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# Application of metallic foams in an electrochemical pulsed flow reactor
## Part II: Oxidation of benzyl alcohol

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Packed beds of nickel foam are suitable porous three-dimensional anodes for the oxidation of organic substrates. The heterogeneous electrocatalytic oxidation of benzyl alcohol on a three-dimensional nickel foam electrode was investigated in a pulsed flow reactor under homogeneous and two phase conditions. The aim of the work was to enhance the aldehyde yield. The activation of the nickel foam electrodes increases the electrolysis current up to 30% and then the alcohol conversion. To prevent further oxidation of aldehyde into acid, variable water/petroleum ether emulsions were studied. The best yields of benzaldehyde are obtained for a 16% petroleum ether volume ratio and a pH range 10–13 of the aqueous phase. Factorial analysis of the electrolysis under galvanostatic conditions showed that the amplitude and frequency of the pulsation are key hydrodynamic factors for the benzaldehyde yield.

### 1. Introduction

The electrooxidation on nickel anodes of organic substrates such as alcohols, aldehydes, amines or related compounds has been extensively reviewed [1]. Oxidation takes place by heterogeneous chemical reaction between the electrogenerated NiOOH and the adsorbed substrate. As the electrooxidation of alcohols is kinetically controlled by the redox reaction on the anode surface, the increase in electrode/substrate contacts should modify the behaviour of the electrooxidation. In the case of primary alcohols, a radical hydrogen abstraction produces a $\alpha$-hydroxy-radical as intermediate, which can be further oxidized to an aldehyde or a carboxylate [2–4]:

$$\mathrm{Ni(OH)_2 + OH^-} \rightleftharpoons \mathrm{NiOOH + H_2O + e^-} \qquad (1)$$

$$\mathrm{RCH_2OH + 2NiOOH} \longrightarrow \mathrm{RCHO + 2Ni(OH)_2} \qquad (2)$$

$$\mathrm{RCH_2OH + 4NiOOH + H_2O} \longrightarrow \mathrm{RCOOH + 4Ni(OH)_2} \qquad (3)$$

Primary alcohols are easily converted in alkaline aqueous solutions into carboxylic acids but oxidation of such substrates can either lead to aldehydes or acids according to the solvent composition. Thus, benzylic type aldehydes can be obtained from the corresponding alcohols in a mixture of water/*tert*-butanol or in two phase media [5]. Unfortunately, these indirect electrocatalytic processes run only with very low current densities (about $<10\,\mathrm{A\,m^{-2}}$) [2–4]. This problem can be overcome either by using modified nickel electrodes or by the use of high surface area nickel electrode.

Modified nickel electrodes, which exhibit special properties in order to increase the reaction rate between the organic compounds and nickel hydroxide, have been recently developed and many applications have been reported [6–11]. Cox and Pletcher [6, 7] have studied the mechanism of organic compound oxidation on spinel electrodes (i.e., $NiCo_2O_4$ etc.) and found similar behaviour to that on nickel. They obtained high current densities for ethanol oxidation in a flow cell system. Budniok and Kozlowska [8] found that oxide layers formed on Ni–P alloys for propanol oxidation were more active than those on a nickel electrode. Current efficiencies obtained by Kunugi *et al.* [9–11] for the electrooxidation of various organic compounds on nickel/poly(tetrafluoroethylene) composite-plated anodes

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were considerably improved, due to the hydrophobicity of the anode. Wen *et al.* [12] reported that the presence of PTFE in a nickel electrode alters the formation pathway of the $\gamma$-phase nickel hydrous oxide, resulting in a high electrocatalytic activity. Furthermore, these authors [13] studied $NiS_x$ electrodes and found that the $Ni(OH)_2/NiOOH$ redox transition formed anodically on such a modified electrode was a suitable electrocatalyst for benzyl alcohol oxidation.

Another way to increase the reaction rate is the use of high surface area anodes. Nickel foam is a reticulated material of high specific surface area and is suitable for the electrooxidation of organic compounds. It has been applied to the electrooxidation of DAS (diacetone-L-sorbose) in DAG (diacetone-keto-2-L-gulonic acid) [14, 15] and high conversion yields were obtained. Moreover, on a laboratory scale, the use of nickel foam in a FM01-LC reactor was shown to be efficient for the oxidation of alcohols into carboxylic acids [16]. Recently, nickel foams have been applied to the electrooxidation of isobutanol to isobutyric acid in a flow cell by Vaze *et al.* [17] who pointed out the importance of the nickel electrode activation.

