield of vanillin. We even notice a decrease, as was already found by Fisher and Marshall (1951b), who had obtained higher yields of production when the waste sulfite liquor was more diluted with the alkaline solution of lime they used to carry out the reaction. They attributed this phenomenon to the use of lime.

It was pointed out by Marshall and Sankey (1950, 1951) and Mathias and Rodrigues (1994) that a minimum concentration of 2 N NaOH is required to provide a good production of vanillin. In run 10 with 1 N NaOH (all other parameters were identical to those of run 3) the yield was only 5% in a reaction time of 10 min, but, thereafter, the concentration of vanillin rapidly decreased, because of further oxidation of vanillin. Therefore, a high concentration of the alkaline species seems to be necessary for efficient oxidation of the lignin polymer, as well as for the protection of the vanillin produced.

Kinetics of the Vanillin Production. We first checked the order of the rate law of vanillin production with regard to lignin and oxygen concentrations. Since lignin concentration was not measured, we are going to consider as a first approximation that there is no degradation of the vanillin produced at the beginning of the reaction and neglect the contribution of eqs 4 or 5. As temperature and oxygen partial pressure change during the run, we will consider the initial values, encountered during the delay of the first sample.

Effect of the Oxygen Partial Pressure on the Reaction Rate of Vanillin Production. In a first series of experiments (runs 2, 3, 5, 6, and 10) the initial lignin concentration (60 g/L), temperature ($\approx 130^\circ\text{C}$), and total pressure (≈ 9.5 bar) were kept constant. The initial oxygen partial pressure P_{O_2i} (average in the time of the first sample) was changed from 1.1 up to 4.5 bar. From a log–log plot of the initial rate of vanillin production $(r_C)_{t=0}$ as a function of the dissolved oxygen concentration, we obtain a straight line with a slope of 1.75 shown in Figure 2; i.e., the reaction order with respect to the oxygen concentration is 1.75.

Effect of the Initial Lignin Concentration on the Reaction Rate of Vanillin Production. In a second series of experiments (runs 2, 3, and 7–9) of vanillin production in alkaline medium at constant temperature ($\approx 125^\circ\text{C}$), constant total pressure (≈ 9.9 bar), and constant oxygen partial pressure (≈ 3 bar), the initial

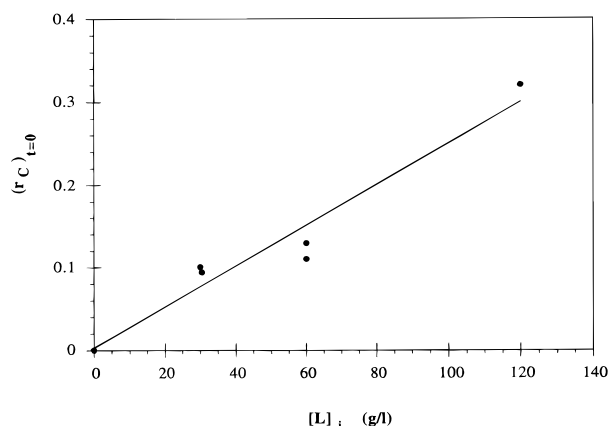


Figure 3. Initial rate of lignin oxidation versus initial lignin concentration: determination of the reaction order with respect to lignin. Experimental points correspond to runs 2, 3, and 7–9.

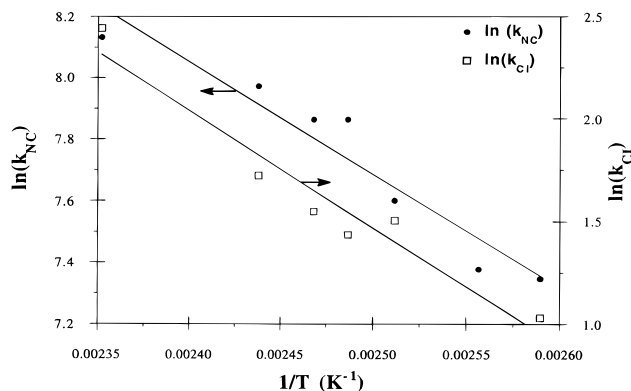


Figure 4. Arrhenius plots, k_{NC} and k_{CI} , versus $1/T$, for the calculation of the activation energy of lignin oxidation (eq 9; runs 1, 2, 4–7, and 9) and vanillin oxidation (eq 4; runs 1, 2, and 4–7) respectively.

concentration of lignin $[L]_i$ was changed in the range 30–120 g/L. Figure 3 shows the initial vanillin formation rate as a function of the initial lignin concentration. From the slope of the straight line we calculate the reaction order with respect to the lignin concentration equal to 1.

