

# Electro-organic reactions. Part 60[1]. The electro-oxidative conversion at laboratory scale of a liginosulfonate into vanillin in an FM01 filter press flow reactor: preparative and mechanistic aspects

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**Abstract** The electrochemical conversion of a spruce liginosulfonate into vanillin, at nickel anodes, was explored in previously unobtainable detail. A flow reactor (FM01), in a rig that permitted considerable variation of electrolysis conditions, allowed up to 150 g to be electrolysed at up to 12 A at a variety of electrode configurations. Samples taken during electrolysis gave detailed reaction profiles. The electrolyser operated at 145 °C/500 kPa/3 M NaOH and yields of vanillin were similar to those obtained industrially using chemical oxidants (about 5–7% w/w). Vanillin production was favoured by low current density and low initial concentration of liginosulfonate. Vanillin, alone, was consumed in a 2.7 F process under the above conditions. Historically, yields in chemical and electrochemical conversions of liginins into vanillin do not exceed 10%; the results herein explain this apparent limit as equilibrium between formation of vanillin, its concomitant oxidative destruction and further condensation of liginins.

**Keywords** Vanillin · Liginin · Electrooxidation · Flow reactor · Biomass conversion

## 1 Introduction

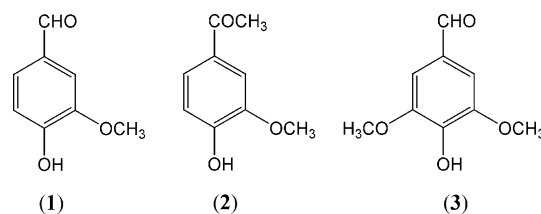
In the context of replacing oil and coal products by renewable resources there is renewed interest [2] in the conversion of liginocellulosic materials into low-molecular weight biofuels (from cellulose and hemicelluloses) and useful fine chemicals (from liginin). Liginocellulosic materials may contain 15–30% liginin and the scale of liginin production worldwide, just as a by-product of paper manufacture from wood, is immense (about  $10^7$  tonnes per year in 2000) [3]. For comparison, oil production [4] in 2007 was  $>10^{13}$  tonnes per year. In this article, we explore the electrochemical oxidation of a cheap liginosulfonate as a method of degradation into, primarily, vanillin (1), a relatively high-priced food additive.

The oxidative conversion of liginins into vanillin and other low-molecular weight products has been much used since the 1940s and processes involving a variety of oxidants have been the subjects of many patents. [5–12]. One leading method involves the treatment of liginins in alkaline solution with oxygen at about 150 °C in the presence of copper or cobalt catalysts [13]. Yields of vanillin are typically 4–7 w/w %. Such processes have been examined in detail, with mechanistic, product, and kinetic studies [13, 14].

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Formulae (1)–(3)

Several attempts have been made to oxidise lignins electrochemically [15, 9, 16]. Oxidation of a lignin (unspecified) at a boron doped diamond anode at pH < 11 represents a new approach, but little information is available, especially about yields of vanillin and related products [17]. However, the boron-doped diamond anodes, under otherwise mild conditions, have been shown [18–20] to effect almost complete electro-oxidative destruction of phenols in aqueous solution, including liginosulfonates. Probably the most successful electrochemical method has been the use of a sealed stainless steel cell equipped with nickel electrodes operating at several atmospheres and at >150 °C. The cell and conditions are well described in a patent [9] and in the open literature [16]; essentially, lignins dissolved in aqueous sodium hydroxide are electrolysed at nickel anodes to give vanillin at >6 w/w% together with other products such as acetovanillone (2) and syringaldehyde (3). The alkaline nickel anode has been shown [21, 22] to involve oxidation at the surface by a Ni(III) species. Oxidation of primary alcohol functions at high area nickel anodes, under flow conditions, has previously been carried out [23, 24] at ambient temperatures and pressures. The usefulness of a batch process involving a sealed cell is clearly limited and herein we describe the exploration of the anodic degradation of a spruce liginosulfonate in a flow reactor capable of reproducing the batch cell conditions.

There is no single, structurally homogenous, lignin and the results of degradative experiments depend crucially on the type and provenance of the lignin sample. Lignins are mixtures of complex three-dimensional polymers composed of oxygenated phenyl propane units and the starting point for lignin biosynthesis is enzymatic oxidation of coniferyl alcohol (4) with subsequent reaction involving quinonemethide radicals (5 in Scheme 1). Key structural features and functionality found in lignins are shown here (6). The  $\beta$ -O-4 linkage is the most common link accounting

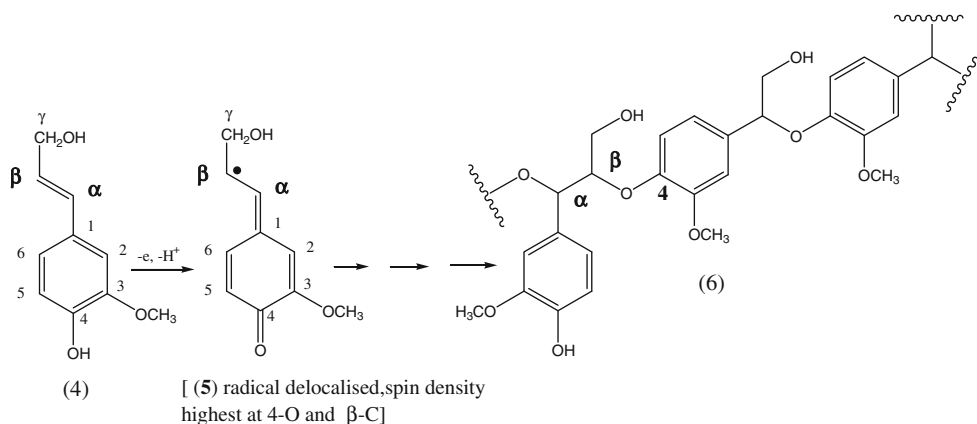
for about 50% of the connections between phenyl propane units in most lignins. Individual samples can be characterised by determination of molecular weight and molecular weight distribution. Functionality can be assessed where solubility is possible by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy [25] or, for the more usual case of solids, by solid-state  $^{13}\text{C}$  NMR spectroscopy [26].

In alkaline solutions or suspensions of lignins, especially at >100 °C, important chemical changes take place. The changes are fairly well understood to involve quinonemethide intermediates, from studies of lignins and of model compounds [27–30]. Whilst there is formation of small amounts of low-molecular weight products the main changes are modification of functionality in the polymer. It has been asserted [31] that substantial oxidation-free conversion of lignins into vanillin can be achieved at 25 °C and pH 8–12. The versatility of the electrolyser described herein allows testing of this claim.

## 2 Experimental

### 2.1 Materials and methods for characterisation

The lignin used was Ultrazine NA, a liginosulfonate supplied by Borregaard Industries Ltd. and produced from spruce by the sulphite process. The lignins, and where appropriate lignin residues following electrolysis, were characterised by  $^{13}\text{C}$  NMR spectroscopy [26, 25] and molecular weight determination using gel permeation chromatography [32]. The equipment was Krauer (HPLC pump 64, variable wavelength monitor, oven control unit and plotter) combined with 30 cm PL gel 5  $\mu\text{m}$  100 and 500 Å columns at 80 °C with elution by 0.1% LiBr in DMF and detection at 256 nm. Molecular weight distributions, especially  $M_n$  (number average) and  $M_w$  (mass average), and polydispersivity ( $D = [M_w/M_n]$ ), were



**Scheme 1** Lignin bond formation from coniferyl alcohol

estimated in the usual way [32] by comparison with elution times for polystyrene standards (low-molecular weight calibration kit [580–22,000] from Jones Chromatography). There are no completely satisfactory standards for lignin analysis, but these are the best available.