We have previously reported the mass transfer performance of the material used in an E3P reactor (E3P:porous percolated pulsed electrode) [18]; results showed that the pulsation increases the mass transfer coefficient of the reactor. Moreover, under pulsation the electroactive species pass through the three-dimensional electrode. As the electrooxidation of alcohols is kinetically controlled by the redox reactions (Equations 2 and 3) on the anode surface [2], the increase in penetration of the electrode by the substrate should modify the course of the electrooxidation. In the present paper we report the electrooxidation of benzyl alcohol on a nickel foam electrode in an E3P reactor. In two phase systems, the organic phase ratio, the pH of the aqueous phase and the working electrode bed height were studied to obtain the highest benzaldehyde yield. Under galvanostatic electrolysis, factorial design was used in planning experiments in order to analyze the effects of hydrodynamic variables on benzyl alcohol current efficiency and benzaldehyde yield.

## 2. Experimental details

### 2.1. *Electrochemical analysis*

Electrochemical experiments were carried out with an ELECTROKEMAT potentiostat/galvanostat system (ISMP, Labège, France [19]) monitored by software using an IBM PS 2 computer. The electrochemical cell was a conventional one with three electrodes (working electrode: polished Ni, diameter 3 mm; counter electrode: Pt wire; reference electrode: SCE). The nickel rod (99.99%) electrode used as the working electrode was polished and rinsed with distilled water, before use. Voltammetry was carried out at a scan rate ranging from 0.05 to $2.0\,V\,s^{-1}$ in 0.1 M KOH aqueous solutions.

### 2.2. *Galvanostatic electrolysis*

Galvanostatic electrolyses were carried out in an undivided E3P reactor whose internal volume was $10^{-3}\,m^3$ [18] (Fig. 1). A peristaltic pump (6 in Fig. 1) was used to control the permanent superficial velocity $U_0$; the overflow was returned to the storage tank (7 in Fig. 1) which was used for sampling. The pulsation was achieved by a Teflon piston (1 in Fig. 1, with an amplitude of $0 < a < 0.014\,m$ and a frequency of $0 < f < 1.24\,Hz$).

A circular bed of nickel foam (MN060 grade, Sorapec, Paris), whose height was fixed by the number of superposed stacks, was used as the working electrode. The specific surface area of MN060 nickel foam was $5500\,m^{-1}$ so that each stack had a $380\,cm^2$ surface area. Before each experiment, the working electrode was first activated in a 0.05 M $NiSO_4$, 0.1 M $CH_3CO_2Na$, 0.005 M NaOH by reverse polarization for 10 s in the oxygen and hydrogen evolution domains, under a current density of $200\,A\,m^{-2}$ for 15 min. The activation procedure ended with positive polarization for 20 min [20]. The solution was then introduced at the bottom of the electrochemical reactor. The configuration of the electrodes system was axial, the counter electrodes were made of expanded stainless steel (area $0.14\,m^2$) and placed at the edges of the working electrode bed. D.c. power was supplied by a 35 V/2 A potentiostat/galvanostat (Tacussel) and experiments were carried out at a constant current density of $2.2\,A\,m^{-2}$. The electrolyses were stopped when the electric charge reached $6\,F\,mol^{-1}$ of benzyl alcohol. The temperature of the solution was controlled at 25 °C. The benzyl alcohol concentration was $20\,mol\,m^{-3}$ in the whole electrolytic volume: 1.2 litre made of aqueous 0.1 M KOH under homogeneous conditions or mixtures of the same aqueous solution with petroleum ether under two phase conditions. When two phase conditions were used, the emulsification was achieved by means of an ultrasonic continuous cell connected to an ultrasonic 500 W generator (Sonics, 5 in Fig. 1) [20]. The pulsation ensured the emulsion stability during the electrolysis. Petroleum ether was chosen as the organic solvent for its high immiscibility in water and easiness to decant. Toluene was shown to give too stable an emulsion. A small amount of benzyl alcohol extracts into petroleum ether but the major part remains in the aqueous phase. The benzyl alcohol concentration was low in order to minimize the electrolysis time.