Therefore, under the conditions previously described the kinetic law for the production of vanillin can be written as:

$$r_C = k_{NC}[O_2]^{1.75}[L] \quad (6)$$

Effect of Temperature on the Reaction Rate of Vanillin Production. In the process of vanillin production from Kraft lignin, temperature can change and therefore it is important to know the temperature dependence of the kinetic constant k_{NC} . A series of experiments (runs 1–4) was performed by changing the temperature from 110 up to 154°C , all other conditions being kept constant. However, as we now know the influence of lignin and oxygen concentrations on the production rate of vanillin, we also use some of the other runs. In the beginning of the reaction, the pH is always higher to 11.5, and the net production rate of vanillin is then the difference between eqs 6 and 4. On the basis of the production rates and temperatures encountered during these runs, we optimize the kinetic constants k_{NC} and k_{CI} . From a semilog plot of k_{NC} and k_{CI} as a function of $1/T$ (Arrhenius plot), we get straight lines, as depicted in Figure 4. From the slope of such lines the activation energies for the vanillin production and oxidation are

calculated. The kinetic constants can be expressed as:

$$k_{\text{NC}} = 1.376 \times 10^7 \exp\left(-\frac{3502}{T}\right) (\text{L/mol})^{1.75}/\text{min} \quad (7)$$

and

$$k_{\text{CI}} = 4.356 \times 10^6 \exp\left(-\frac{5530}{T}\right) \text{L}/(\text{mol}\cdot\text{min}) \quad (8)$$

The activation energies for lignin oxidation and vanillin oxidation are 29.1 and 46.0 kJ/mol, respectively. The kinetic constant k_{CI} had been previously determined, in the case of the oxidation of the vanillin alone (Fargues et al., 1995). The dependency with the temperature was

$$k_{\text{CI}} = 3.61 \times 10^{10} \exp\left(-\frac{9706.2}{T}\right) \text{L}/(\text{mol}\cdot\text{min}) \quad (9)$$

The kinetic constant of degradation of the vanillin produced is higher in the conditions encountered now, when the oxidation process starts with the molecule of lignin. This can be easily explained by the presence in that case of a greater number of intermediate and final products created as shown in reactions (2). The factor between results given by eqs 8 and 9 is around 9 at 100 °C but decreases to 3 when the temperature increases to 140 °C

Model Validation. Equations 4–6 were used to simulate the production of vanillin in a batch reactor. Average experimental temperature, pH, and oxygen partial pressure were calculated for the time during two samples and used in these equations:

$$\text{for pH} > 11.5 \quad r_{\text{C}} = k_{\text{NC}}[\text{O}_2]^{1.75}[\text{L}] - k_{\text{CI}}[\text{O}_2][\text{C}] \quad (10)$$

$$\text{for pH} < 11.5 \quad r_{\text{C}} = k_{\text{NC}}[\text{O}_2]^{1.75}[\text{L}] - A f(\text{pH})[\text{C}]^2 \quad (11)$$

Equations 7 and 8 were used for k_{NC} and k_{CI} and for pH < 11.5, with constants A and B previously calculated (Fargues et al., 1995):

$$A = 4071 \exp\left(-\frac{3103.7}{T}\right) \text{L}/(\text{mol}\cdot\text{min}) \quad (12)$$

and

$$B = 8.88 \times 10^{12} \exp\left(-\frac{1936.6}{T}\right) \text{L}/\text{mol} \quad (13)$$

Parts a and b of Figure 5 show the vanillin concentration and pH as a function of reaction time for two temperatures, 110 and 154 °C (runs 1 and 4). When the temperature increases, the vanillin yield slightly decreases; however, the reaction time required for the maximum yield is much lower at high temperature.

Parts a and b of Figure 6 show experimental results for two different partial pressures of oxygen, 1.2 and 5 bar (runs 5 and 6). Increasing the oxygen partial pressure leads to a much better operation in terms of reaction time required to obtain good vanillin yields.

