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Application of an electrochemical pulsed flow reactor to electroorganic synthesis Part II: Oxidation of cyclohexanol and pilot plant operation

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A pilot plant electrolyser was built, which, in design, was similar to an industrial reactor used for metal recovery from waste waters. Increased mass transport rates were achieved by applying a pulse to the reactor solution. The first reaction tested on this new cell was the indirect oxidation of cyclohexanol in aqueous solution by means of an iodinated intermediate species. Several electrochemical methods, such as cyclic and linear sweep voltammetry and chronoamperometry, were used for the study of the reacting system. The results from these analyses have allowed optimization of the reactor operating conditions. A mathematical model for the process has been established which predicts the reactor yield and conversion as a function of the main operating parameters.

Keywords: *cyclohexanol*, *indirect oxidation*, *iodide mediator*, *pilot plant*

List of symbols

a	amplitude of the pulsating movement (m)
C_e	cyclohexanol concentration in the exit of the reactor (mol dm^{-3})
C_f	cyclohexanol concentration in the feed of the reactor (mol dm^{-3})
C_{I^-}	iodine concentration (mol dm^{-3})
$C_{[I^+]}$	intermediate concentration (mol dm^{-3})
C_0	initial concentration on cyclohexanol (mol dm^{-3})
E	working electrode potential (V)
$E_{1/2}$	half wave potential (V)
f	frequency of the pulsating movement (s^{-1})
j	current density (A m^{-2})
I	current (A)
I_0	initial current (A)
I_t	current at time t (A)
I_s	stabilized current (A)
p	Electron transfer rate constant (s^{-1})
Q	volumetric flow rate (dm^3 s^{-1})
q	current passed (F mol^{-1})
K	apparent reaction rate constant (s^{-1})
K_0	apparent reaction rate constant without pulsation (s^{-1})
k'	pseudo first order kinetic constant (s^{-1})
Sr	Strouhal number
t	time (s)
v	instant liquid flow velocity (m s^{-1})
v_0	steady liquid flow velocity (m s^{-1})
V_1	reaction zone volume (dm^3)
V_2	solution tank volume (dm^3)
X	conversion rate
Y	ketone yield

Greek letters

γ	Ratio of the chemical step rate constant to the electrochemical one
τ_1	Electrolyte residence time in the reaction zone (s)
τ_2	Electrolyte residence time in the solution tank (s)

1. Introduction

This paper describes a new kind of electrolyser for industrial organic synthesis, which was conceived following the design of a metal recovery electrochemical cell, the pulsated percolated porous electrode (E3P) [1]. At the laboratory scale, this reactor has been successfully applied to ferrocene oxidation in liquid–liquid dispersions [2], acetophenone reduction to the corresponding pinacol [3], benzylic alcohol oxidation [4] and the cleavage of diols on nickel foam electrodes [5, 6]. The results from these experiments have led to the construction of a pilot plant reactor.

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The reaction employed to test the reactor performance is the indirect oxidation of cyclohexanol to cyclohexanone, which is carried out in an aqueous, homogenous phase by means of an inorganic catalytic electron carrier.

2. Pilot plant reactor

The process is depicted in Fig. 1. The electrolyte solution is prepared in the tank; it is fed to the base of the reactor, then passes through a mixing zone followed by the reaction zone. The solution is fully recycled. In the present configuration of the process, reactor and tank volumes are $V_1 = 2\,\mathrm{dm}^3$ and $V_2 = 10\,\mathrm{dm}^3$, respectively.

A pulsating movement is applied to the electrolyte in the mixing and reaction zones to maintain high mass transfer coefficients between the solution and the electrode. The pulsating device is a pneumatic system operating at 7 bar over a Teflon membrane 0.4 m in diameter. The pulsating movement follows a signal of the type: $y = a\cos(2\pi ft)$, where a is the amplitude, f the frequency and t the time. If v_0 is the steady flow velocity, the instantaneous velocity of the liquid phase is given by

$$v = v_0 + 2\pi fa\,\sin(2\pi ft) \qquad (1)$$

The hydrodynamics of a pulsed flow system are characterized by the Strouhal number, expressed as

$$Sr = (2\pi fa)/v_0 \qquad (2)$$

In a pulsated device the mass transfer coefficients are a function of the Strouhal number. The piston frequency can be set between 0 and $1.5\,\mathrm{s}^{-1}$ and the amplitude varies from 0.01 to 0.1 m.

