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Electrocatalytic hydrogenolysis of lignin model dimers at Raney nickel electrodes

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The electrocatalytic hydrogenolysis (ECH) of lignin model compounds has been investigated under galvanostatic control at Raney nickel electrodes in aqueous ethanol. The influence of current density, concentration of substrate and temperature on the efficiency of the carbon–oxygen bond hydrogenolysis was studied with benzyl phenyl ether and the optimum conditions leading to its total conversion were found. The effect, on the current efficiency, of replacing the phenyl group by an alkyl group (e.g. benzyl methyl ether) and of substituting hydrogens on aromatic rings by methoxy groups was investigated using the optimum electrolysis conditions. The electrocatalytic hydrogenolysis of β-phenoxyethylbenzene and α -phenoxyacetophenone, representatives of two other kinds of carbon–oxygen linkage in lignin, was also carried out.

1. Introduction

Lignin is one of the major renewable components of biomass and is available for conversion into useful organic materials. Thus, in an era of uncertainty about oil supplies and prices and rising concern over environmental issues, it has become increasingly attractive to a variety of material based industries [1]. Lignin, native or as a waste product of the pulp industry, has found very little use due to its complex structure. Its main use is as fuel for the paper and pulp industry but it is often discarded as polluting effluent [1]. Lignin is a three-dimensional polymer with carbon–oxygen bonds at the α and (or) β postition of a phenyl ring [2, 3]. The compounds of Fig.1 represent models of structural units of lignin with such carbon-oxygen bonds. Cleavage of these α-aryl and β-aryl ethers is an important reaction in the depolymerization of lignin. A large amount of work has been done on its degradation to useful and commercially valuable low molecular weight products. Degradation is achieved typically by oxidation with nitro aromatics [4], by air oxidation in alkaline solution at high temperatures [5], by electrochemical oxidation [6], by a combined nitro aromatic/electrochemical oxidation [7] and by reductive degradation (catalytic hydrogenation mainly [8, 9]). The oxidative degradation suffers from important side reactions and the reductive degradation from lack of selectivity [8, 9]. The electrooxidation has the disadvantage of generating radicals (phenoxy radicals) during the electrolysis which trigger polymerization of lignin fragments through reaction mechanisms similar to those involved in lignin biosysnthesis [1, 10, 11, 12]. The products formed are aldehydes and the corresponding carboxylic acids. In catalytic hydrogenation, depending on the catalyst and the reaction conditions, lignin is more or less degraded to monomeric phenols [13]. In fact, two hydrogenation processes can occur: addition of chemisorbed hydrogen to C–O single bonds with their concomitant cleavage (hydrogenolysis); addition of chemisorbed hydrogen to aromatic rings (hydrogenation) before and(or) after hydrogenolysis of ether linkages [14, 15]. If hydrogenation of the aromatic rings occurs first, hydrogenolysis of the ether bonds becomes extremely difficult and there is little or no degradation of lignin. Indeed, the ease of hydrogenolysis of a C–O bond decreases in the order: benzyl-O-phenyl, benzyl-O-alkyl, alkyl-O-alkyl [9]. Therefore, to degrade lignin efficiently by an hydrogenation process, hydrogenolysis of the ether bonds must be faster than hydrogenation of the aromatic rings. Such chemoselective hydrogenolysis of the ether bonds is difficult to achieve by classical catalytic hydrogenation because of the severe conditions used (high temperature and pressure) [8, 9, 16]. Electrocatalytic hydrogenation (ECH), a judicious and advantageous combination of electrochemical and catalytic methods, is an alternative method [17, 18]†. In ECH, the chemisorbed hydrogen (H)M, which is generated *in situ* on the electrocatalyst surface by water electrolysis at low overpotential [17] (Reaction 1), reacts with the adsorbed organic substrate (R)M (Reactions 2–4).

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† For a short review on the ECH of organic compounds from 1906, see [17] and [18].