Parts a and b of Figure 7 display results of runs for two different concentrations of lignin, 30 and 120 g/L (runs 7 and 9). Vanillin yield increases with lignin concentration as shown in Table 1 up to 60 g/L but then decreases.

Simulation results for run 2, which corresponds to the near optimized production of vanillin, are shown in Figure 8. In these figures the experimental evolution

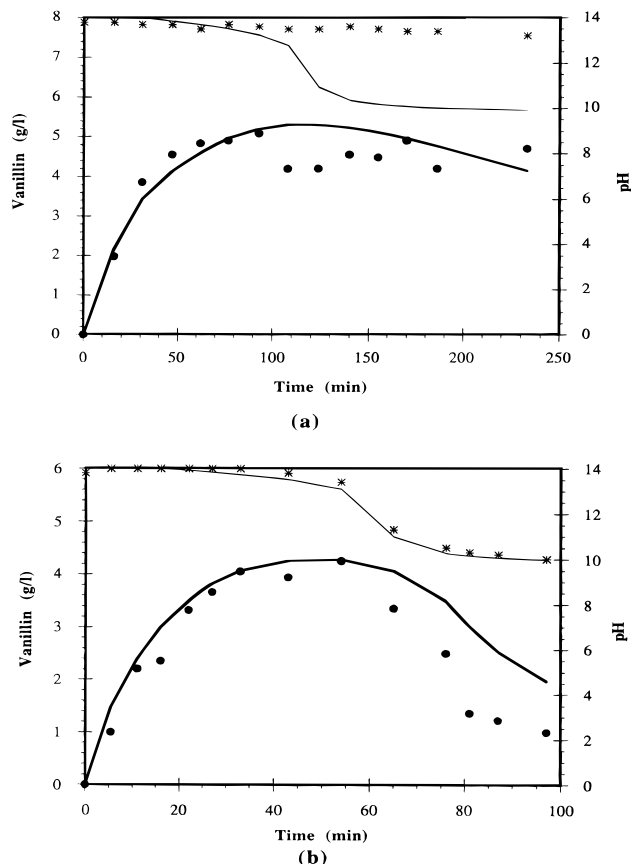


Figure 5. Vanillin concentration (●) and pH (*) versus reaction time. (a) Run 1: $T = 110$ °C, $[\text{L}]_i = 60$ g/L, $P_{\text{O}_2} = 3.5$ bar, $P_{\text{tot}} = 9.7$ bar. (b) Run 4: $T = 154$ °C, $[\text{L}]_i = 60$ g/L, $P_{\text{O}_2} = 4$ bar, $P_{\text{tot}} = 9.7$ bar. Lines are model results obtained with rate equations (12) and (13) for vanillin and eqs A.1–A.4 (appendix) for the pH.

of the pH is plotted as well as an attempt of its prediction, as discussed later. The parameters k_{NC} and k_{CI} previously calculated allow reasonable simulation of experimental results in all these conditions, when the pH stays higher than 11.5. The model results obtained when eq 11 is taken into account, i.e., when pH decreases below 11.5, stay higher than the experimental decrease in the vanillin concentration. This is more obvious on Figures 5b, 7b, and 8 (runs 4, 9, 2, respectively). The disappearance of vanillin under “acid” conditions is much higher than the one predicted with A and B calculated from the oxidation of vanillin alone (eqs 12 and 13). The radical mechanisms that were responsible for the oxidation of vanillin are probably enhanced by the presence of a great number of new radical species, appearing in the sketch of reactions (2).

For runs 1 (Figure 5a) and 7 (Figure 7a), where pH stays above 11.5, the predicted optimal times are 92 and 65 min, respectively; the corresponding maximum vanillin concentrations are 5.1 and 2.5 g/L, respectively. These predicted values are in good agreement with experimental results. They are obtained from $d[\text{C}]/dt = r_{\text{C}} = 0$, where r_{C} is given by eq 10, leading to:

$$t_{\text{max}} = \frac{\ln\left\{\frac{k_{\text{NC}}[\text{O}_2]^{0.75}}{k_{\text{CI}}}\right\}}{k_{\text{NC}}[\text{O}_2]^{1.75} - k_{\text{CI}}[\text{O}_2]} \quad (14)$$