## 2.2 Analysis of products of electrolysis

Samples of the electrolysis liquor were analysed by HPLC using a  $\mu$ bondapak 10C18, 25 cm  $\times$  0.4 cm ID column with a  $\mu$ bondapak C18 guard column. The mobile phase was 1% aqueous acetic acid (solvent A) with gradient elution over 40 min with methanol (solvent B) at a flow rate of 1.5 mL min<sup>-1</sup> with uv detection at 280 nm.

A measured volume of the electrolysis liquor (containing ca. 250–500 mg of lignin) was transferred to a 50 mL volumetric flask. This solution was diluted with solvent A (ca. 15 mL, cooled in an ice bath) and made acidic (pH 3) with glacial acetic acid. Methanol (ca. 15 mL) was added and the resulting suspension made up to volume (50 mL) with solvent A. The supernatant was filtered through a syringe filter (0.5  $\mu$ m, nylon). Stock solutions in methanol were prepared (vanillin, 4.0 mg mL<sup>-1</sup>; 4-hydroxybenzaldehyde, 7.0 mg mL<sup>-1</sup>; vanillic acid, 5.0 mg mL<sup>-1</sup>; acetovanillone, 6.0 mg mL<sup>-1</sup>) from which standard solutions were prepared by mixing aliquots of the solutions of vanillin (5.0 mL), 4-hydroxybenzaldehyde (1.5 mL), vanillic acid (1.5 mL), and acetovanillone (1.5 mL) with subsequent dilution to 100 mL with solvent A. An appropriate volume (ca. 2–6  $\mu$ L) of the filtered sample was injected and compared with the standard in the usual way.

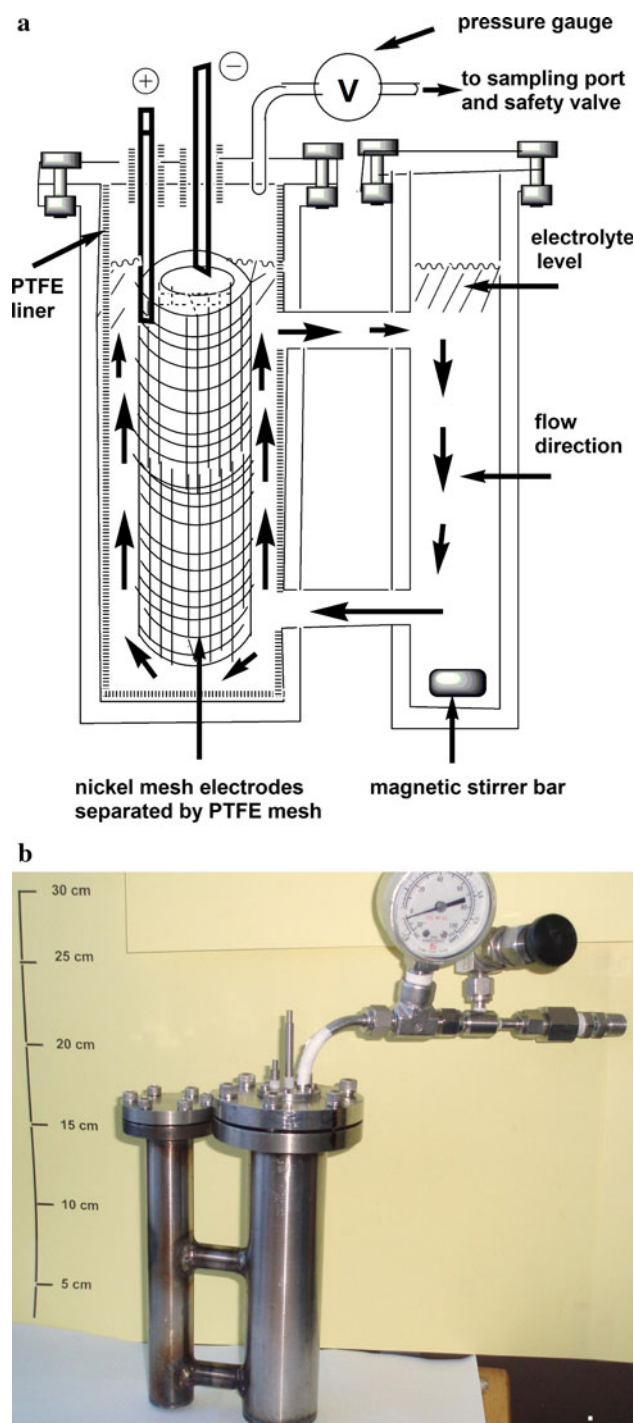
## 2.3 Electrolysis procedures

### 2.3.1 The batch cell

The batch cell is shown in Fig. 1 and was used for preliminary experiments. It was based on the stainless steel pressure cell (total volume 96 mL) used in earlier work, where it, and its operation, has been described in detail [9]. For this study, it was fitted with cylindrical nickel electrodes with an anode area of 57 cm<sup>2</sup>. A pressure gauge (max 100 psi [689.4 kPa]) and a safety valve (variable 50–250 psi) were fitted together with a gas-sampling valve. The cell was flushed out with O<sub>2</sub> free nitrogen before sealing; gas evolved during electrolysis was analysed by mass spectrometry (MS50RF).

### 2.3.2 The flow reactor rig

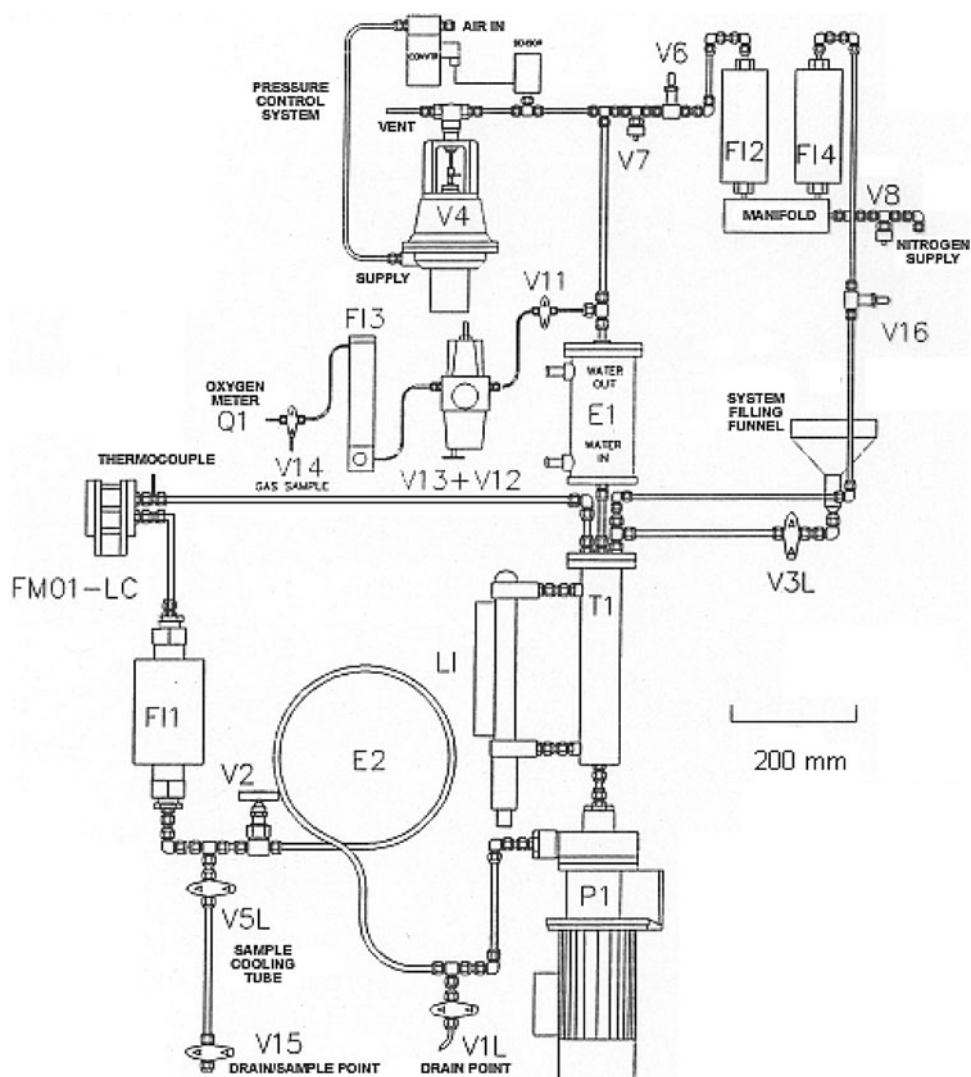
Strictly this electrolyser should be described as “semi-batch” because the system is sealed. The assembly (Figs. 2, 3) was designed to electrolyse multigram samples