Under pulsation, the instantaneous velocity of the liquid is given by

$$U = U_0 + a\omega \sin \omega t \qquad (4)$$

and the hydrodynamic conditions can be characterized by the Strouhal number $Sr = a\omega/U_0$ [18]. In the present study, as $Sr \gg 1$, the electrochemical cell

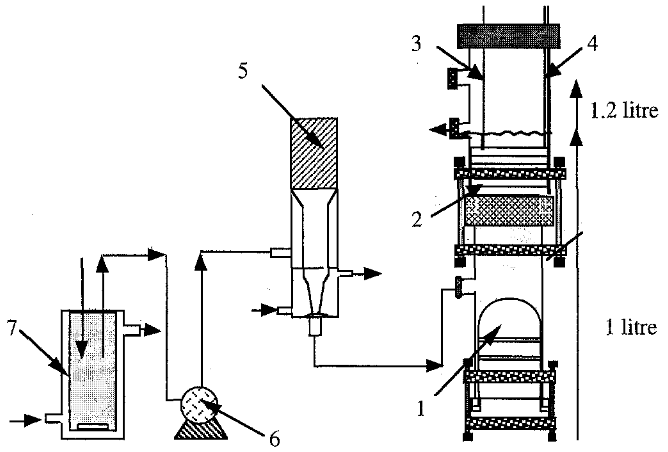

Fig. 1. Schematic view of the experimental apparatus: (1) Teflon piston, (2) electrodes, (3) Luggin capillary (SCE reference electrode), (4) current feeder, (5) sonication cell, (6) peristaltic pump and (7) storage tank.

can be considered as a perfectly stirred tank [20]. The effects of the following electrolysis parameters on conversion, benzaldehyde yield and current efficiency were investigated: (A) overall flow velocity, (B) pulsation amplitude, (C) pulsation frequency. Fixed levels of these parameters are given in Table 1.

### 2.3. *Product analysis*

During electrolysis in homogeneous conditions, 1 ml samples of the electrolyte were acidified with hydrochloric acid prior to analysis by high performance liquid chromatography (on a C-18 column): all the products were then identified. In the case of the two phase system, samples of the organic phase were analyzed by GPC (on a DB-1 column, 30 m) by the internal standard method. No benzaldehyde was found in the aqueous phase.

## 3. Results and discussion

### 3.1. *Electrochemical analysis*

Typical cyclic voltammograms of nickel electrodes in KOH solutions [2] have been described. On the anodic scan, the polished nickel electrode exhibits an anodic peak at about 0.4 V vs SCE corresponding to the Ni(II)/Ni(III) redox transition before the oxygen evolution reaction beginning at about 0.5 V (Fig. 2). On the reverse scan, the reduction peak of Ni(III) is observed at about 0.3 V. The oxidation peak current is linearly related to the square root of the potential scan rate as for a diffusion controlled process; this result accounts for thick oxide layers as observed by Fleischmann [2]. The value of the peak ratio $RI_p$ (reduction current/oxidation current) lies around 1 which shows the reversibility of the redox system, Equation 1. When benzyl alcohol is added (Fig. 2), the voltammogram is wave shaped as for a catalytic process. The plateau current is linearly related to the benzyl alcohol concentration. However, the catalytic effect is weak and the process is limited to low current density.

*Table 1. Factors and levels for the $2^3$ factorial design*

| *Factors* | *Levels* | |
|---|---|---|
| | – | + |
| A, volume flow rate/ml min$^{-1}$ | 50 | 340 |
| B, pulsation amplitude/cm | 0.24 | 1.20 |
| C, pulsation frequency/Hz | 0.20 | 1.20 |

To increase the electrocatalytic properties of the nickel electrode, the electrode was activated by anodic polarization in order to increase the NiOOH amount. The activation of the electrode was demonstrated by cyclic voltammetry: the anodic peak current increased with the number of scans. Figure 3 shows the influence of hydroxide ion concentration and activation time on the anodic peak current. The electrode was activated by reverse polarization as mentioned above. The peak current increased with both activation time and hydroxide ion concentration. The activation is the most influent parameter, while a concentration of 0.1 M KOH is sufficient to ensure the efficiency of the electrode.