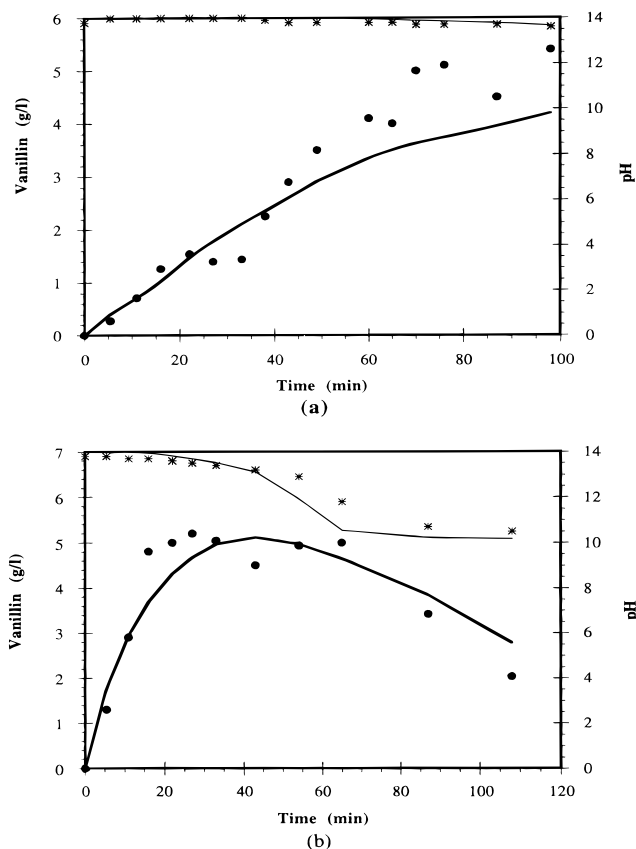


Figure 6. Vanillin concentration (●) and pH (*) versus reaction time. (a) Run 5: $T = 130\text{ }^{\circ}\text{C}$, $[L]_i = 60\text{ g/L}$, $P_{O_2} = 1.2\text{ bar}$, $P_{\text{tot}} = 9\text{ bar}$. (b) Run 6: $T = 135\text{ }^{\circ}\text{C}$, $[L]_i = 60\text{ g/L}$, $P_{O_2} = 5\text{ bar}$, $P_{\text{tot}} = 9.5\text{ bar}$. Lines are model results obtained with the rate equations (12) and (13) for vanillin and eqs A.1–A.4 (appendix) for the pH.

and

$$[C]_{\text{max}} = [L]_i \left\{ \frac{k_{\text{NC}}[O_2]^{0.75}}{k_{\text{CI}}} \right\}^{1/[1-(k_{\text{NC}}[O_2]^{0.75}/k_{\text{CI}})]} \quad (15)$$

We should also add that the model predicts a much higher production of vanillin in run 10, carried out with 1 N NaOH. In that case, the hydrolysis of the lignin polymer must have been affected by the lack of alkaline species, leading to a much lower production.

We also made an attempt for the prediction of the pH evolution, based on the theoretical oxidation curve of the lignin nucleus and on simple assumptions described in the appendix. Figures 5b–7b as well as figure 8 show that the pH prediction is very close to the experimental pH. On the contrary, for run 1 (Figure 5a), carried out at lower temperature, the prediction fails. In this case, the inflection point of the experimental pH curve occurs for a theoretical oxidation of lignin much higher than for the other experiments; this could be ascribed to a smaller postoxidation of the reaction products, leading to a smaller production of molecules of high acidity like oxalic acid.

Overall Process of Vanillin Production. Examples of commercial processes for the production of vanillin from air oxidation of sulfite lignin are those of Salvo Chemical Co. (U.S.A.), Monsanto (U.S.A.), and Ontario Paper Co. (Canada) (Diddams and Krum, 1970). The extraction of vanillin from the reactant medium can be achieved in various ways:

(1) Acidification of the medium to precipitate the components of high molecular weights, followed by liquid–liquid extraction of the vanillin in the super-