**Fig. 1** a Schematic of batch cell. b Photograph of batch cell

of lignin dissolved in 1 L of concentrated aqueous sodium hydroxide. This could be heated at up to 170 °C at a consequent pressure of up to 4.0 barg (=5.0 bar = 5.0  $\times$  10<sup>2</sup> kPa). A stabilised DC power supply (Farnell) could supply up to 50 A at up to 60 V; the current was typically 6–12 A. The pressure gauges for the batch cell and for the flow rig were supplied in engineering format, i.e. psi (pounds force per square inch) and barg (bar gauge

**Fig. 2** Schematic diagram of flow rig (see text for explanation of labelling)



whereby calibration is such that zero = 1 bar). In discussing the results of experiments, pressure has been converted into kilo pascals (kPa) according to the factors 1 psi = 6.894 kPa and 1 bar = 100 kPa.

The key labelled components are: P1, stainless steel pump (motor Brook Parkinson Motors, 1 HP, model PCL 80L; pump head Global Pumping Systems, 30 bar; non-corrosive flowmeter, Platon serial 62384, scale 0–60 L h<sup>-1</sup> water); nitrogen flowmeters (F12, F14) Platon C60 with range 6–400 L h<sup>-1</sup>; oxygen flowmeter (F13) Platon with range 2–250 cm<sup>3</sup> min; pressure control system (pressure transmitter Amot Spot model 8302AAB1A-AA, range 0–10 barg, converter Watson Smith type 100X, 8A0114008, input 4–20 mA, output 0.1–1.0 barg, inlet 5.5 barg maximum, control valve (V4) Platon # 062378, type 14 SCR with built-in valve positioner model 73 N/12F; level indicator (L1) Weka CH8620, pressure controller Eurotherm; heater controller RS; temperature sensor/indicator (T1), The Control House TCH 2000. Heating of the loop E2 was by heating tape, Hotfoil GW.



**Fig. 3** The flow rig (photograph courtesy of Dr. Carlos Ponce de Leon (University of Southampton))

The components were connected using stainless steel tubing of internal diameters 6.6, 4 and 2 mm as appropriate and mounted on a wheeled metal frame. Samples of the



electrolyte could be taken without interrupting electrolysis using the valves V5L and V15.

Normal flow rates were: N<sub>2</sub> purge to vent, 180 L h<sup>-1</sup>; N<sub>2</sub> purge to tank (T1, Fig. 3), 20 L h<sup>-1</sup>; vent gas flow to oxygen meter, 10 L h<sup>-1</sup>; electrolyte, 300 L h<sup>-1</sup>. An essential safety requirement was that the operation of the oxygen meter was checked before each run and that every 2 weeks the oxygen meter was recalibrated using oxygen free nitrogen and standard 1.5 v/v% O<sub>2</sub> in nitrogen (alarm set to trigger at 1.5% O<sub>2</sub>).

2.3.3 The cell (reactor)

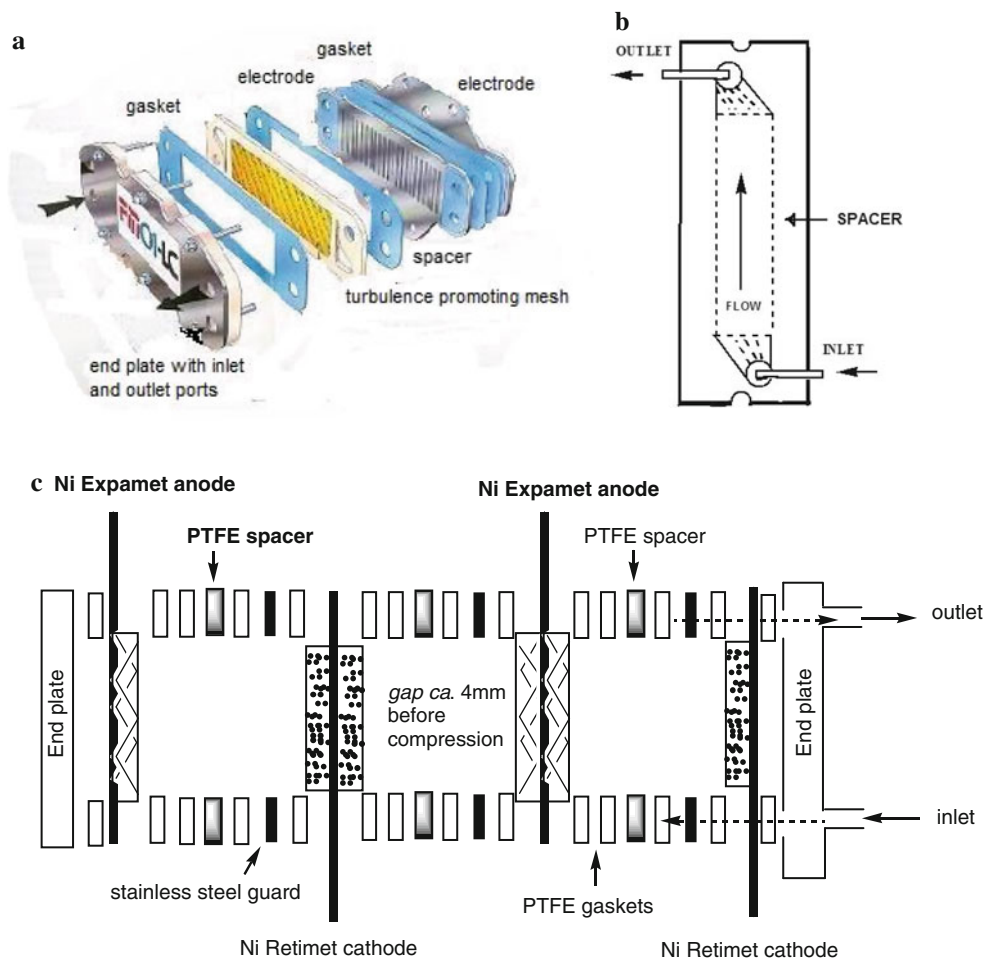
This was an FM01-LC laboratory electrolyser supplied by ICI the construction of which, and its main characteristics, have been well described in the open literature [33–35, 24]. It was supplied with a variety of standard, commercial, nickel or stainless steel electrodes (ICI), some of which presented expanded nickel surfaces (Retimet foam, Expamet mesh) with enhanced surface area (a factor of 20 is quoted by the manufacturers); the cell is of a parallel plate design. The reactor design is versatile and allows the