### 3.2. *Optimization of some operating parameters*

The electrooxidation of benzyl alcohol was carried

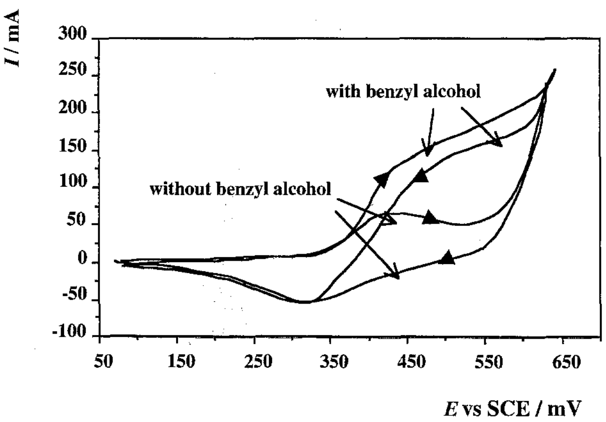

Fig. 2. Cyclic voltammograms at a nickel electrode in a 1 M KOH solution with and without benzyl alcohol (0.005 M): potential scan rate, $v = 0.01\ \mathrm{V\,s^{-1}}$.

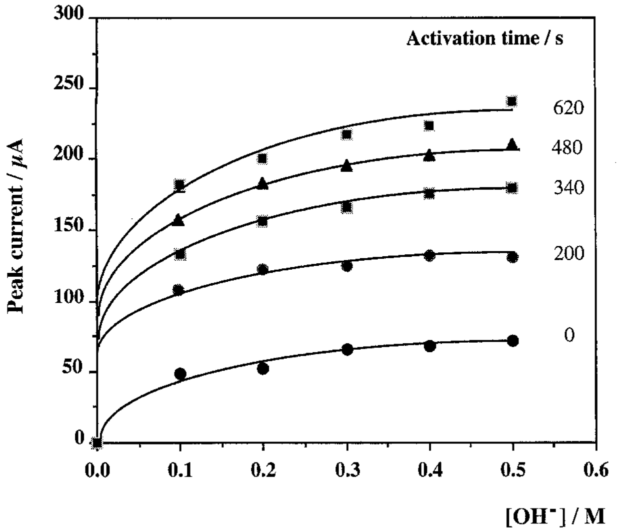

Fig. 3. Variation of the anodic peak current at a nickel electrode as a function of both [OH$^-$] and activation time: potential scan rate, $v = 0.1\,\mathrm{V\,s^{-1}}$.

out in the E3P reactor under homogeneous aqueous conditions and a two phase system. Figure 4 shows the preliminary results obtained with homogeneous and two phase electrolysis; it shows the benzaldehyde yield as a function of electrolysis time. For the two media, it is observed, at the beginning of the electrolysis, that the benzaldehyde yield is linearly related to time, that is to the electric charge, which corresponds to a simple oxidation process. Then, the yields decrease because benzaldehyde is further oxidized into acid. In each case, the benzaldehyde yields show a maximum. As shown in Fig. 4, the maximum benzaldehyde yield is not obtained for the same electrolysis time and it is more than twice higher in the two phase electrolysis case. A yield of 35% was found without optimization under two phase conditions. From these preliminary results, two phase electrolysis appears of interest and requires optimization. Thus, the following parameters were studied in order to enhance the benzaldehyde yield: organic phase volume, pH of the aqueous continuous phase, electrode bed height.

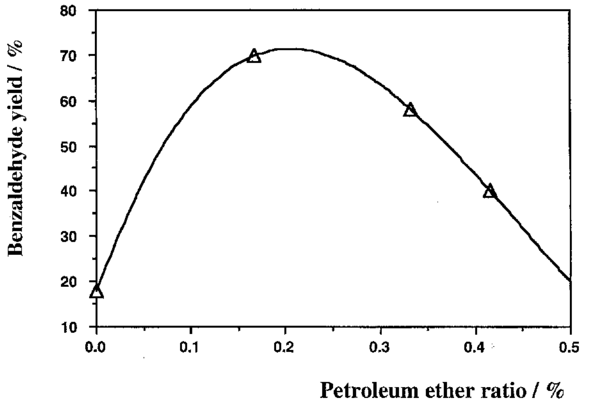

Fig. 5. Benzaldehyde maximum yield as a function of the petroleum ether ratio: intensity 0.5 A; electrode surface area $0.228\,\mathrm{m^2}$; total volume $1.2 \times 10^{-3}\,\mathrm{m^3}$; benzyl alcohol concentration $2 \times 10^{-2}$ M; temperature 25 °C; aqueous phase pH = 13.