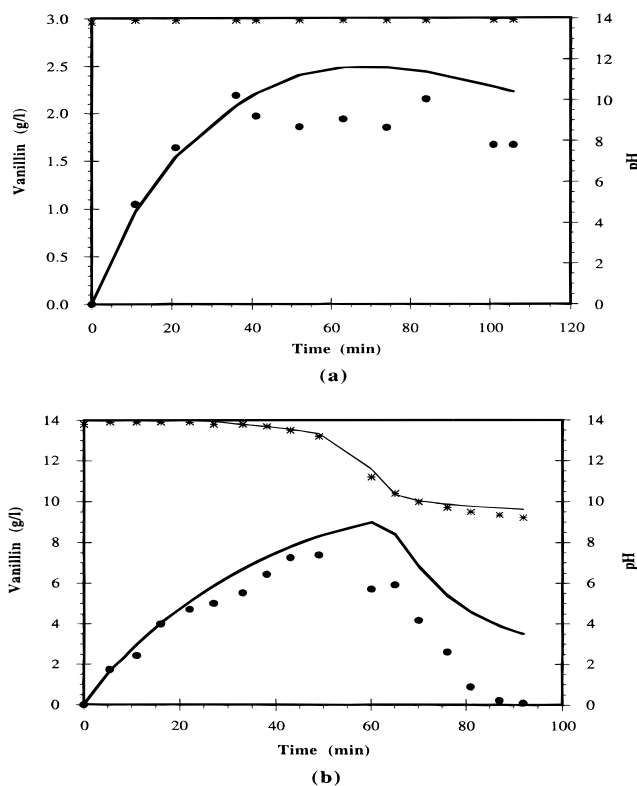


Figure 7. Vanillin concentration (●) and pH (*) versus reaction time. (a) Run 7: $T = 128\text{ }^{\circ}\text{C}$, $[L]_i = 30\text{ g/L}$, $P_{O_2} = 3\text{ bar}$, $P_{\text{tot}} = 10\text{ bar}$. (b) Run 9: $T = 120\text{ }^{\circ}\text{C}$, $[L]_i = 120\text{ g/L}$, $P_{O_2} = 2.5\text{ bar}$, $P_{\text{tot}} = 9.6\text{ bar}$. Lines are model results obtained with the rate equations (12) and (13) for vanillin and eqs A.1–A.4 (appendix) for the pH.

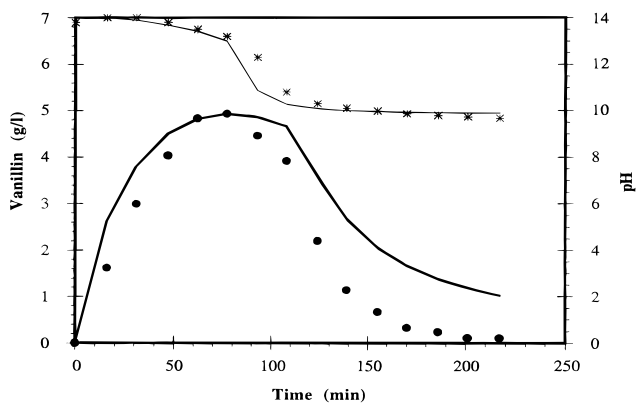


Figure 8. Vanillin concentration (●) and pH (*) versus reaction time. Run 2: $T = 125\text{ }^{\circ}\text{C}$, $[L]_i = 60\text{ g/L}$, $P_{O_2} = 3\text{ bar}$, $P_{\text{tot}} = 9.7\text{ bar}$. Lines are model results obtained with the rate equations (12) and (13) for vanillin and eqs A.1–A.4 (appendix) for the pH.

natant (with benzene, toluene, or ethyl ether). The vanillin is then further reextracted by an aqueous solution of sodium bisulfite, creating an insoluble bisulfite–vanillin complex which is further solubilized by acid addition (Sandborn and Howard, 1938).

(2) Direct extraction of the vanillin from the reaction medium proposed by Bryan (1955) with propylic alcohol.

(3) Adsorption of the vanillate on a cationic resin (Forss et al., 1981). The separation of the vanillin from sulfite lignin sodium carbonate and sodium hydroxide comes from a smaller retention of these components on the resin. The advantage of this method is to avoid the acidification of the medium.