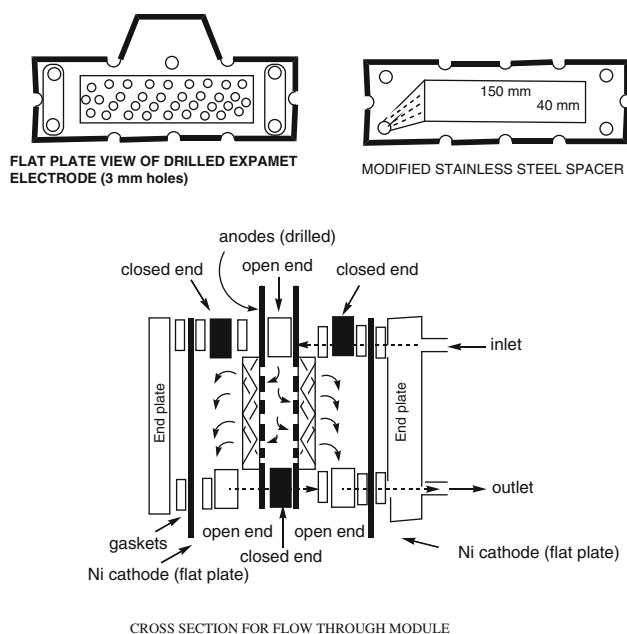
exploration of many electrode configurations. The cell was always used in the undivided mode.

Commercially available components, such as electrodes, spacers, gaskets and turbulence promoters may be combined in a variety of ways and such elements are shown in Fig. 4a. Figure 4b shows the transverse flow direction resulting from the spacer design and Fig. 4c illustrates, in cross section, one of several arrangements used in this study. By varying the number of modules, and therefore with different electrode areas, experiments may be run at a constant cell current but at different current densities. To take full advantage of the high surface area of the 3D nickel Expamet, electrodes drilled (40 × 3 mm holes) from the flat side, combined with spacers that direct the flow from one end only, were constructed. This allowed the assembly of flow-through cells of the type shown in Fig. 5.

It is important to note that the effective areas of the three-dimensional nickel Expamet electrodes are much greater than the nominal areas obtained by measuring their dimensions; the manufacturer’s estimate of an area enhancement of 20 may well be too low. It has been shown [24] that some expanded nickel electrodes can lead to an

Fig. 4 Schematic of a elements of a modular cell, b end view and c arrangements for a transverse flow cell, in cross section





**Fig. 5** Elements of flow-through cell

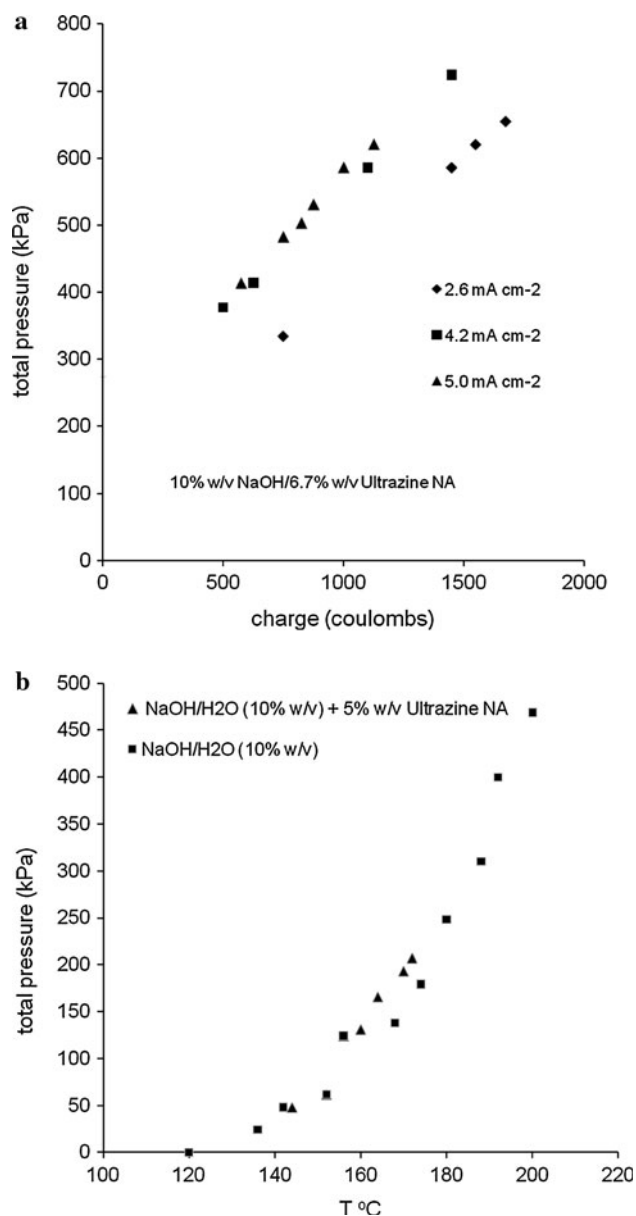
increase in cell current compared with flat plate electrodes of up to 100-fold. Current densities in the experiments described herein are calculated using the enhancement factor 20 but with the proviso that the real current densities may be much smaller. An important advantage of the flow cells is the capability of running at significant currents (several amps), thereby converting multigram quantities of lignin on a convenient timescale (usually under 3 h).

### 3 Results

#### 3.1 Experiments using the batch cell

Preliminary experiments were concerned with monitoring pressure build up as the cell temperature was increased and gas evolution during electrolysis of the aqueous alkali electrolyte to establish safe working conditions. Any substantial evolution of oxygen would clearly be dangerous.

During electrolysis of aqueous NaOH (2 M)/Ultrazine in the batch cell, at 170 °C, a steady build up of pressure is observed that increases with charge and initially with current density (Fig. 6a). When pressure was allowed to build up by electrolysis to 655 kPa (95 psi) the residual pressure when cooled to room temperature was 345 kPa (50 psi), which reflects the amount of gas generated during electrolysis. Analysis by mass spectrometry indicated that the evolved gas was substantially hydrogen with barely detectable amounts of oxygen. This qualitative result was confirmed in operation of the flow cell (see Sect. 4.1).



**Fig. 6** **a** Total pressure as a function of charge; **b** as a function of temperature

Figure 6b illustrates the pressure build up of 10% w/v NaOH/H<sub>2</sub>O alone and with dissolution of 5% w/v Ultrazine NA. It is evident that the build up is smooth at up to 345 kPa (50 psi)/200 °C. Furthermore, the dissolution of Ultrazine has little effect on the pressure/temperature curve indicating that no volatile products are produced by chemical reaction.

