



Biomass conversion: attempted electrooxidation of lignin for vanillin production

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Abstract

Electrochemical oxidative degradation of Kraft lignin was investigated in batch and flow cells on Pt, Au, Ni, Cu, DSA–O₂ and PbO₂ anodes. Production of vanillin was evaluated by means of formal kinetic analyses. Conversion and chemical yields were found to be dependent mainly on the applied current density, that is on the partial pressure of oxygen at the interface, while the nature of the electrode influenced the reaction rates.

1. Introduction

The structure of lignin has not been fully elucidated but its empirical formula is usually represented as C₉H_{8.83}O_{2.37}(OCH₃)_{0.96} [1]. Degradation of lignin polymers reveals three basic structures assembled through ether or C–C bonds as shown in Scheme 1. Oxidative depolymerization involves α and β aryl-ether. Typically, it results in the conversion of phenolic nuclei to *o*- or *p*-quinonoid structures or in the rupture of the aromatics leading to enoic or dienoic acids. Vanillin is obtained from the cleavage of the propanoid side chain in the presence of oxidizing agent. The theoretical yield can reach 30% with respect to the lignin. Successful conversion of lignin into vanillin (27%) by chemical methods as nitrobenzene or metallic oxides oxidation was reported during the first half of the century [2–5].

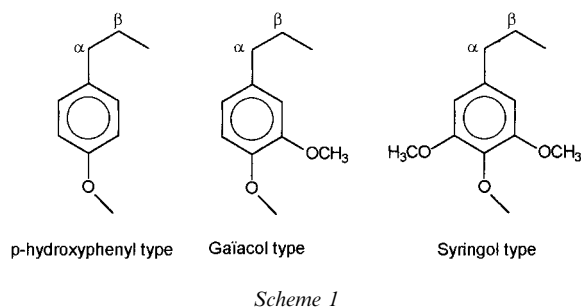
During the 1970s, electrochemical properties of lignin and model compounds of lignin were investigated by Kovalenko, Vodzinskii or Koryttseva and coworkers [6]. The yields of monomers obtained from lignin oxidation varied according to the nature of the anode. When the lignin concentration was 50 g L⁻¹, the maximum yield (absolute, not relative) of vanillin obtained at 1 A h⁻¹ g⁻¹ did not exceed 3%, which is far from the 27% claimed by chemical methods. Otherwise, oxidation of acetone-soluble spruce lignin was performed using nitroaromatic oxidants and the possibility of their anodic regeneration was explored [10]. The chemical yields in vanillin could reach 15% and the selectivity 74% at low conversion (2%). Most of these results were patented [11, 12] but economical problems, such as the cost of the sodium hydroxide, did not allow scale up of the process.

More recently, the mechanism for oxidative cleavage of model phenolic ethers of lignin was studied by Pardini et al. [7]. The authors demonstrated the crucial role of the substituents (4-hydroxyl, α -keto, β -*o*-aryl and β -hydroxymethyl) using nickel anodes at which polymerization processes were found to be predominant, although small amounts of aldehydes and corresponding acids were produced. Fargues et al. [9] have reported kinetic results of vanillin production from 30–120 g L⁻¹ lignin solutions under partial pressure of oxygen (1–5 bar) and relatively low temperature (110–150 °C) in 2 N NaOH. Maximum yield (10%) was obtained at 133 °C and 3 bars of O₂.

From what is currently known about electrocatalysis, such transformations can be carried out by associating the concepts and the methods of interfacial electrochemistry with those of heterogeneous catalysis. The carbon–carbon cleavage and the oxygen transfer can be achieved through the catalytic properties of the working electrode and its potential.

2. Experimental details

Voltammetric measurements were performed in a thermostated three electrode glass cell using a HI-TEK generator/potentiostat and a Philips X–Y recorder. Working electrodes were pretreated before each measurement (flame annealing for noble metals, polishing for the others). The working electrode was introduced into the solution at controlled potential and the first and the following voltammograms were recorded versus a saturated calomel electrode (SCE). Supporting electrolyte was prepared from ultrapure water (E-pure system)



and analytical grade NaOH (Pronalab). Kraft lignin, vanillin, eugenol, guaiacol and vanillyl alcohol were purchased from Aldrich. The solutions were deaerated with ultrapure argon (U quality from L'Air Liquide).

Electrolyses were performed in a double compartment batch cell and in a filter press cell (FM01-LC from ICI and Watson–Marlow peristaltic pump). The two compartments were separated by an ion exchange membrane (Ionac 3475). The constant current and constant potential electrolyses were performed using a DC power supply (IKA-EN 500) and a galvanostat/potentiostat (Amel 2055), respectively.