A study was carried out in our laboratory on the retention of vanillin on a classical cationic resin, Duolite C20 (Rohm and Haas, France). A sorption isotherm was

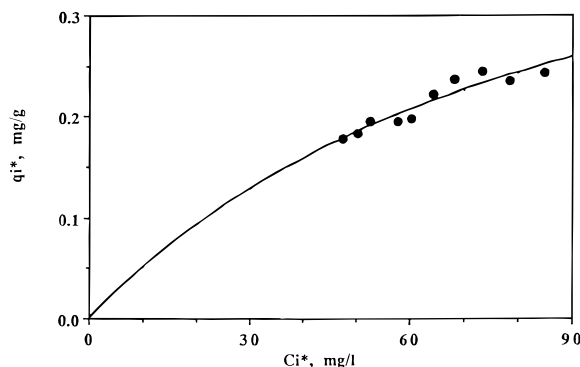


Figure 9. Sorption equilibrium isotherm of vanillin in Duolite C20 resin: vanillin concentration in the resin, q_i^* , versus vanillin concentration in the solution, C_i^* .

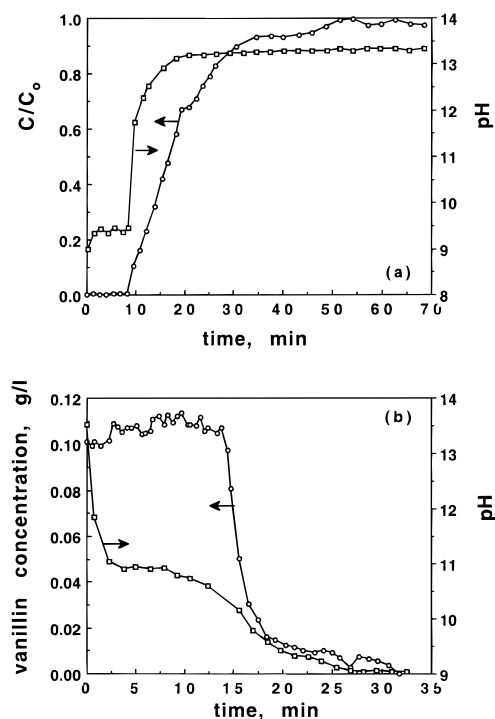


Figure 10. Experimental breakthrough curve: vanillin concentration (\circ) in the liquid phase at the bed outlet versus time and pH (\square) versus time (a) and desorption of vanillin from a fixed bed of Duolite C20 saturated with vanillin (b).

measured by batch equilibration. Experimental results were fitted by the Langmuir equation with $Q = 0.518$ mg of adsorbed/g of dry resin and $K_L = 11$ L/g. The adsorption equilibrium isotherm is shown in Figure 9.

Fixed-bed experiments for vanillin adsorption/desorption were carried out in a 1×27 cm column, packed with particles with $d_p = 0.06$ cm at 20°C and flow rate

2.15 mL/min. The feed was a solution of pure vanillin ($C_0 = 0.1$ g/L) prepared in NaOH (1 N). Under such conditions the space time traveled by a nonadsorbed species is 4.74 min and the expected stoichiometric time is 18 min since the capacity factor $q_i^* \rho_b / \epsilon C_0$ is 2.8. The experimental breakthrough curve, i.e., vanillin concentration at the bed outlet as a function of time, is shown in Figure 10a.

The desorption (recovery of vanillin) is shown in Figure 10b; desorption was carried out by passing water through the fixed bed previously saturated with vanillin.

The proposed overall flowsheet is shown in Figure 11. The black liquor from pulp industry using the Kraft process is oxidized with air in an alkaline medium. The vanillin produced is present in a medium containing high molecular weight compounds which are separated in the sorption column. The residual lignin has various applications. Vanillin is then extracted after acidification: with benzene, sodium salts are recovered, and with sodium bisulfite, the solvent is recovered. After acidification and stripping with air to remove sulfur dioxide, the crude vanillin stream is further purified before sale.

Conclusions

A kinetic study of vanillin production from chemical oxidation of Kraft lignin was carried out to measure reaction orders with regard to lignin, oxygen, and vanillin species, as well as the influence of temperature on the kinetic rate constants. From a series of experiments under different oxygen partial pressures an order 1.75 relative to oxygen was found; also from runs at different initial lignin concentrations an order 1 relative to the lignin was obtained. The dependency of the kinetic constant of vanillin production with the temperature was also calculated.