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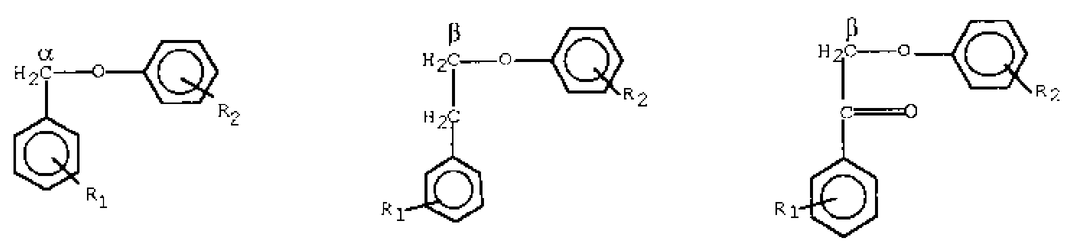
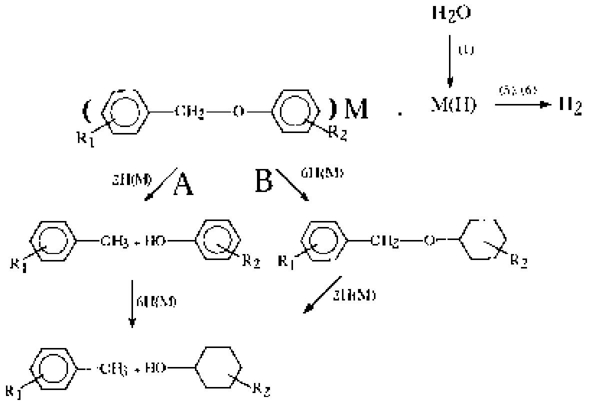


Fig. 1. R_1 and R_2 = H or OCH_3



R_1 = H or OCH_3; R_2 = H or OCH_3

Scheme 1

Therefore, the kinetic barrier related to the low solubility of hydrogen and to its dissociative adsorption is bypassed and, as a consequence, the hydrogenation can be carried out at relatively low pressures and temperatures with little or no side reactions [17]. Furthermore, the concentration of chemisorbed hydrogen can be controlled by adjusting the current density which makes the reaction easier to handle and may also help to control the reaction selectivity [19]. Thus, ECH is expected to be more selective than catalytic hydrogenation [17, 19] and cleaner than a direct electrochemical method [17]. However the competing hydrogen evolution reaction (HER) (Reactions 5 and 6) can drastically lower the current efficiency of ECH and, in the worst cases, can even prevent the hydrogenation of the organic compound [17]. The relative rates of these two competing processes depend on several parameters among which, for a given electrode, the strength of the bond to be hydrogenated [17], the current density [19, 20] and the local concentration [19] of the organic substrate adsorbed on the catalyst are particularly important.

$$2H_2O + 2e^- + M \rightarrow 2(H)M + 2OH^- \qquad (1)$$

$$R + M \rightarrow (R)M \qquad (2)$$

$$(R)M + 2(H)M \rightarrow (RH_2)M \qquad (3)$$

$$(RH_2)M \rightarrow RH_2 + M \qquad (4)$$

$$(H)M + H_2O + e^- \rightarrow H_2 + M + OH^- \qquad (5)$$

$$(H)M + (H)M \rightarrow H_2 + M \qquad (6)$$

To evaluate the potential of the ECH method for the degradation of lignin and to appreciate some of the factors affecting the efficiency of the process, we have studied the ECH of simple lignin model compounds in aqueous ethanol at Raney nickel electrodes prepared by pressing a mixture of Raney alloy powder and fractal nickel powder (80:20, v/v) and leaching out the aluminium afterwards (RaNi/Ni electrodes). We report the results in this paper. First, we describe the results of a study of the influence of the electrolysis conditions on the efficiency and the selectivity of the ECH of benzyl phenyl ether, which allowed the determination of the best conditions for its total conversion. Then, the effect, on the efficiency, of replacing the phenyl group by an alkyl group (e.g., benzyl methyl ether) and of substituting some hydrogens on the aromatic rings by a methoxy group is evaluated under the optimum conditions. Finally, the results of the ECH of β-phenoxyethylbenzene and α-phenoxyacetophenone, carried out under the optimum conditions, are described.