Direct quantitative analyses of the anolyte were performed on HPLC (pump and UV detector from Jasco, LiChrospher RP18 column from Merck, H₂O/ACN 80/20 0.2% TFAA) after precipitation, centrifugation and filtration of the samples. The aqueous solution was also extracted using an accelerated one-step extractor/concentrator and analysed by GC–MS (INCOS 500 and ITS 40, Varian). A gas chromatograph (Chrompack) equipped with a capillary column (DB-5, J&W) was also used for the quantitative analyses.

Blank experiments were performed according to the standard procedures. Specifically, vanillin production from 0.5% of Kraft lignin/NaOH 1 M/room temperature in contact with the anode under stirred conditions for 6 h (in order to be sure that no pure catalytic reaction by the anode material could take place) was evaluated. It was found that the concentration of vanillin rapidly reached a stable value (within 30 min). This concentration was reported in Figures 5, 6, 7, 8 and 9 and corresponds to the analyses at $t = 0$ (electrolyses were started 1 h after the preparation of the anolyte).

3. Results and discussion

3.1. Voltammetric study

It was found that the passivation of the anodes during lignin electrolyses was related to processes involving phenolic compounds [8]. Oxidation of guaiacol, eugenol, vanillin alcohol and vanillin were investigated by cyclic voltammetry on several electrodes (Pt, Au, Ni and C). Except in the case of vanillin, the anodes were deactivated after the first cycle. For example, on nickel electrodes in the presence of guaiacol (Figure 1), the

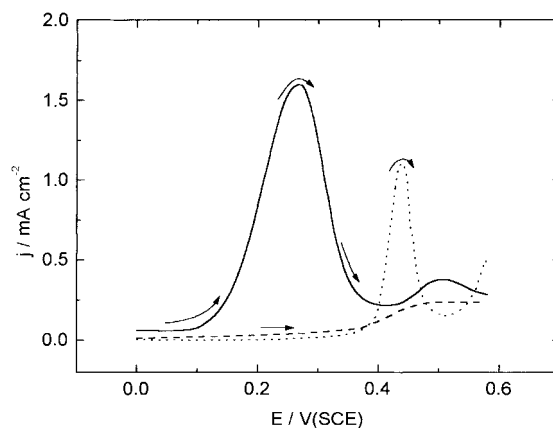


Fig. 1. Electrooxidation of guaiacol 10^{-2} M on nickel electrode in 1 M NaOH. Voltammograms recorded at 50 mV s^{-1} at room temperature. Dotted line: in the absence of guaiacol; solid line: first cycle in the presence of guaiacol; dashed line: second cycle in the presence of guaiacol.

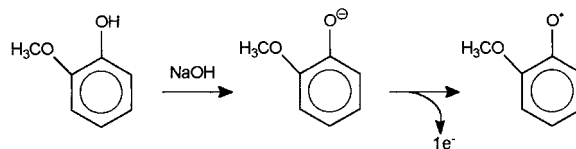
oxidation wave observed during the first cycle (solid line) diminished drastically during the second one (dashed lines).

During the first positive sweep of the potential, guaiacol is oxidized before the so called 'NiOOH region' [13]. This means that the processes does not involve oxygen species. The current is due to a direct electron transfer leading to a radical which initiates the polymerization as shown in Scheme 2 [8].

Vitreous carbon, gold and platinum electrodes underwent the same phenomenon. The i.r. spectra of the polymeric film formed during guaiacol oxidation on platinum in alkaline medium revealed the characteristic bands of aryl–alkyl ether at 1174 and 1033 cm^{-1} and of polymeric OH vibration at 3386 cm^{-1} .

Figures 2 and 3 represent $j = f(E)$ curves recorded during the first positive sweep on gold and nickel, respectively.