*3.2.1. Effect of the organic phase ratio.* Figure 5 shows the variation of the benzaldehyde yield as a function of the organic phase ratio (volume ratio). There is an optimum for the organic phase. The best benzaldehyde yield is obtained for a volume of $2 \times 10^{-4}\,\mathrm{m^3}$ petroleum ether (60–80 °C), around 20% of the total volume as shown in Fig. 5. The organic average droplet size for the optimum value of petroleum ether ratio was estimated by laser screening to be approximately 1 μm [18]. The emulsion stability inside the reactor was ensured by pulsation.

*3.2.2. Effect of the aqueous phase pH.* A sufficient hydroxide concentration is needed to ensure good activation of the nickel foam electrode. On the other hand, a too highly alkaline medium can lead to side reactions such as benzaldehyde disproportionation. Figure 6 shows the variation of the benzaldehyde yield as a function of pH. There is an optimum pH: the best benzaldehyde yields are obtained for a 10–13 pH range. In the following experiments, KOH concentration was 0.1 M.

*3.2.3. Effect of the electrode bed height.* Nickel foam was supplied as sheet of 2 mm thickness; stacking of

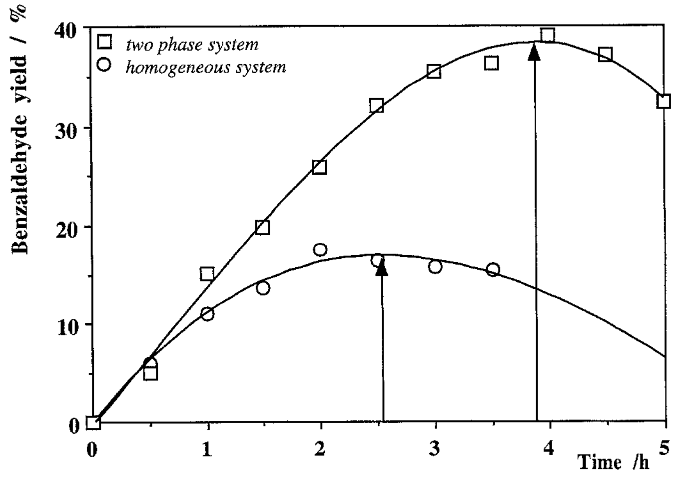

Fig. 4. Benzaldehyde yield as a function of electrolysis time under homogeneous and two phase conditions (petroleum ether volume: $5 \times 10^{-3}\,\mathrm{m^3}$): intensity 0.5 A; electrode surface area $0.228\,\mathrm{m^2}$; total volume $1.2 \times 10^{-3}\,\mathrm{m^3}$; benzyl alcohol concentration $2 \times 10^{-2}$ M; temperature 25 °C; aqueous phase pH 13. Key: (○) homogeneous system; (□) two phase system.

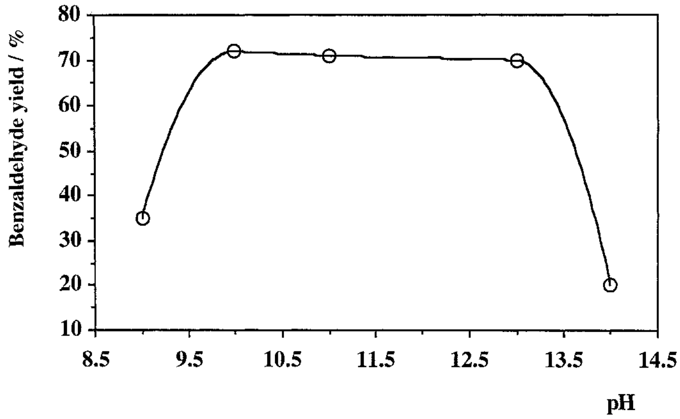

Fig. 6. Benzaldehyde maximum yield as a function of the aqueous phase pH: intensity 0.5 A (current density 2.2 A $m^{-2}$); electrode surface area 0.228 $m^2$; total volume $1.2 \times 10^{-3}$ $m^3$; petroleum ether volume $2 \times 10^{-4}$ $m^3$; benzyl alcohol concentration $2 \times 10^{-2}$ M; temperature 25 °C.