2. Experimental details

2.1. *General*

Vapour phase chromatographic analyses were performed on a Hewlett Packard 5890A chromatograph equipped with a flame ionization detector, an HP 3390A integrator and a DB-1 capillary column 30 m long (0.25 μm). ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AC-300 instrument. Mass spectra were obtained with a HP 5890 series II gas chromatograph coupled with a HP 5971 series mass selective detector.

2.2. *Electrolyses*

The electrolyses were carried out with a 410 potentiostatic controller coupled to a 640 digital coulometer and a 2830 digital multimeter (Electrosynthesis Company). A two-compartment glass H-cell with a jacketed cathodic compartment (volume of each compartment 25 mL) having a Nafion-324 (E.I. du Pont de Nemours & Co.) membrane (1.8 cm^2) as separator was connected to a Haake D8 constant temperature circulating bath filled with water/ethylene glycol. The counter electrode was a glassy carbon plate (~ 12 cm^2). The substrate was dissolved in a stock solution (25 mL) of sodium chloride (0.1 M) in ethanol–water (75:25, v/v) by stirring and sometimes heating slightly on a hot plate then the solution was poured in the cathodic compartment. The anodic compartment was filled with the above stock solution (25 mL). The cathode and the counter electrode were immersed and the electrolysis was performed at constant current. The catholyte was stirred with a magnetic bar and stirrer. The apparent pH was measured with a Sargent Welch 6000 pH meter and a Cole Parmer glass electrode which was calibrated in aqueous buffer. Aliquots (0.2 mL) from the catholyte were acidified and extracted with diethyl ether after the addition of a saturated NaCl solution (1 mL) and analysed by VPC. The products were identified by GCMS and by comparison of retention times with those of authentic samples. The mass balance was determined by the internal standard method using authentic samples, after extraction of the catholyte with diethyl ether and thorough rinsing (EtOH then diethyl ether) of the electrode. The material balance was closed to 100% (±8%) in all cases. There was no organic product in the anolyte after completion of the electrolysis according to VPC analysis.

2.3. *Electrodes*

The Raney nickel alloy (Ni–Al 50:50 w/w) powder (particle size of 45–125 μm) was purchased from BDH. The specific surface area of the spongy Raney nickel (RaNi) particles (average diameter < 40 μm) after leaching in aqueous NaOH is of the order of 65 $m^2\ g^{-1}$ [21]. The filamentary nickel powder (particle size of 2.2–2.8 μm and specific surface area of 0.68 $m^2\,g^{-1}$) was purchased from INCO (type 255 nickel powder) and consisted of spiky (fractal characteristics) spheres. The Raney nickel/nickel pressed powder (RaNi/Ni) electrodes were prepared by pressing a 4:1 (w/w) mixture of Raney nickel alloy powder and fractal nickel powder at $p = 300$ MPa and at room temperature followed by leaching in 10% aqueous NaOH for 1 h at 50 °C [22]. The geometric area of the electrodes was $2\pi r^2\,cm^2$ ($r = 1$) considering that both faces of the disc were used. An electrode made from a 4:1 (w/w) mixture of Raney alloy and fractal nickel had the same activity (both apparent and intrinsic) but a better mechanical stability than an electrode made from 100% Raney alloy.