The mixing zone is made of glass and filled with glass beads as turbulence promoters for the solution. The ratio of the lower to upper diameter is 2 to 1. The diameter reduction in the mixing zone makes it possible to have a wider amplitude range and a uniform velocity profile entering the reaction zone.

The electrodes are made of a series of rigid expanded platinized titanium grids of high surface area, placed in the reaction zone, which consists of a glass cylinder that allows for different electrode configurations. The characteristic dimensions of the grids employed in this work are shown in Fig. 2. The reaction zone arrangement (shown in Fig. 3) used for the cyclohexanol oxidation reaction has a working electrode surface area of $0.4\,\mathrm{m}^2$. The grids are interchangeable and their number can be increased. A radial configuration, used when a divided cell is required, can easily be installed.

3. Cyclohexanol oxidation

3.1. *Reaction system*

The direct electrochemical oxidation of alcohols is usually difficult to accomplish because it requires electrode potentials greater than 2 V vs SCE [7]. Indirect oxidation of primary and secondary alcohols can be achieved by means of an electrocatalytic couple. Indirect electrochemical oxidation or reduction has been studied during the last twenty years, and the applications of organic and inorganic intermediates such as iodide [8], bromide [9], nitrate [10], manganese dioxide [11], NaCl–RuO_2 [12], PVH [13], *N*-hydroxilamine [14], *N*-hydroxiphthalimide [15] and triarylamine [16] have been developed.

Cyclohexanol oxidation is carried out by the anodic oxidation of iodide, to an intermediate product $[I^+]$ which reacts with cyclohexanol to give cyclohexanone and to regenerate I^-. Tertiary alcohols cannot be oxidized this way.

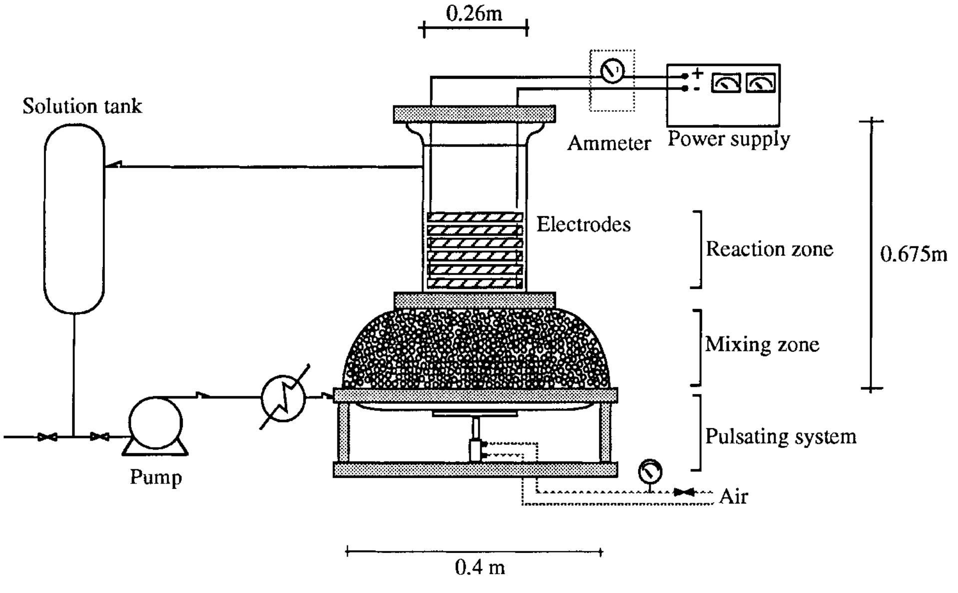


Fig. 1. The organic electrosynthesis pilot reactor.