nickel foam discs give electrode bed heights between 2 and 12 mm. As a consequence, the electrode surface varied from 380 to 2280 $cm^2$. A constant current density of 2.2 A $m^{-2}$ was applied. In Table 2, the benzaldehyde yields are reported as a function of electrode bed height. Surprisingly, the use of one nickel foam leads to the best benzaldehyde yield together with the best current efficiency but the electrolyses are long. To shorten the electrolysis time, the maximum surface area consisting in the stack of six nickel foam discs was used in the following studies.

### 3.3. *Comparison between homogeneous and two phase system electrolysis*

Products of benzyl alcohol electrooxidation on the nickel electrode in alkaline solution containing organic solvent (*t*-butanol) were reported to be benzaldehyde and benzoic acid, and the yield of aldehyde was strongly affected by electrolysis conditions [1, 4, 7]. The yield of benzaldehyde can also be strongly affected by the presence of an extractive organic phase [1]. In this study, the factorial design method [21] was established to identify the key hydrodynamic variables influencing aldehyde yield and the current efficiency from the following variables: (A) volume flow, (B) pulsation amplitude and (C) pulsation frequency. Current efficiency is calculated from the benzaldehyde yield. Both homogeneous and two phase electrolysis conditions were studied. This experimental design allows study of the influence of selected process variables; moreover, the interaction effects among the variables can be drawn.

The design factors and levels for the $2^3$ factorial experiments are listed in Table 1 and the results of these experiments are given in Tables 3 and 4. The level of each variable during a run in homogeneous electrolyte is indicated in columns 2 to 4 of Table 3, with the conversion rate obtained for the highest benzaldehyde yield and benzaldehyde selectivity corresponding to each set of conditions being shown in columns 5, 6 and 7, respectively. For two phase conditions, the level of each variable during a run is indicated in columns 2 to 4 of Table 4, with the highest benzaldehyde yield corresponding to each set of conditions being shown in column 5.

Estimates of the experimental variable effects for both homogeneous and two phase electrolysis were algebraically calculated following the procedure recommended by Sado *et al.* [21] and are given in Tables 5 and 6, respectively.

Table 5 deals with the homogeneous aqueous electrolyte. Table 5 shows that the conversion of benzyl alcohol increases with decreasing volume flow rate and pulsation frequency. The conversion mainly depends on three interaction effects: A–C which is negative, B–C negative and A–B positive which have opposite effects. We consider the conversion corresponding to the highest benzaldehyde yield obtainable in the conditions of the run and not the

*Table 2. Maximum benzaldehyde yield and current efficiency as a function of the nickel foam electrode bed height; volumic flow: 110 ml $min^{-1}$; pulsation amplitude 1 cm; pulsation frequency 0.6 Hz*

| *Run* | *Number of stacks and electrode surface area* | *Intensity /mA* | *Electrolysis time /h* | *Maximum benzaldehyde yield /%* | *Benzaldehyde current efficiency /%* |
|---|---|---|---|---|---|
| 1 | 1 → 380 $cm^2$ | 83 | 5 | 68 | 88 |
| 2 | 2 → 760 $cm^2$ | 167 | 4,17 | 39 | 30 |
| 3 | 3 → 1140 $cm^2$ | 250 | 3 | 45 | 32 |
| 4 | 4 → 1520 $cm^2$ | 333 | 2 | 30 | 24 |
| 5 | 5 → 1900 $cm^2$ | 417 | 1,83 | 24 | 17 |
| 6 | 6 → 2280 $cm^2$ | 500 | 1,75 | 45 | 28 |