Concerning the similarity of the oxidation peaks of guaiacol, eugenol, vanillic alcohol (2nd peak) on both nickel and gold electrodes, the assumption of a direct electron transfer during this wave is confirmed. On gold and in the presence of vanillic alcohol the first peak can be attributed to the oxidation of the primary alcohol group (dehydrogenation). If the upper limit of the potential is maintained at lower values than the second wave, the voltammograms are stable during cycling and no polymer formation is observed. The vanillin oxidation occurs at more positive potential, just before oxygen evolution. As lignin is oxidized at lower poten-



Scheme 2

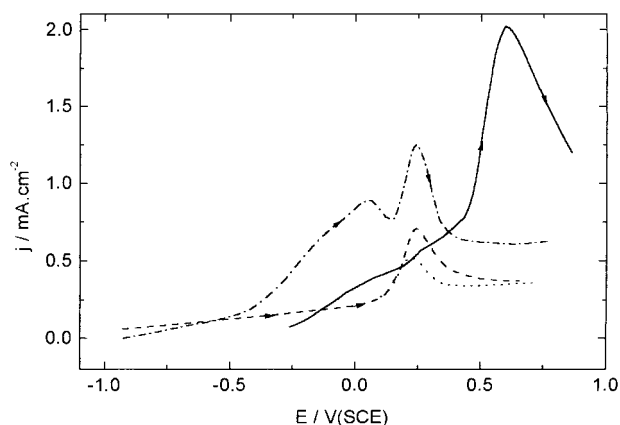


Fig. 2. Electrooxidation of model compounds 10^{-2} M on gold electrode in 1 M NaOH at room temperature. First positive sweep recorded at 50 mV s^{-1} . Solid line: vanillin; dash-dotted line: vanillic alcohol; dashed line: guaiacol; dotted line: eugenol.

tials (Figure 4) it would be expected that the vanillin produced would not undergo further oxidation.

Unfortunately, all the electrolyses carried out in the range of the stability of the solvent led to rapid and strong anode passivation. Oxidative depolymerization of lignin also led to substituted phenolates, which were further oxidized to radicals following Scheme 2.

3.2. Preparative electrolyses

3.2.1. In batch cell

The results obtained by cyclic voltammetry showed that electrochemical depolymerization of kraft lignin can only be performed at very positive potentials corresponding to oxygen evolution to avoid the passivation of the electrode. The catalytic effect of the electrode material is lowered and the oxidative depolymerisation is carried out through activated oxygen.

The formal kinetics of the reaction were investigated in a batch cell on nickel, platinum and copper anodes.

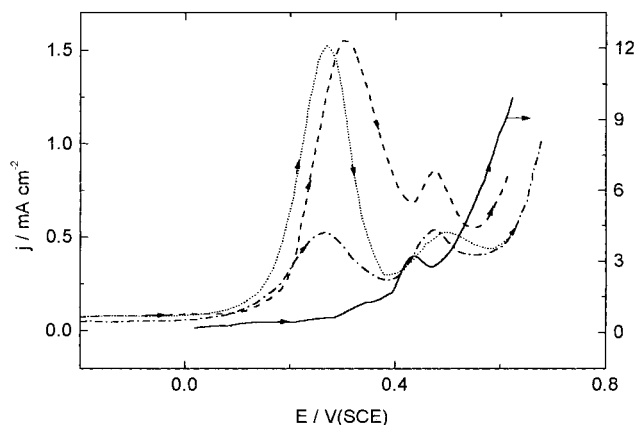


Fig. 3. Electrooxidation of model compounds 10^{-2} M on nickel electrode in NaOH 1 M at room temperature. First positive sweep recorded at 50 mV s^{-1} . Solid line: vanillin; dash-dotted line: vanillic alcohol; dashed line: guaiacol; dotted line: eugenol.

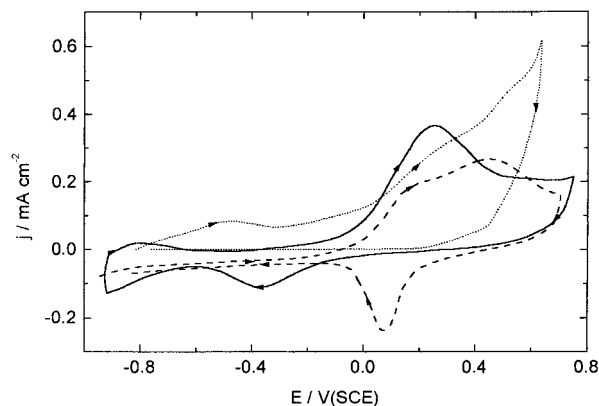


Fig. 4. Electrooxidation of 2% lignin in NaOH 1 M. Voltammograms recorded at 50 mV s^{-1} . Solid line: on platinum; dashed line: on gold; dotted line: on nickel.

172 cm^3 of anolyte containing 0.5% Kraft lignin (0.9 g) and 1 M NaOH was electrolysed at 700 A m^{-2} (the cell potential was almost constant and equal to 12–13 V). The results plotted in Figure 5 show that the production rate of vanillin is higher on copper than on platinum or nickel.