Preliminary experiments in the batch cell, followed up systematically using the flow cell, are displayed in Table 1. In 3 M aqueous NaOH at 170 °C, after 6.5 h, measurable degradation of the Ultrazine NA into vanillin is observed (entry 1). However, these conditions are much more severe than those described [31] for rot wood and kraft lignins

**Table 1** Preliminary observations using batch cell

Entry	Conditions	Lignin (C g <sup>-1</sup> )	Vanillin (%w/w) <sup>a</sup>	M <sub>n</sub>	M <sub>w</sub>	D <sup>b</sup>
1	6.5 h; 4.2% w/v lignin	0	3.5	9328	13721	1.47
2	5.5 h; 4.2% w/v lignin	1026 <sup>c</sup>	6.7	7474	31724	4.3
3	2.5 h; 0.52% w/v lignin	6300 <sup>c</sup>	5.6			
4	2.5 h; 1.04% w/v lignin	3150 <sup>c</sup>	9.6			
5	15 h hydrolysis, 5 h electrolysis; 4.2% w/v lignin	1117 <sup>c,d</sup>	4.8			

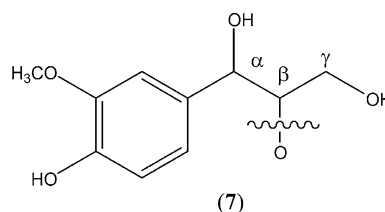
In 3 M aqueous NaOH at 170 °C. <sup>a</sup> By hplc—vanillin as % of weight of starting lignin; <sup>b</sup> untreated Ultrazine NA was M<sub>n</sub> = 28,665, M<sub>w</sub> = 73,073, D = 2.5; <sup>c</sup> 350 mA (6.1 mA cm<sup>-2</sup>); <sup>d</sup> Elemental analysis (C/S) gives 167, for reference C/S for Ultrazine NA was 21.7

where substantial hydrolysis is claimed at room temperature and pH 8–12 on a time-scale of a few hours. In the latter study, the products of degradation were presumed by comparison of polarographic reduction peaks for the hydrolysate with those for samples of vanillin and other aromatic aldehydes, i.e. direct analysis, e.g. by hplc, was not attempted. Chemical changes to lignins under alkaline conditions are well documented [36] and aldehyde, ketone, and quinone functions may be formed without the lignin polymer being ‘unzipped’. It is probably these functions, in the alkali-modified lignin, that are being detected polarographically and confused with monomeric products. A much clearer comparison of chemical as opposed to electrochemical conversion was possible from the results of flow cell experiments.

From a comparison of entries 1 and 2, it is evident that electrochemical oxidation is effective in causing substantial degradation to vanillin. The lower yield of vanillin on further electrolysis (entry 3) is the first indication that vanillin is sensitive to overoxidation. The highest yield of vanillin (9.6% w/w), from these preliminary experiments, was obtained using a lower concentration of lignin and less extensive electrolysis (entry 4). These factors were explored in more detail using the flow cell, which permitted sampling during electrolysis. Changes are evident in the molecular weights of residual lignin after degradation by both hydrolysis and electrooxidation (entries 1 and 2). Compared with the molecular weight profile of Ultrazine NA (footnote to Table 1), M<sub>n</sub> and M<sub>w</sub> are much reduced in both cases. However, the dispersivity, D, is increased considerably after electrooxidation, probably an indication of further condensation.

Elemental analysis of Ultrazine NA suggests an empirical formula C<sub>10</sub>H<sub>13</sub>O<sub>4</sub>·½SO<sub>3</sub>Na, consistent with the C<sub>10</sub> unit approximating to structure (7). In particular, this is consistent with the observed ratios H/C = 1.31 (1.25 experimental) and C/S = 19.9 (21.7 experimental). After electrolysis (Table 1, entry 5), the C/S ratio is greatly increased (to 167) in recovered lignin reflecting substantial removal of sulphur. Other significant changes are revealed by <sup>13</sup>C NMR spectroscopy before and after electrolysis.

Prominent signals at δ (ppm) 190, 175, 108–158 and 56 are assigned, respectively, to CO (ketone, quinone), CO<sub>2</sub>H, aromatic carbons and ArOCH<sub>3</sub>. The CO<sub>2</sub>H and CO functions are not detected in Ultrazine NA, but after electrolysis (752 C g<sup>-1</sup>) signals assigned to these functions appear for the recovered lignin and their significance can be judged by comparing the integrated areas with that for the six aromatic carbons—i.e. Ar (24.5):CO<sub>2</sub>H (3.0):CO (1.0). Thus, there is substantial oxidation of functional groups without cleavage to low-molecular weight compounds. There appears to be little cleavage of methoxyl groups upon electrolysis; the ratios of aromatic carbons:OCH<sub>3</sub> are 5.9 (before electrolysis) and 6.0 (after).



Formula (7)

## 4 Experiments using the flow cell

### 4.1 Approach and choice of standard conditions

The use of the flow cell allowed a thorough exploration of the factors influencing large scale electro-oxidative degradation of Ultrazine NA. Key parameters that can be varied are: nominal current density, electrode configuration, temperature, concentration of lignin and of alkali. The reservoir was charged with 1 L of electrolyte containing 15–150 g of Ultrazine NA; samples were withdrawn at intervals and products analysed.

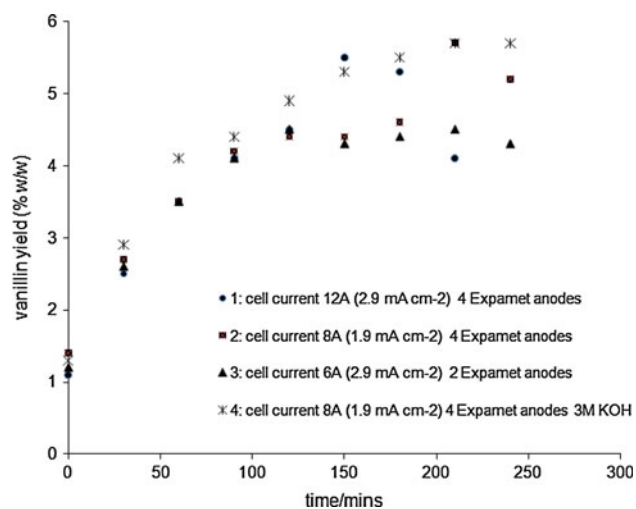
The temperature controller could theoretically operate at up to 170 °C, the temperature for batch cell electrolyses. However, preliminary experiments showed that, at the optimal flow rate of 300 L h<sup>-1</sup>, lowering of the temperature to 130 °C gave a much reduced yield of vanillin and there

**Table 2** Vanillin yields (%w/w) as function of cell configuration and consequent parameters: see Fig. 7

Time/min	C g <sup>-1</sup>	6 A (2.9 mA cm <sup>-2</sup> ) 2 Expamet anodes Yield	C g <sup>-1</sup>	8 A (1.9 mA cm <sup>-2</sup> ) 4 Expamet anodes Yield	C g <sup>-1</sup>	12 A (2.9 mA cm <sup>-2</sup> ) 4 Expamet anodes Yield	C g <sup>-1</sup>	8 A (1.9 mA cm <sup>-2</sup> ) <sup>a</sup> 4 Expamet anodes Yield
0	0	1.2	0	1.4	0	1.1	0	1.3
30	177	2.6	236	2.7	4140	2.5	236	2.9
60	354	3.5	472	3.5	8280	3.5	472	4.1
90	531	4.1	708	4.2	12420	4.1	708	4.4
120	708	4.5	944	4.4	16560	4.5	944	4.9
150	885	4.3	1180	4.4	20700	5.5	1180	5.3
180	1062	4.4	1416	4.6	24840	5.3	1416	5.5
210	1239	4.5	1652	5.7	28980	4.1	1652	5.7
240	1416	4.3	1889	5.2	33120		1889	5.7

Standard electrolysis conditions (see text), 61 g Ultrazine NA in 1 L electrolyte

<sup>a</sup> 3 M KOH



**Fig. 7** Electrolysis in the flow-through cell (see Fig. 5)—Ultrazine concentration 6.1%w/v

was no advantage in operating at 156 °C/4.6 barg. Consequently, standard conditions of 145 °C, a flow rate of 300 L h<sup>-1</sup>, with a consequent pressure of 4.0 ± 0.1 barg (=5.0 bar = 5.0 × 10<sup>2</sup> kPa), were chosen for the series of electrolyses described herein. Control experiments also showed that poor conversion into vanillin was achieved at 1.0 and 6.0 M NaOH with 3.0 M being the chosen concentration.