2.4. *Synthesis of model compounds*

Starting materials were all commercially available: benzylbromide, (2-bromoethyl)benzene, 2-bromoacetophenone, 3-methoxybenzyl chloride, guaiacol, 2,6-dimethoxyphenol, 3,5-dimethoxyphenol were purchased from Aldrich; phenol and cyclohexanol from BDH. Distilled water and solvents (from ACP company) were used for the solutions. The lignin models (ethers **(1)** to **(9)**, see Table 2 and 3 for structures) were synthesized by a S_N2 type reaction between a halide (benzylbromide, (2-bromoethyl)benzene, 2-bromoacetophenone and 3-methoxybenzyl chloride) and the conjugate base of a phenol (phenol, guaiacol, 2,6-dimethoxyphenol, 3,5-dimethoxyphenol) or aliphatic alcohol (cyclohexanol and methanol) in refluxing THF–H_2O (90:10, v/v)(except for **7** where MeOH was the solvent) containing 0.4 M LiOH. The products were identified by GCMS, ^1H NMR and by ^{13}C NMR spectroscopy after extraction with ether and, when needed, thick-layer chromatographic separation (Merck Silica Gel 60 F_{254}, layer thickness: 250 μm). All compounds had a ^1H and a ^{13}C NMR spectrum and a GCMS consistent with their structure.

3. Results and discussion

3.1. *Electrocatalytic hydrogenation of benzyl phenyl ether on Raney nickel electrodes*

We studied the influence of current density, substrate concentration and temperature on the process efficiency and the selectivity of the electrocatalytic hydrogenolysis of the carbon-oxygen bond of benzyl phenyl ether in ethanol–water (75:25, v/v) solutions under constant current conditions. As mentioned in the introduction, in order to degrade lignin efficiently by an hydrogenation process, hydrogenolysis of the ether bonds must be faster than hydrogenation of the aromatic rings (see path A of Scheme 1) and, in order to get acceptable current efficiencies, hydrogen evolution which competes with the hydrogenation reactions must be minimized. The efficiency of the electrohydrogenation of benzyl phenyl ether was evaluated from the conversion rate and the current efficiency. The selectivity of the electrohydrogenolysis is defined as the ratio of the yield of products obtained by path A (Scheme 1) to the conversion rate. The charge passed corresponded to two moles of electrons per mole of substrate, which is the charge required for complete hydrogenolysis of the benzyl-O-aryl bond. The results obtained under the different electrolysis conditions are summarized in Table 1. As shown in entry 1, three different RaNi/Ni electrodes gave very reproducible results (range of conversion rate of 49–52%) as in the case of the ECH of phenanthrene [22]. An ethanol–water mixture (75:25, v/v) was chosen as solvent because it permits a range of organic substrate and supporting electrolytes to dissolve easily. Furthermore, working in an alcohol–water mixture may allow to extrapolate the results to water in which lignin is soluble. The effect of current density on the efficiency and on the selectivity of the ECH of benzyl phenyl ether is shown in entries 1 to 4 of Table 1. In all cases, the selectivity is 100% which means that any hydrogenation of aromatic rings occurred only after hydrogenolysis of the C–O bond (path A). The conversion rate and current efficiency increase from 30% (entry 4) to 76% (entry 3) as the current density decreases from 160 to 20 mA dm^{-2} (geometric area) which shows that a decrease of

Table 1. Electrocatalytic hydrogenolysis of benzyl phenyl ether (**1**) *at RaNi/Ni* (*80:20*)[a] *electrodes: effect of current density, concentration of substrate, pH and temperature*[b]

Entry	*J*[c] /mA dm^{-2}	*C* /mM	pH_i–pH_f[d]	*T* /°C	*Conversion*[e] (Current efficiency)[f] /%	*Selectivity*[g] /%
1	80	9	6.5–11.9	25	49-52 (*49–52*)[h]	100
2	40	9	6.5–11.9	25	69 (*69*)	100
3	20	9	6.5–11.9	25	76 (*76*)	100
4	160	9	6.5–11.9	25	30 (*30*)	100
5	80	18	6.5–11.9	25	68 (*68*)	100
6	80	26	6.5–11.9	25	81 (*81*)	100
7	80	9	11.5–11.5[i]	25	42 (*42*)	100
8	80	9	6.5–11.9	30	62 (*62*)	100
9	80	9	6.5–11.9	40	71 (*71*)	100
10	20	26	6.5–11.9	40	100 (*124*)[j]	100