Nevertheless, vanillin seems to be a primary product which can be further oxidized to vanillic acid and other products of low molecular weight (mainly aliphatic carboxylic acids). Otherwise, increasing the applied current increases the rate of vanillin formation and shifts the maximum towards more positive values (Figure 6). In all cases the yields were low and never exceeded 10% conversion by mass of the initial Kraft lignin.

3.2.2. In 'filter press' cell

As the yields were found to be connected with the applied current and, therefore, with the partial pressure of oxygen at the interface, preparative electrolyses in the filter press cell were performed on Ni, DSA- O_2 and

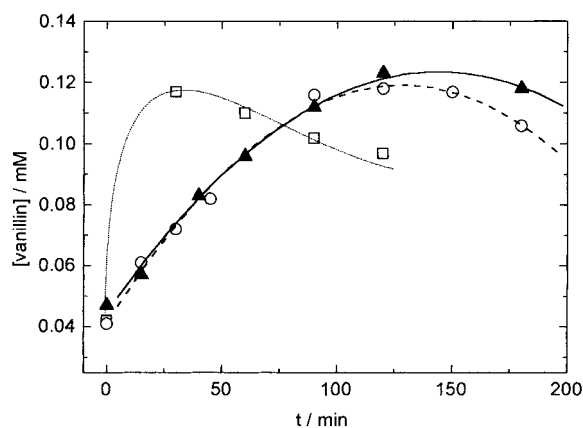


Fig. 5. Constant current electrolysis of 0.5% lignin in a batch cell at 700 A m^{-2} and room temperature. Effect of the nature of the anode on vanillin production. Key: (\blacktriangle) on nickel; (\circ) on platinum; (\square) on copper.

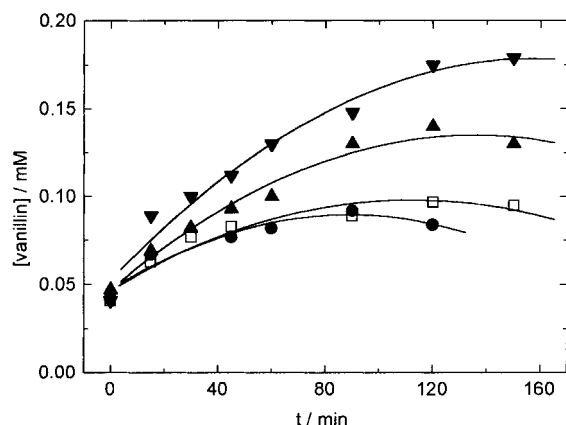


Fig. 6. Constant current electrolysis of 0.5% lignin in a batch cell on nickel anode at room temperature. Effect of the current density. Key: (▼) 850, (▲) 700, (□) 500 and (●) 350 A m⁻².

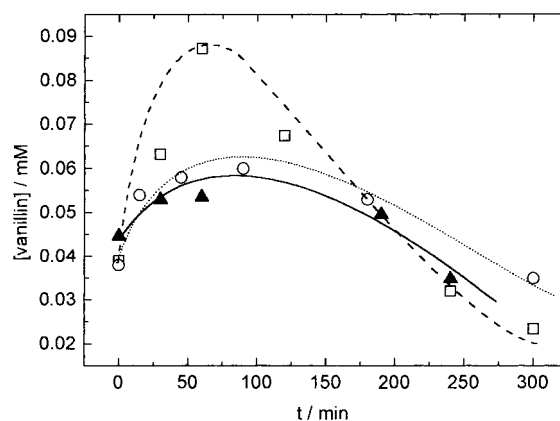


Fig. 7. Constant current electrolysis of 0.5% lignin in a filter press cell on DSA-O₂ at room temperature. Effect of the current density on vanillin production. Key: (□) 1500, (○) 750, (◻) 500 and (▲) 150 A m⁻².

PbO₂. The results obtained after 3 h are summarized in Table 1 [8].

Other oxidative derivatives (eugenol, catechol,...) were identified but in a rather small amount in comparison with those reported in Table 1 which represent more than 98%. The conversion yield is expressed as the ratio of the total amount of identified products and the initial weight of lignin.

The change in nature of the anode and of the initial concentration, otherwise under the same conditions, had no particular effect neither on selectivity towards vanillin nor on the conversion yield. As the processes are connected with the activated oxygen produced at the anode, the applied current density was expected to be a determining parameter. This effect is illustrated in Figure 7.