*Table 3. Homogeneous system electrolysis: design matrix and experimental data from the $2^3$ factorial design*

| Run | Factors | | | Conversion /% | Aldehyde yield /% | Aldehyde selectivity /% |
|---|---|---|---|---|---|---|
| | *A* Volume flow rate | *B* Pulsation amplitude | *C* Pulsation frequency | | | |
| 1 | − | − | − | 66.2 | 10.6 | 16.0 |
| 2 | + | − | − | 72.3 | 18.8 | 26.0 |
| 3 | − | + | − | 72.0 | 19.8 | 27.5 |
| 4 | + | + | − | 81.8 | 26.2 | 39.2 |
| 5 | − | − | + | 85.8 | 17.0 | 19.8 |
| 6 | + | − | + | 58.8 | 19.4 | 33.9 |
| 7 | − | + | + | 70.4 | 16.2 | 23.0 |
| 8 | + | + | + | 63.4 | 32.1* | 50.6 |

*Table 4. Two phase system electrolysis: design matrix and experimental data from the $2^3$ factorial design*

| Run | Factors | | | Aldehyde yield /% |
|---|---|---|---|---|
| | *A* Volume flow rate | *B* Pulsation amplitude | *C* Pulsation frequency | |
| 1 | − | − | − | 21.1 |
| 2 | + | − | − | 22.3 |
| 3 | − | + | − | 16.4 |
| 4 | + | + | − | 28.6 |
| 5 | − | − | + | 32.0 |
| 6 | + | − | + | 25.4 |
| 7 | − | + | + | 60.0 |
| 8 | + | + | + | 27.6 |

*Table 5. Homogeneous system electrolysis: estimates of the effects from the $2^3$ fractional design*

| Effects | Estimate | | |
|---|---|---|---|
| | Conversion /% | Aldehyde yield /% | Aldehyde selectivity /% |
| A (volume flow rate) | −2.26 | 4.11 | 7.92 |
| B (pulsation amplitude) | 0.56 | 2.29 | 5.57 |
| C (pulsation frequency) | −1.74 | 1.16 | 2.32 |
| AB | 2.96 | 1.46 | 1.9 |
| BC | −3.26 | −0.59 | −0.6 |
| AC | −6.24 | 0.46 | 2.5 |
| ABC | 2.04 | 1.91 | 1.47 |

*Table 6. Two phase system electrolysis: estimates of the effects from the $2^3$ fractional design*

| Effects | Estimate |
|---|---|
| | Aldehyde yield /% |
| A (volume flow rate) | −3.2 |
| B (pulsation amplitude) | 3.97 |
| C (pulsation frequency) | 7.07 |
| AB | −1.85 |
| BC | 3.57 |
| AC | −6.55 |
| ABC | −4.6 |

conversion of benzyl alcohol obtained for a given electricity consumption. Table 5 also reveals that benzaldehyde yield is positively influenced by volume flow, amplitude and frequency of pulsation. This maximum benzaldehyde yield obtainable during a run strongly depends on the volume flow rate but also depends on the pulsation parameters whose positive effects are reinforced. Finally, all the hydrodynamic parameters positively influence the corresponding selectivity.

Table 6 gives results related to the two phase electrolysis. For practical reasons only the benzaldehyde yield was taken into account. The maximum benzaldehyde yield obtained with petroleum ether as the organic extractive phase was 60%. This is twice the value obtained in homogeneous medium. Table 6 reveals that benzaldehyde yield is positively influenced by both pulsation amplitude and frequency. The effect of pulsation frequency is the most important. The effect of pulsation amplitude and frequency is enhanced in two phase medium, probably because of the efficiency of the pulsed columns in extraction processes as is the case in our work. It is also noticed that almost all parameter interaction effects must be taken into account and can not be neglected.

In alkaline solution, the electrooxidation of primary alcohol on nickel leads mainly to acid [13]. Accordingly, in an aqueous solution the major product of benzyl alcohol oxidation was benzoic acid. Conversely, in an emulsion electrolysis, alcohol can be converted to aldehyde as main product [13]. Our results show that the aldehyde yield and selectivity increase in two phase conditions. This confirms that the intermediate aldehyde is extracted into the organic phase and thus prevented from further oxidation into acid.