The cell current was controlled at values in the range 6–12 A and the consequent cell voltages were steady in the range 1.3 V (at 6 A) to 1.6 V (at 12 A). In some cases, the cathode type and material was varied (flat nickel, Retimet, Expamet, stainless steel) with no significant effect on conversion at the anode.

No oxygen was detected under any of the conditions explored and conversion into vanillin was clean; in one case acetovanillone was formed in addition to vanillin.

#### 4.2 Cell configuration; change of alkali

The flow-through cell (Fig. 5) was used with 1 or 2 modules combined (2 or 4 drilled Expamet anodes) and this allowed experiments to be run at 6, 8 and 12 A. In one case, 3.0 M KOH was substituted for NaOH. The results are summarised in Table 2 and Fig. 7.

The rates of vanillin production for much of the reaction time are almost identical and independent of the cell configuration, absolute cell current and current density. The use of KOH at low current density is marginally beneficial. Vanillin production levels off and the later points suggest (a) that a higher yield is reached at low current density (plot 3) and (b) at high current density (plot 1) vanillin is consumed (overoxidation). These observations are explored in subsequent experiments.

#### 4.3 Effect of current density

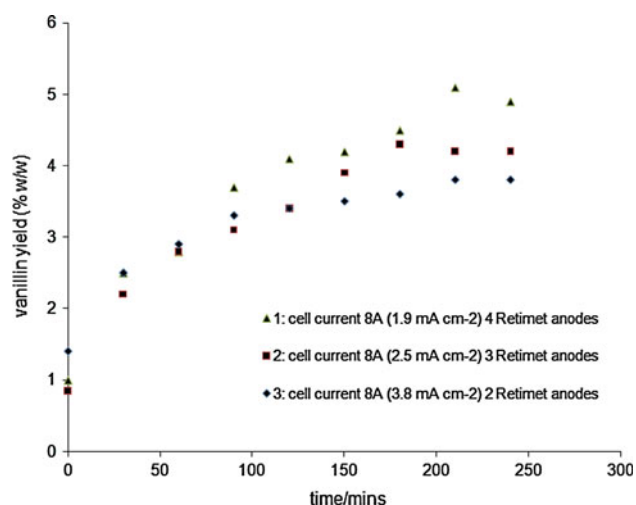
The modular transverse flow arrangement (Fig. 4) was used with current density varied by altering the anode area (i.e. number of cell units combined), whilst maintaining the cell current at 8 A. The results (Table 3 and Fig. 8) clearly show that at long reaction times (>100 min) vanillin yield is favoured by lower current density (plot 1 compared with 2 and 3) and the levelling off is again seen. The highest yield is 5.1% w/w, disappointing in comparison with the nearly 10% obtained using the batch cell or the 7% from chemical oxidation (aqueous NaOH/air/Cu<sup>2+</sup>). For reaction times <100 min the rates of conversion are similar.



**Table 3** Vanillin yield as a function of current density: see Fig. 8

Time/min	C g <sup>-1</sup>	Yield (1.9 mA cm <sup>-2</sup> ) <sup>a</sup>	Yield (2.5 mA cm <sup>-2</sup> ) <sup>b</sup>	Yield (3.8 mA cm <sup>-2</sup> ) <sup>c</sup>
0	0	1.0	0.8	1.4
30	236	2.5	2.2	2.5
60	472	2.8	2.8	2.9
90	708	3.7	3.1	3.3
120	944	4.1	3.4	3.4
150	1180	4.2	3.9	3.5
180	1416	4.5	4.3	3.6
210	1652	5.1	4.2	3.8
240	1889	4.9	4.2	3.8

Standard electrolysis conditions (see text), 61 g Ultrazine NA in 1 L electrolyte  
<sup>a</sup> 8 A, 4 Retimet anodes; <sup>b</sup> 8 A, 3 Retimet anodes; <sup>c</sup> 8 A, 2 Retimet anodes

**Fig. 8** Effect of current density in the modular transverse flow cell

#### 4.4 Initial concentration of lignin

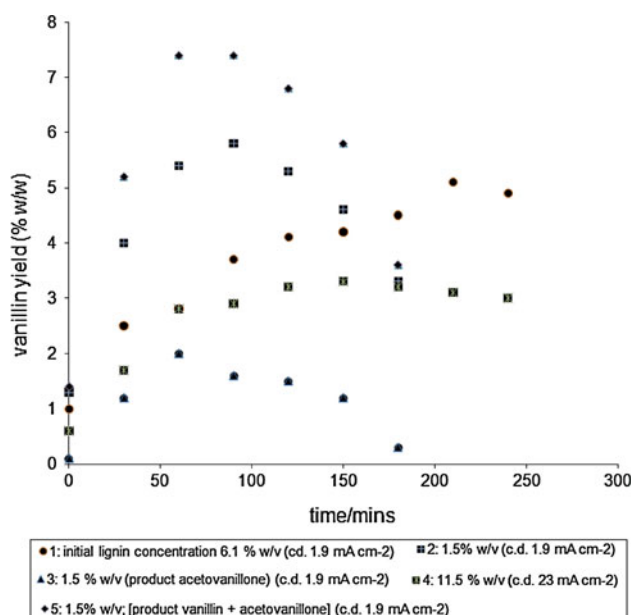
For electrolysis in the batch cell entry 4 in Table 1 (9.6% yield of vanillin) suggests that the desired reaction is favoured at a low initial concentration of the lignin (1% w/v).

**Table 4** Yield of vanillin as a function of initial concentration: see Fig. 9

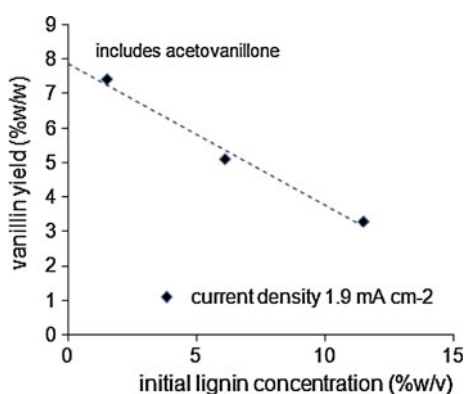
Time/min	C g <sup>-1</sup>	Yield <sup>a</sup> (1.5% w/w)	Yield <sup>b</sup> (1.5% w/w)	Yield <sup>c</sup> (1.5% w/w)	C g <sup>-1</sup>	Yield <sup>d</sup> (6.1% w/w)	C g <sup>-1</sup>	Yield <sup>e</sup> (11.5% w/w)
0	0	1.3	0.1	1.4	0	1.0	0	0.6
30	960	4.0	1.2	5.2	236	2.5	125	1.7
60	1920	5.4	2.0	7.4	472	2.8	250	2.8
90	2880	5.8	1.6	7.4	708	3.7	376	2.9
120	3840	5.3	1.5	6.8	944	4.1	501	3.2
150	4800	4.6	1.2	5.8	1180	4.2	626	3.3
180	5760	3.3	0.3	3.6	1416	4.5	751	3.2
210					1652	5.1	877	3.1
240					1889	4.9	1002	3.0