Contrary to what was observed on nickel in the batch cell (Figure 6), the maximum concentration of vanillin is reached at a constant time. Its rate of consumption is proportional to the applied current, which means that the optimum is reached using the shortest electrolysis time and the highest applied current.

Table 1. Electrooxidation of Kraft lignin in 1 M NaOH (250 cm³) in a filter press cell at room temperature. Effect of the nature of the anode on the distribution of the oxidative derivatives determined by GC analyses after precipitation, centrifugation and extraction

	DSA-O ₂	PbO ₂	Ni
<i>j</i> /A m ⁻²	600	600	300
Initial concentration of Lignin*/%	2	0.2	0.2
Conversion Yield/%	15	17	7
Vanillin [†] /%	63; 3.1 [‡]	64; 0.14 [‡]	56
Vanillic acid [†] /%	1	4	5
Guaiacol [†] /%	8; 0.5 [‡]	12; 0.05 [‡]	16
Hydroxymethoxyphenyl ethanone [†] /%	15; 0.7 [‡]	11; 0.02 [‡]	12
Hydroxymethoxybenzene acetic acid [†] /%	8; 0.35 [‡]	5; 0.01 [‡]	5
Hydroxybenzaldehyde [†] /%	2	2	4

* expressed as wt %

[†] relative yields

[‡] number of mmoles

On both nickel and DSA-O₂ electrodes the kinetic law is similar with high initial rates of vanillin production. Under the same experimental conditions nickel electrodes are more efficient (Figure 8).

The vanillin consumption may be due to the positive shift of the potential during galvanostatic electrolysis. Potentiostatic electrolyses at 1 V (controlled potential vs SCE) on DSA-O₂ electrode were performed. Quantitative analyses of vanillin and vanillic acid are plotted in Figure 9. The kinetics and the yields are similar to those observed under galvanostatic conditions until the vanillin concentration reaches a maximum, then the further oxidation rates are lowered.

To conclude, vanillin is produced by electrochemical oxidative degradation of Kraft lignin. The processes are initiated by activated oxygen produced at the electrode. To a certain extent, it is not necessary to control the potential. On both nickel and DSA-O₂ electrodes the effect of applied current density was found to be more important from 500 A m⁻². This is unambiguously associated with processes involving oxygen species from the solvent. As the vanillin

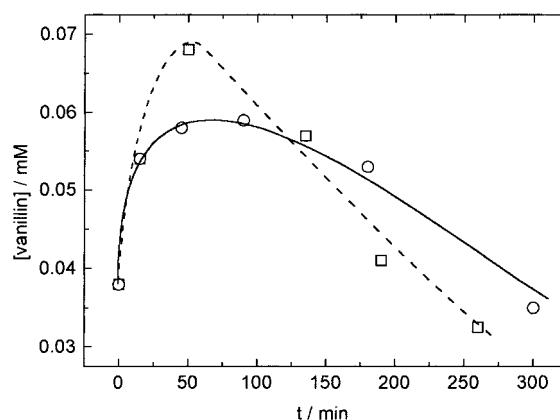


Fig. 8. Constant current electrolysis of 0.5% lignin in a filter press cell at 750 A m⁻² and room temperature. Effect of the nature of the anode on vanillin production. Key: (□) on nickel and (○) on DSA-O₂.

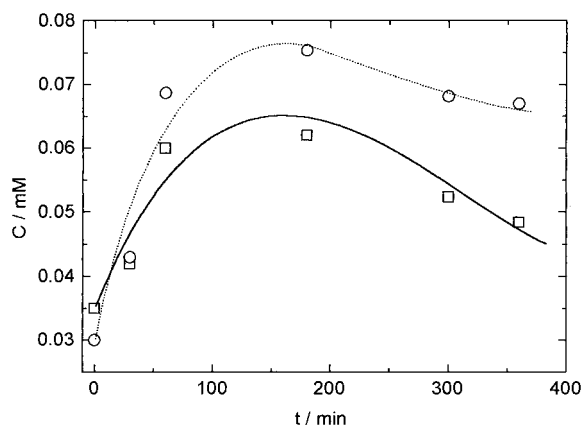


Fig. 9. Constant potential electrolysis of 0.5% lignin in a filter press cell on DSA-O₂ at 1 V vs SCE and room temperature. Key: (○) vanillin and (□) vanillic acid.

concentration rapidly reaches a maximum, vanillin must be extracted continuously during electrolysis to prevent its further oxidation.

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