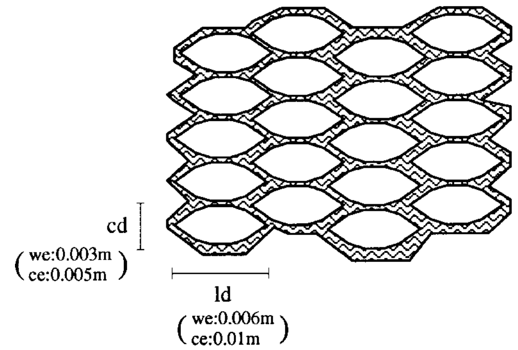
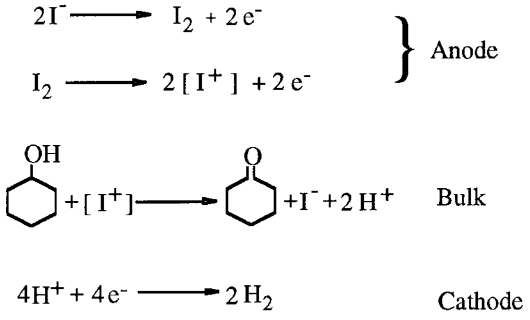
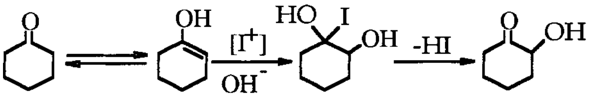


Fig. 2. Geometry and dimensions of platinized titanium electrodes.

The reactions are as follows:



Reaction byproducts are iodine, which can react at the cathode to regenerate iodide, and 2-hydroxy-cyclohexanone, which is generated from the enolic form of cyclohexanone.



The actual structure of the intermediate $[I^+]$ is not known with certainty, and has been a subject of discussion by several authors. Kolthoff and Jordan [17] have taken the intermediate as unipositive iodine:

$$I_2 + 2x\,H_2O \longrightarrow 2\,[I(H_2O)_x]^+ + 2\,e^-$$

Ogumi *et al.* [18] and Dryhurst and Elving [19] reported that $[I^+]$ is the hypoiodite ion:

$$I_2 + 2\,H_2O \longrightarrow 2\,HOI + 2\,H^+ + 2\,e^-$$

All of these species exist in stable form only in extremely acidic medium [20].

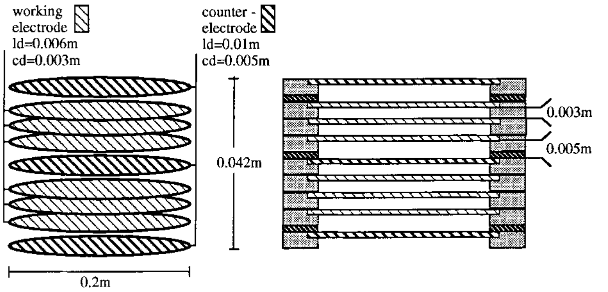


Fig. 3. Electrodes arrangement.

From a global point of view, the advantages of the use of this indirect oxidation system are (i) that a small quantity of energy is employed because the intermediate species has a low oxidation potential; (ii) that $[I^+]$ is constantly regenerated, so it can be used in small quantities; and (iii) that the electrolysis can be carried out at a constant current density.

3.2. *Kinetics*

The kinetics of an EC reaction (electrochemical step–chemical step catalytic mechanism), assuming a pseudo first order reaction with a large excess of alcohol compared to iodide concentration [21], can be expressed by the following equations:

$$\frac{dC_{I^-}}{dt} = -pC_{I^-} + k'C_{[I^+]} \tag{3}$$

$$\frac{dC_{[I^+]}}{dt} = pC_{I^-} - k'C_{[I^+]} \tag{4}$$

where p is the diffusion controlled rate constant for the electrochemical step and k' is the pseudo first order rate constant for the chemical step. Combination of these equations gives:

$$(C_{[I^+]})_t = (C_{I^-})_0 - (C_{I^-})_t \tag{5}$$

Integration of Equation 3 and introduction of the ratio of the two steps rate constants $\gamma = k'/p$, leads to

$$(C_{I^-})_t = (C_{I^-})_0\left(\frac{\gamma + \exp(-p(1+\gamma)t)}{1+\gamma}\right) \tag{6}$$