Standard electrolysis conditions (see text): <sup>a</sup> 8 A, 1.9 mA cm<sup>-2</sup>; <sup>b</sup> acetovanillone, conditions as for <sup>a</sup>; <sup>c</sup> vanillin + acetovanillone, conditions as for <sup>a</sup>; <sup>d</sup> 8 A, 1.9 mA cm<sup>-2</sup>; <sup>e</sup> 16 A, 23 mA cm<sup>-2</sup>

The experiments summarised in Table 4 and Fig. 9, carried out at a relatively low current density, confirm that best results are obtained at low initial concentrations of lignin and low current densities. Furthermore, a second low-molecular weight product [acetovanillone (2)] is produced (plot 5). The total conversion is 7.4% w/w comprising vanillin (5.8% w/w) and acetovanillone (1.6% w/w). Selected results from Fig. 9 have been re-plotted (Fig. 10) to emphasise the effect of initial lignin concentration. At 1.9 mA cm<sup>-2</sup>, the disappointing conclusion is that the yield of vanillin (plus acetovanillone) is unlikely to exceed 8% w/w. Although comparable with yields from existing processes there is probably no great advantage to be found in electrooxidative degradation. It is likely that operation at even lower current densities would raise the yield (see results from the batch cell) but this would entail the design of flow cells with even higher electrode areas to provide useful rates of conversion. The results do, however, throw light onto the fact that no oxidative method seems capable of producing more than 10% vanillin. Another striking feature of the results displayed in Fig. 9 is the overoxidation whereby both vanillin and acetovanillone are destroyed. Consequently, this aspect has been explored further.



**Fig. 9** Effect of initial lignin concentration at low current density



**Fig. 10** Vanillin yield as function of lignin concentration

#### 4.5 Stability and reactivity of vanillin under the conditions of electrolysis

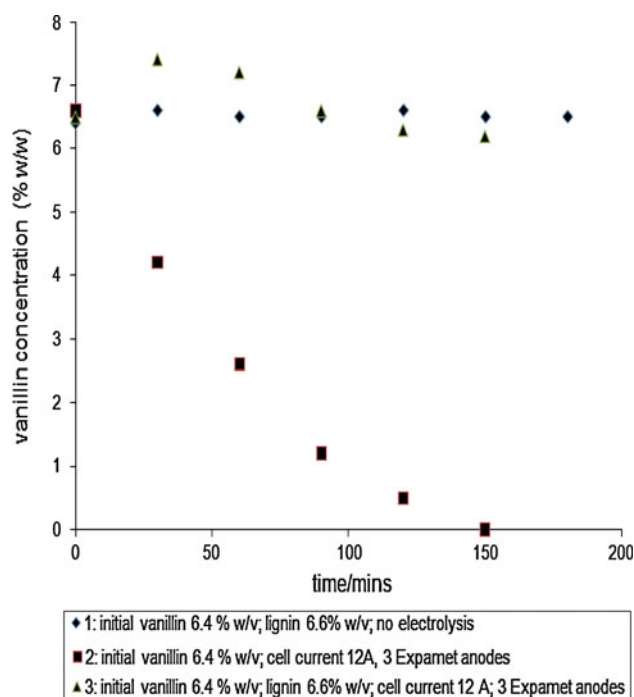
In a series of experiments: (a) vanillin was subjected to the conditions of electrolysis but without the passage of current; (b) vanillin was electrolysed under the standard conditions; and (c) vanillin was electrolysed in the

**Table 5** Stability of vanillin in electrolyte; steady state conditions; see Fig. 11

Time/min	Vanillin (6.4% w/v) no current	Charge (F) <sup>a</sup>	Vanillin (6.4% w/v) 12A (3.4 mA cm <sup>-2</sup> )	Vanillin (6.4% w/v) lignin (6.6% w/v) 12 A (3.4 mA cm <sup>-2</sup> )
0	6.4	0	6.6	6.5
30	6.6	0.5	4.2	7.4
60	6.5	1.1	2.6	7.2
90	6.5	1.6	1.2	6.6
120	6.6	2.1	0.5	6.3
150	6.5	2.7	0	6.2

Standard conditions (see text)

<sup>a</sup> Electrolysis of 64 g (0.42 mol) of vanillin



**Fig. 11** Vulnerability of vanillin to electrooxidation

presence of a similar concentration of lignin. The results are displayed in Table 5 and Fig. 11.

Vanillin is stable over a period of 200 min at 145 °C in 3 M aqueous NaOH in the presence of lignin (plot 1). However, vanillin alone is smoothly and completely oxidised when current is passed, in this case at about 3.4 mA cm<sup>-2</sup> (plot 2). In the experiment imitating the conditions of the preparative electrolyses, i.e. vanillin being formed in the presence of lignin, the vanillin appears to be ‘protected’ by the lignin (plot 3); at about 3.4 mA cm<sup>-2</sup> the concentration of vanillin remains close to its initial value for the duration of the electrolysis (180 min).

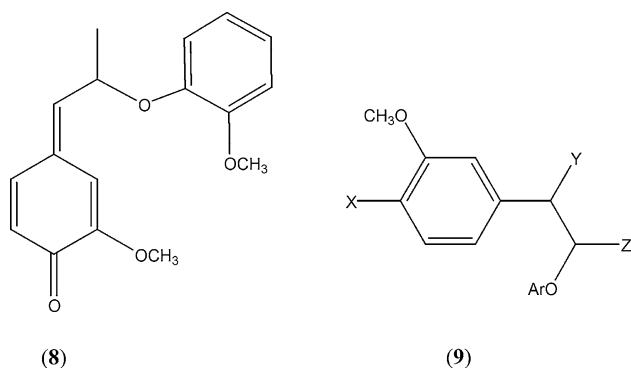
## 5 Discussion

### 5.1 Background

In nature, lignins are formed by oxidation [37, 38] of coniferyl alcohol with subsequent polymerisation of the