The vanillin produced by lignin oxidation is also degraded by oxidation whose importance depends on the pH and the temperature of the solution. The influence of these two parameters on the kinetics of vanillin degradation had been previously studied on vanillin alone. The relationships obtained were applied directly to the case of the vanillin produced by lignin oxidation; however, the simulation thus predicts a smaller degradation than the experimental one. This is probably due to the creation of new radical species during the oxidation of lignin, that enhances the postoxidation reactions of vanillin. Therefore, by a slight modification of the vanillin oxidation constant under alkaline conditions, the modeling of vanillin production from Kraft lignin in a batch reactor is reasonably predicted over a wide range of experimental conditions.

An overall scheme for vanillin production from Kraft black liquor is proposed which considers the recovery

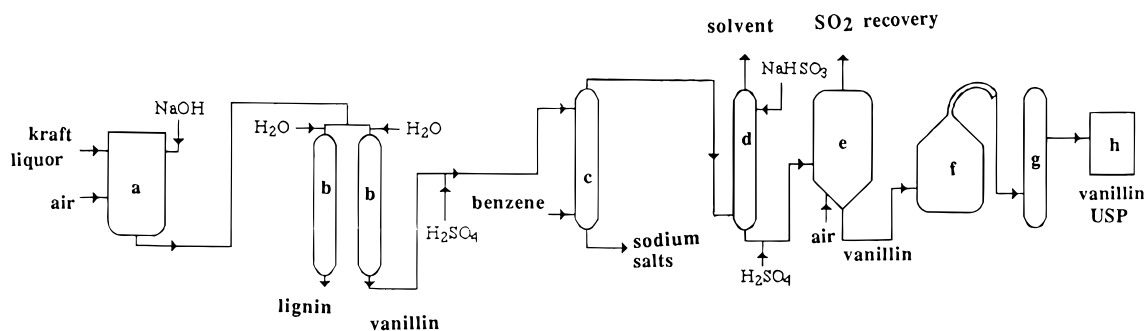


Figure 11. Overall flowsheet for the production of vanillin from Kraft lignin oxidation. (a) reactor; (b) sorption columns; (c) liquid-liquid extractor; (d) solvent recovery; (e) gas scrubber; (f) vacuum distillation; (g) crystallizer; (h) market.

of vanillin from the reactant medium by sorption in a cationic resin.

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Nomenclature

A = parameters in eq 5
 B = parameters in eq 5
 E = activation energy of the reaction, J/mol
 I = ionic strength, mol/L
 K = constant of the equation of Arrhenius
 k_{CI} = kinetic constant in eq 4, L/(mol·min)
 k_{NC} = kinetic constant in eq 3, (L/mol)^{1.75}/min
 m = reaction order with respect to oxygen in eq 3
 n = reaction order with respect to lignin in eq 3
 P_{O_2} = partial pressure of oxygen in the reactor, bar
 $P_{O_{2i}}$ = initial partial pressure of oxygen in the reactor, bar
 P_{tot} = total pressure in the reactor, bar
 R = ideal gas constant, J/(mol·K)
 r = reaction rate, mol/(L·min)
 T = temperature, K
 t = time, min
 $[C]$ = concentration of vanillin (or vanilate), g/L or mol/L
 $[L]$ = concentration of lignin, g/L or mol/L
 $[L]_i$ = initial concentration of lignin, g/L or mol/L
 $[O_2]$ = concentration of dissolved oxygen in the liquid phase, mol/L
 $[O_2]_i$ = initial concentration of dissolved oxygen in the liquid phase, mol/L

Component Abbreviations

N^- = useful lignin nucleus giving bearth to vanillin
 C^- = vanillate anion
 E = vanillin hydroperoxide
 F^* = radical created from the decomposition of E
 G^* = hydroxyl radical (HO^*)
 I^- = vanillate hydroperoxide
 Q = quinonic compound
 LOH = lignin polymer

Appendix: Prediction of the pH

In the case of lignin oxidation we did not try to construct a theoretical relation between lignin degradation and pH of the medium, from detailed chemical reactions as we did in the case of vanillin oxidation (Fargues et al., 1995). The detailed description of the rate of lignin oxidation (as well as the creation of acid products) is a very difficult task as it would be necessary to consider many crossover reactions between various intermediates.