The current passing through the solution is a measure of the diffusion controlled reaction rate, thus it can be written as

$$\frac{I_t}{I_0} = \frac{\gamma + \exp(-p(1+\gamma)t)}{1+\gamma} \tag{7}$$

where I_0 is the measured current at time $t = 0$. For a catalytic system the current intensity does not decrease to zero, but to a constant value I_s for an infinite time, because the active species is constantly regenerated. Thus,

$$\frac{I_s}{I_0} = \frac{\gamma}{1+\gamma} \tag{8}$$

The value for γ providing the information about the relative reaction rates for both steps can be calculated by controlled potential chronoamperometry. The values for the $I^-/[I^+]$ couple are presented in Section 4.1.

4. Experimental details

4.1. *Analytic study*

Chronoamperometry experiments were carried out with solutions containing 0.2 M NaCl, at a platinized titanium electrode of surface area $1 \times 10^{-4}\,m^2$. The current potential plots and cyclic voltammograms were obtained with solutions containing 0.005 M KI, 0.005 M cyclohexanol, 0.1 M NaCl. *Ter*-butanol (5%

volume) was added to increase the cyclohexanol solubility. A 0.001 m diameter platinum rotating disc electrode was used.

4.1.1. Chronoamperometry. The results from controlled potential chronoamperometry experiments are presented in Fig. 4. They show high reaction rates for the chemical step compared to the electrochemical one. The γ values, calculated from the ratio $I_s/(I_0 - I_s)$, are 11, 12 and 12 for concentrations of KI of 0.2, 0.1 and 0.05 M, respectively. The diffusion of the mediator being the rate controlling step of the process, the current reaches a stable value within a few seconds, proving that $[I^+]$ has an extremely short life time. The anodic potential was kept at 1.1 V vs SCE.

4.1.2. Current–potential plots. Linear sweep voltammograms for this system were calculated at a rotating disc Pt electrode (sweep rate $0.005\,V\,s^{-1}$; electrode rotation 1500 rpm) and the plot is shown on Fig. 5.

The first wave presents a half wave potential of 0.57 V vs SCE. This wave corresponds to the oxidation of iodide to iodine. The second wave is due to the oxidation of iodine to the intermediate $[I^+]$. In neutral solution the half wave potential for this reaction is 0.83 V vs SCE. A small peak is observed at a potential of 1.2 V vs SCE; this is likely caused by an interaction product between iodine and cyclohexanol. More generally, the half wave potential of the second wave is pH dependent [19], in accordance with

$$E_{1/2} = 0.99 - 0.049\,\mathrm{pH} \qquad (9)$$

An alkaline pH can reduce the electrode potential at which the reaction takes place, but a very high pH could lead to iodine decomposition:

$$3\,I_2 + 3\,H_2O \longrightarrow IO_3^- + 5\,I^- + 6\,H^+$$

The best conditions to carry out cyclohexanol oxidation are neutral or slightly alkaline solutions. An acidic pH would lead to iodine accumulation and to its eventual adsorption on the electrode surface. In the case of pilot reactor operation, pulsated flow helps to minimize this problem.

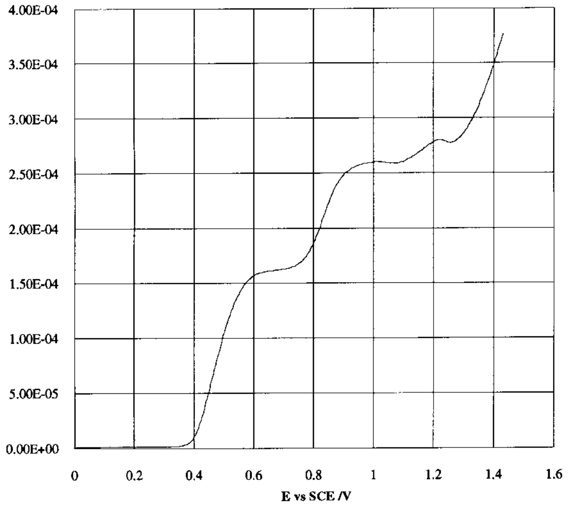


Fig. 5. Current–potential plot. Solution containing 0.005 M KI; 0.005 M cyclohexanol; 0.1 M NaCl; 5% volume *ter*-butanol.