[a] The electrodes were prepared by pressing fractal nickel and Raney alloy powders at $p = 3\times10^7$ kg m^{-2}, then leaching in 10% aqueous NaOH for 1 h at 50 °C. The RaNi/Ni ratio refers to the weight ratio of Raney alloy and fractal nickel before leaching.

[b] Electrolysis conditions: EtOH–H_2O (75:25, v/v); 0.1 M NaCl; charge passed = 2 moles of electrons per mole of substrate.

[c] Based on the geometric area.

[d] pH_i = pH at the beginning of the electrolysis, pH_f = pH at the end. The pH-meter was calibrated using buffers in aqueous solutions.

[e] The conversion rate and yield of products were determined by VPC analysis. The yields are based on converted benzyl phenyl ether.

[f] Current efficiencies are not corrected for the amount of chemisorbed hydrogen present on the electrode after leaching, approximatly 0.6 mmoles [17], because part of this chemisorbed hydrogen was also converted to molecular hydrogen.

[g] Selectivity = 100 (yield of products formed through path A (Scheme 1) / conversion rate).

[h] Range obtained from 3 different electrolyses.

[i] NaOH was added at the beginning of the electrolysis.

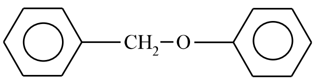
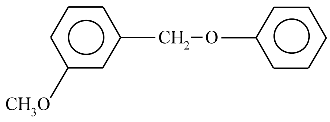
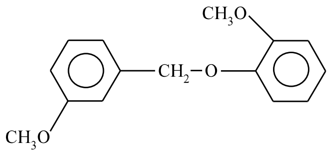
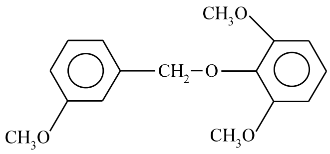
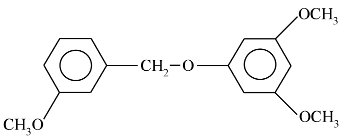
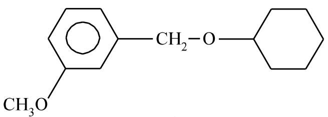
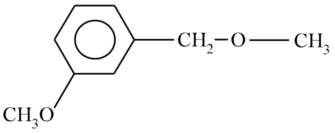
[j] Cyclohexanol (8%) was formed.