We made an attempt to predict the experimental pH curve, based on logical observations of our results. We noticed a certain reproducibility in the evolution of the pH compared to the calculated oxidation curve of lignin, based on eq 6. It must be noticed that the oxidation of the vanillin produced during a typical experiment (oxidation of 0.8 g of vanillin in a volume of 500 mL) cannot be alone responsible for the observed pH decrease during the production process; it has been shown that this would create around 0.015 mol of equivalent H^+ , not sufficient to neutralize a solution containing 1 equiv of OH^- (solution of 2 N NaOH). We are also going to consider that the concentration of hydroxyl ions in the initial solution of lignin is still 2 N, which means

that there is no interaction (buffer power) of the molecule of lignin with the hydroxyl ions.

We enclose all possible acid products of the lignin oxidation (including vanillin as well) in a global designation PH^+ , responsible for the changes in pH, i.e., $LO^- + O_2 \rightarrow PH^+$.

Comparing the experimental pH curve with the theoretical curve of the disappearance of lignin (eq 6), we notice that the inflection point of pH occurs in many cases (at least for the experiments where $[L]_i = 60$ g/L) for an oxidation of around 53 g/L of lignin. We also observe that the pH stabilizes around 9, probably due to a buffering power of the products PH^+ . On this basis, we construct a model with the following assumptions:

(a) 500 mL of the initial solution of lignin ($[L]_i$ from 30 to 120 g/L) still contains 1 equiv of OH^- .

(b) The oxidation of 26.5 g of lignin neutralizes 1 equiv of OH^- ; it means 1 equiv of PH^+ is created. The relation between $[PH^+]$ in equiv/L and $[L]$ in g/L is then

$$[PH^+] = x = 0.03774([L]_i - [L])$$

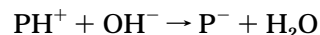
(c) The products PH^+ have a buffering power around $pK_a = 9$.

The titration curve of NaOH by PH^+ can be calculated in three steps:

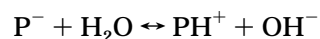
$$[1] \text{ for } x < 1 \text{ N} \quad pH = 14 \quad (A.1)$$

$$[2] \text{ for } 1 \text{ N} < x < 2 \text{ N} \quad pH = 14 + \log [OH^-] = 14 + \log(2 - x) \quad (A.2)$$

During these two steps, all molecules of PH^+ are transformed in the corresponding base P^- :



[3] for $x > 2$ N, the value of the pH comes from the proportion of P^- and PH^+ in the solution



$[P^-] = 2 \text{ N}$ and $[PH^+] = x - 2$, leading to:

$$pH = pK_a + \log \frac{[P^-]}{[PH^+]} = pK_a + \log \frac{2}{x - 2} \quad (A.3)$$

with $pK_a = pK_{(P^-/PH^+)} = 9$.

[4] we must add a fourth step of transition between steps 2 and 3: for x near 2, $[P^-]$ becomes the main species controlling the pH

If $[PH^+] = [OH^-] = y$, $[P^-] = x - y$, then

$$\frac{[PH^+][OH^-]}{[P^-]} = \frac{K_e}{K_a} = \frac{y^2}{x - y}$$

Neglecting y compared with x , $[PH^+] = y = (K_e x / K_a)^{1/2}$, leading to

$$pH = pK_a + \log \frac{x - (K_e x / K_a)^{1/2}}{(K_e x / K_a)^{1/2}} \quad (A.4)$$

The transition x between the expressions 2 and 4 has been calculated as 1.9955.

The pH evolutions of run 2 ($[L]_i = 60$ g/L, Figure 8) and run 4 ($T = 154^\circ\text{C}$, Figure 5b) have been successfully

predicted with the above model, as well as runs 5 ($P_{O_2} = 1.2$ bar, Figure 6a) and 7 ($[L]_i = 30$ g/L, Figure 7a) which exhibit less than 50 g/L of oxidation of lignin. In the case of run 6 ($P_{O_2} = 5$ bar, Figure 6b), a better simulation is obtained with a value of $pK_a = 9.5$, and the concentration of lignin oxidated to obtain the inflection point is a little higher (57 g/L).

For the run 9 ($[L]_i = 120$ g/L, Figure 7b), the experimental inflection point of the pH curve occurs for a greater oxidation of lignin (≈ 80 g/L); therefore, eq A.4 for pH prediction is now $[PH^+] = x = 0.025([L]_i - [L])$.

The pH variation for run 1 ($T = 110$ °C, Figure 5a) is not correctly predicted; combined effects of the oxidation products PH^+ and the postoxidation products of PH^+ (as oxalic acid) are probably responsible for the decrease in the pH.

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