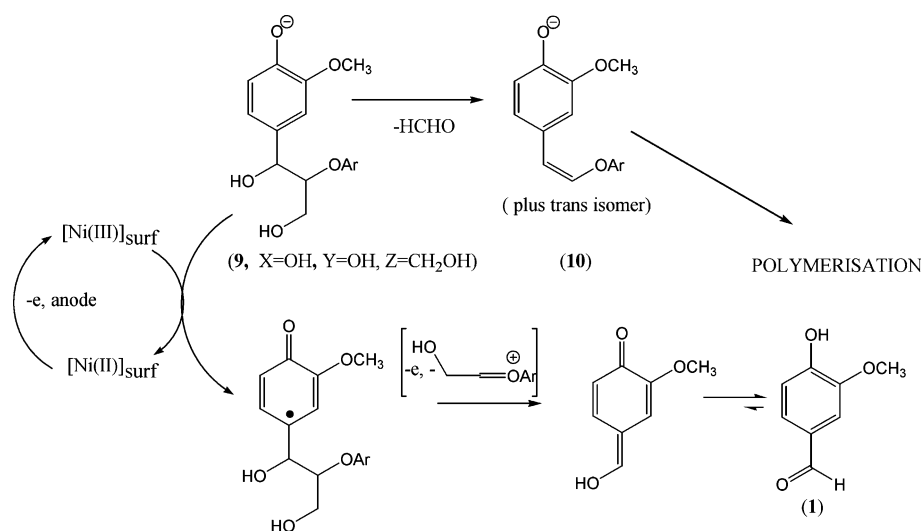
quinonemethide product as, outlined in Scheme 1, which also rationalises formation of the most common linkage ( $\beta$ -O-4). The process has been demonstrated in the laboratory, one example being the formation, by chemical oxidation of the corresponding phenol, of a quinonemethide (**8**) which undergoes [39] base-catalysed or electrochemically initiated polymerisation. Much information on the mechanism of electrooxidation of lignins was obtained by the detailed examination of the oxidation of variously substituted lignin-model compounds (**9**) at a nickel anode in 2–3 M aqueous NaOH at 150–160 °C or, in acetonitrile, by tris-(4-bromophenol)amine radical-cation as a homogeneous single electron oxidant [29]. These experiments allowed identification of functionality that was essential for oxidative cleavage.

Particularly relevant to the results from flow cell electrolyses is the earlier finding [28] that base-promoted polymerisation competes effectively with oxidative cleavage for several of the phenolic ethers (**9**). For vanillin formation, this competition is illustrated in Scheme 2; the enol ether (**10**) has been characterised as an intermediate. It is stable in alkaline solution but decomposes rapidly in neutral or acidic media [28, 29].



Formulae (8) and (9)

**Scheme 2** Mechanism of oxidative cleavage of lignin-model compounds

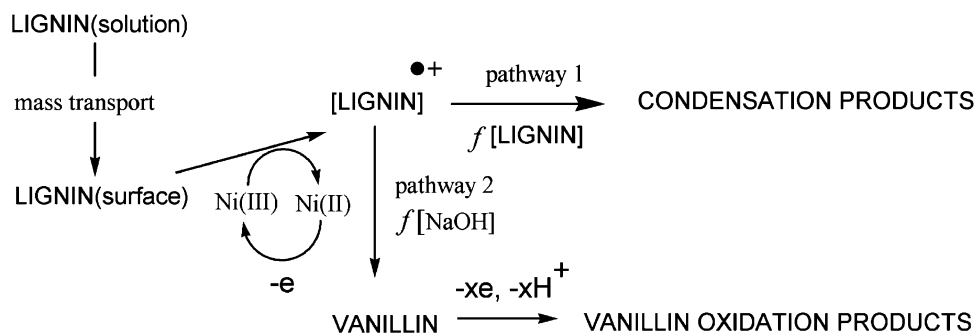


## 5.2 Mechanistic rationalisation in the light of results from flow cell electrolyses

Oxidation of organic compounds, especially primary alcohols, at nickel anodes in alkaline solution has been well-studied and reviewed [21, 22] and oxidation is at the surface via an oxygenated Ni(III) species (possibly Ni(III)OOH) and favoured at low current density. The results of experiments in the batch and flow reactor also indicate that better yields of vanillin are obtained at lower current densities; overoxidation was evident in the batch experiments at high conversion (Table 1, entry 3). Results from the flow reactor electrolyses are more revealing than those from the batch cell and may be interpreted in terms of the mechanism proposed for lignin-model compounds (Scheme 2). It is reasonable to regard lignins as being three-dimensional macromolecules with exposed functionality, structurally close to the model compounds (phenolates in alkaline solution) as depicted in Scheme 2. These will, therefore, be oxidised with cleavage to vanillin and with competing condensation of the residual lignin. Thus, the main features of the bulk electrooxidation of lignins are incorporated into Scheme 3.

Cell configuration, current and current density, and change of alkali, have little effect on the rate of vanillin production during the first 100 min (>50%) of electrolysis (Fig. 7). This is consistent with effective mass transport followed by oxidation limited by the relatively slow regeneration of the surface bound Ni(III) species. In one set of conditions (Fig. 7, plot 1), consumption of vanillin is observed in the later stages of electrolysis. Experiments at different current densities but otherwise comparable conditions (Fig. 8) again display closely similar rates of vanillin formation for much of the reaction. However, at an advanced stage of reaction higher yields are found at lower

**Scheme 3** Competing processes in lignin oxidation in the flow cell



current density. As electrolysis proceeds, the concentration of accessible oxidisable functions decreases so that pathway 2 (Scheme 3) is favoured over pathway 1 and, at the lower current densities, the Ni anode is operating under the preferred conditions.

The marked effect of initial lignin concentration (Fig. 9) is also consistent with Scheme 3; at high lignin concentration pathway 1 is predominant, whereas at low concentration pathway 2 is favoured. Pathway 2 (vanillin formation) is also, as observed, favoured by higher concentration of alkali, which facilitates cleavage from the lignin radical-cation. The results in Fig. 9 clearly indicate that after an optimum passage of charge vanillin is destroyed by further oxidation. Acetovanillone (2) is often found among the products of chemical oxidation but it is not obvious why in electrochemical oxidation at low concentration it should be co-produced with vanillin.

Vanillin, which is stable in 3.0 M NaOH at 145 °C, is consumed smoothly (Fig. 11, plot 1) by electrooxidation in a 2.7 F reaction (64 g of vanillin consumed after passage of  $1.08 \times 10^5$  C); in such alkaline conditions vanillin will be present as a sodium phenolate. Similarly, the accessible oxidisable functions in the lignin will be in the phenolate form. In co-electrolysis of equal concentrations of vanillin and lignin (Fig. 11, plot 3) the vanillin concentration increases slightly at first but then falls and is maintained at close to the starting value. This is good evidence for Scheme 3 with lignin and vanillin oxidation proceeding at similar rates with vanillin destruction being balanced by its formation. An alternative explanation is that the nickel anode is covered by lignin, thus preventing vanillin oxidation. However, if this were so, it is difficult to see why the adsorbed lignin is not oxidised, in which case the total concentration of vanillin should increase and not remain steady.

Finally, one other important conclusion can be drawn from the experiments described in Figs. 7, 8, and 9. The electrolysis procedure involved filling of the reservoir of the flow reactor rig with 1 L of electrolyte at room temperature with subsequent circulation and heating until conditions were steady at 145 °C and  $4.0 \pm 0.1$  barg

(=5.0 bar =  $5.0 \times 10^2$  kPa); typically this took 15–30 min before the current was switched on. Consequently, the  $t = 0$  axes on Figs. 7, 8, and 9 refer to vanillin concentrations produced by hydrolysis, under  $N_2$ , of Ultrazine NA at rather severe conditions. Thus the yields of vanillin from hydrolysis (at  $t = 0$ ) average  $1.10 \pm 0.03\%$  w/v. This remarkably consistent low degree of hydrolysis contrasts with the more extensive reaction claimed for other lignins at pH 8–12 at 25 °C during 60 min [31].

**Acknowledgments** The flow rig was designed by Dr J.K. Hammond (ICI) and it centred on an FM01-LC filter press flow reactor (donated by ICI). Components, including Expamet and Retimet nickel electrodes, were donated by ICI and the rig was constructed in The Queen Mary Faculty of Science Mechanical Workshop under the supervision of Mr F. Hands. We are also grateful for substantial financial and material support from Borregaard Industries Ltd., PO Box 162, N-1701 Sarpsborg, Norway and for crucial help and discussions with Dr Hans Evju of that company.

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