It is concluded that the benzaldehyde yield and selectivity can be increased by using an organic extractive phase dispersed in an aqueous continuous phase by using ultrasonics. The pulsation amplitude and frequency enhance the benzaldehyde yield. The value of the volume flow must be kept low in order to achieve a reasonable residence time. To confirm the validity of the statistical experimental strategy, an additional confirmatory experiment was performed under the following conditions: 0.2 litre of petroleum ether (60–80 °C) dispersed into one litre of 0.1 M KOH solution containing $2 \times 10^{-2}$ M of benzyl alcohol, current density of $2.2\,\mathrm{A\,m^{-2}}$, volume flow $40\,\mathrm{ml\,min^{-1}}$, pulsation amplitude 1.3 cm, pulsation frequency 1.20 Hz. The resulting aldehyde yield and current efficiency were 62 and 60%, respectively, which is in agreement with Table 4. This resulting benzaldehyde yield is lower than that obtained on a single nickel foam disc. This is attributed to the change in electrode bed height (from 0.2 to 1.2 cm). A large electrode bed height leads to greater acid production (Table 2) but permits shorter electrolysis time.

## 4. Conclusion

Nickel foam electrodes present large active surface areas and were found to be suitable as catalyst for benzyl alcohol oxidation. Best results were obtained for two phase electrolysis. The organic phase extracts the benzaldehyde, which prevents further oxidation to acid. The organic phase was dispersed in the aqueous phase using ultrasonication and the emulsion was maintained by pulsation. The effects of the following electrolysis parameters: organic phase ratio, aqueous phase pH, bed height, volumic flow, pulsation amplitude and frequency on the benzaldehyde yield were experimentally investigated. The results from the factorial design experiments showed that the aldehyde yield increased with increasing pulsation amplitude and frequency.

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## References

[1] H. J. Schäfer, *Topics in Current Chemistry* **142** (1986) 101.
[2] M. Fleischmann, K. Korinek and D. Pletcher, *J. Electroanal. Chem.* **31** (1971) 39.
[3] M. Fleischmann, K. Korinek and D. Pletcher, *J. Chem. Soc., Perkins Trans II* (1972) 1396.
[4] M. Amjad, D. Pletcher and C. Smith, *J. Electrochem. Soc.* **124** (1977) 203.
[5] R. Schneider and H.-J. Schäfer, *Synthesis* (1989) 742.
[6] P. Cox and D. Pletcher, *J. Appl. Electrochem.* **20** (1990) 549.
[7] *Idem, ibid.* **21** (1991) 11.
[8] A. Budniok and E. Kozlowska, *Thin Solid Films* **204** (1991) 341.
[9] Y. Kunugi, T. Fuchigami, T. Nonaka and S. Matsumura, *J. Electroanal. Chem.* **287** (1990) 385.
[10] Y. Kunugi, T. Nonaka, Y.-B. Chong and N. Watanabe, *ibid.* **318** (1991) 321.
[11] Y. Kunugi, R. Kumada, T. Nonaka, Y.-B. Chong and N. Watanabe, *ibid.* **313** (1991) 215.
[12] T.-C. Wen, C. C. Hu and Y. J. Li, *J. Electrochem. Soc.* **140** (1993) 2554.
[13] T.-C. Wen, S.-M. Lin and J.-M. Tsai, *J. Appl. Electrochem.* **24** (1994) 449.
[14] J. Nanzer, S. Langlois and F. Coeuret, *ibid.* **22** (1993) 471.
[15] J. Nanzer, S. Langois and F. Coeuret, *ibid.* **23** (1993) 477.
[16] C. J. Brown, D. Pletcher, F. C. Walsh, J. K. Hammond and D. Robinson, *ibid.* **24** (1994) 95.
[17] A. S. Vaze, S. B. Sawant and V. G. Pangarkar, *ibid.* **25** (1995) 27.
[18] P. Cognet, J. Berlan, G. Lacoste, P.-L. Fabre and J.-M. Jud, *ibid.* **25** (1995).
[19] P. Cassoux, R. Dartiguepeyron, C. David, D. de Montauzon, J.-B. Tommasino and P.-L. Fabre, *Actual. Chim.* **1–2** (1994) 49.
[20] P. Cognet, Thèse de Doctorat I.N.P.T., Toulouse (1994).
[21] G. Sado and M.-C. Sado, Les plans d'expériences: méthode Taguchi, Les éditions d'organisation (1988).