current density favours hydrogenolysis over hydrogen evolution (Scheme 1). Assuming that the mechanism of the HER in ethanol–water on Raney nickel electrodes is the same as in aqueous alkaline solutions [23], that is a Volmer–Heyrovsky mechanism (Reactions 1 and 5), the competition between hydrogenation and hydrogen evolution (Scheme 1) becomes a competition between a chemical process (Reactions 2 to 4) and an electrochemical process (Reaction 5) (Scheme 1). The increase of the ECH efficiency upon decreasing the current density would then result from a decrease of the rate of the electrochemical desorption of hydrogen (Equation 5). A similar behaviour has been observed in the case of the ECH of cyclohex-2-en-one [19] but in this case, both the selectivity and the efficiency were affected by current density. The effect of increasing the benzyl phenyl ether **(1)** concentration from 9 mM to 26 mM is shown in entries 1, 5 and 6 of Table 1. The efficiency of the process increases upon increasing the concentration of the substrate due to an increase of the rate of the hydrogenation step (Reaction 3, see A and B, Scheme 1). A current efficiency of 81% was obtained for a 26 mM solution (entry 6). As expected, the substrate concentration had no effect on the selectivity of the hydrogenolysis which was always 100%. As shown in Reaction 1, the ECH process produces hydroxide ions at the surface of the cathode so the pH of an unbuffered electrolysis medium increases as the electrolysis proceeds. In fact, in the medium used (EtOH–H_2O:75:25 v/v, NaCl 0.1 M), the pH had increased from 6.5 to 10.5 after the passage of 1 C and therefore, 98 to 99 % of the electrolysis was actually carried out in alkaline medium. The result of entry 7 shows that, indeed, adding NaOH at the beginning of the electrolysis to bring the pH at 11.5 had practically no effect (compare entries 7 and 1). Since lignin is soluble only in alkaline aqueous medium, the study of lignin model compounds in neutral or acidic medium does not have any practical interest. Increasing the temperature from 25 to 40 °C caused an increase of the conversion rate and current efficiency from 50 to 71% (compare entries 1,8 and 9). Thus, upon increasing the temperature, the rate of hydrogenolysis must increase more rapidly than that of hydrogen evolution. The results of entries 1 to 9 of Table 1 discussed above allowed us to choose the optimum conditions which are: EtOH/H_2O (75–25 v/v) as solvent, a current density of 20 mA dm^{-2} (geometric area), a substrate concentration of 26 mM and a temperature of 40 °C. Under these conditions (entry 10), the selectivity remained at 100%, the conversion rate was 100% and the current efficiency was higher than 100% for the hydrogenolysis of the C–O bond; further hydrogenation of the phenol formed occurred to a small extent (8%). A current efficiency higher than 100% reflects the fact that chemisorbed hydrogen generated during the leaching of the Raney alloy was present on the electrode at the beginning of the electrolysis [17, 19]. Current efficiencies higher than 100% have been observed also in the electrocatalytic hydrogenation of cyclohexenone [19] and phenanthrene [17] on freshly leached RaNi electrodes made from the pressed alloy or consisting of RaNi particles embedded in a nickel matrix.

3.2. *ECH of methoxylated benzyl phenyl ethers and of benzyl alkyl ethers*

In the structure of lignin, there are methoxy groups on both aryl rings of the benzyl phenyl ether moieties [9, 24] (see in particular model compounds **(3)** and **(4)** in Table 2). Steric interactions can sometimes decrease drastically the efficiency of the ECH process [19]. In fact, an increase in steric interactions makes the adsorption of the substrate on the catalytic surface more difficult [25]) and, as a result, its reaction with chemisorbed hydrogens is also more difficult. To

Table 2. Electrocatalytic hydrogenolysis of some methoxylated benzyl phenyl ethers[a]

Entry	*Substrate*	*Conversion* (Current efficiency)[b] /%	*Selectivity*[c] /%
1[d]	 **1**	100 (*124*)	100
2	 **2**	93 (*111*)[e]	100
3	 **3**	94 (*103*)[f]	100
4	 **4**	71 (*71*)	100
5	 **5**	84 (*84*)	100
6	 **6**	9 (*9*)	100
7	 **7**	14 (*14*)	100

[a] Electrolysis conditions: EtOH–H_2O (72:25, v/v); 0.1 M NaCl; electrodes: RaNi/Ni (80/20); current density: 20 mA dm^{-2}; substrate concentration: 26 mM; pH_i–pH_f: 6.5–11.9; temperature 40 ° C.

[b] See footnote[e] of Table 1.

[c] See footnote[g] of Table 1.

[d] Taken from Table 1. Cyclohexanol (8%) was formed.

[e] Cyclohexanol (6%) was formed.

[f] Phenol (3%) and cyclohexanol (3%) were formed.

verify if the presence of methoxy groups on the aryl rings could affect drastically the efficiency of the ECH process or not, the electrocatalytic hydrogenolysis of the methoxylated derivatives **(2)** to **(5)** was investigated under the conditions of entry 1, Table 1, which gave the highest efficiency with benzyl methyl ether. The results are reported in Table 2. The comparison was made at a charge corresponding to two moles of electrons per mole of substrate (the theoretical charge for the hydrogenolysis of the benzyl-O-aryl bond). The efficiency of the ECH process evaluated from the conversion rate and the current efficiency, which both depend on the relative rates of hydrogenolysis and hydrogen desorption (Scheme 1), the latter being constant under given conditions, reflects the ease of hydrogenolysis of the benzyl-O-aryl bond also referred to as the ${}^{\alpha}$C–O arylether bond. The comparison of entries 2 to 5 of Table 2 with entry 1 shows that the presence of methoxy groups on the aryl rings does not affect drastically the efficiency of the ECH process even when they are at the ortho position. Further hydrogenation of the phenol formed was observed again (entry 2) and even some hydrogenolysis of the O–CH_3 bond (entry 3).

As shown by a comparison of entries 6 and 7 of Table 2 with entry 2, the electrohydrogenolysis of a benzyl-O-alkyl bond is much less efficient than that of a benzyl-O-phenyl bond as anticipated from the fact that the latter is stronger [9]. Indeed, both the conversion rates and current efficiencies in entries 6 and 7 are much lower than in entry 2. The more difficult (slower) the hydrogenolysis, the more important is the hydrogen evolution as already pointed out.

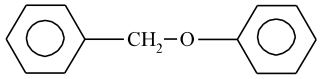
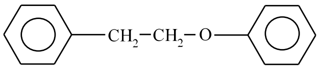
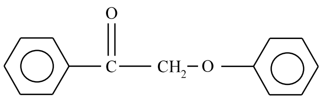
3.3. *ECH of representatives of two other types of C–O bonds in lignin*

The results for the electrocatalytic hydrogenolysis of β-phenoxyethylbenzene and α-phenoxyacetophenone are summarized in Table 3; they are representatives of two other kinds of carbon-oxygen linkage in lignin. The three model compounds of Table 3 represent about 70% of the lignin linkages, the rest being mostly C–C bonds. The electrolysis conditions were the optimum conditions determined with benzyl phenyl ether. The results of entry 2 show that when the C–O bond is conjugated to one phenyl ring only as in ether **(8)** (${}^{\beta}$C–O bond), the electrohydrogenolysis is less efficient (lower conversion rate and current efficiency) than when it is conjugated to two phenyl rings (${}^{\alpha}$C–O bond) as in benzyl phenyl ether **(1)** (see entry 1). This is expected from the fact that the former bond is stronger. When the C–O bond is conjugated to both a phenyl group and a carbonyl group as in a-phenoxyacetone **(9)** (entry 3), it is also easily hydrogenolysed as shown by the high conversion rate and current efficiency.

4. Conclusion

We have shown that, in the electrocatalytic hydrogenolysis of benzyl phenyl ether at Raney nickel electrodes in aqueous ehthanol, the efficiency of hydrogenolysis of the C–O bond can be optimized to 100% by choosing the proper substrate concentration, current density and temperature. Under the optimum conditions, further hydrogenation of the

Table 3. Electrocatalytic hydrogenolysis of lignin model dimers[a]

Entry	*Substrate*	*Conversion*[b] (Current efficiency)[c] /%	*Selectivity*[d] /%
1[e]	 **1**	100 (*124*)[e]	100
2	 **8**	39 (*63*)[e]	100
3	 **9**	100 (*121*)[f]	100

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[a] See footnote a of Table 2.

[b] See footnote e of Table 1.

[c] See footnote f of Table 1.

[d] See footnote g of Table 1.

[e] Cyclohexanol (8 %) was formed.

[f] Cyclohexanol (7 %) was formed.

products formed (phenol to cyclohexanol, 2-methoxy phenol to phenol) occurred to a small extent (6 to 8%). These results show that the depolymerization of lignin by electrocatalytic hydrogenolysis of C–O linkages appears feasible. The ECH method has the advantage of being clean and selective.

Acknowledgements

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