4.1.3. Cyclic voltammetry. Cyclic voltammograms were carried out at potential sweep rates ranging from 0.01 to $2\,V\,s^{-1}$. The results are presented in Fig. 6.

The first peak corresponds to the iodide to iodine oxidation, the reverse peak is slightly larger than the anodic wave, showing some adsorption of iodine on the electrode surface. The second couple ($[I^+]$ formation) has a well defined anodic wave and a cathodic wave that increases with the sweep rate. Dryhurst and Elving [19] found no reverse peak for this second couple with iodide in K_2SO_4 and K_2SO_4–H_2SO_4 solutions at a stationary pyrolitic graphite electrode and low scan rates ($0.01\,V\,s^{-1}$). Our results show a well defined cathodic peak at all sweep rates. It is possible that the intermediate is stabilized by the

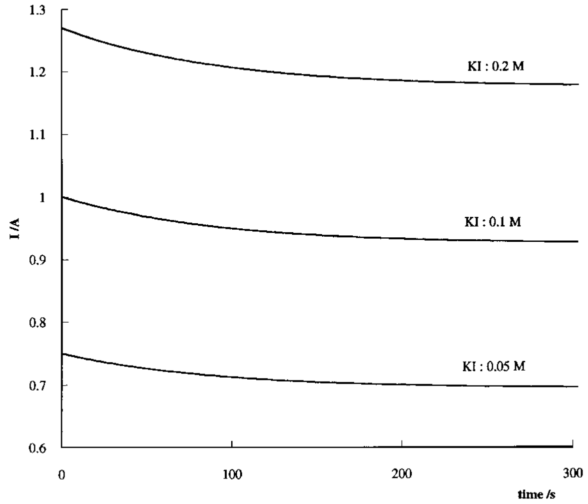


Fig. 4. Chronoamperometry results. Solutions containing 0.2 M NaCl. The concentrations in KI are indicated on every plot.

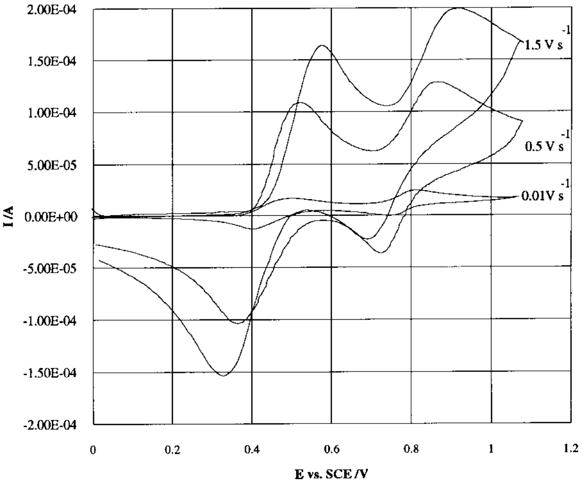


Fig. 6. Cyclic voltammetry graphs. Solution with 0.005 M KI; 0.005 M cyclohexanol; 0.1 M NaCl; 5% volume *ter*-butanol. Sweep rates are indicated on every plot.

presence of cyclohexanol or ter-butanol. For both couples, the peak current is a linear function of the sweep rate, showing that the whole process is diffusion controlled [22].

Chronoamperometry experiments allowed us to determine the correct current density values to be used in pilot plant operation, and showed that the intermediate species has a very short life time. This result, however, does not agree with the cyclic voltammetry plots, in which we find a significant cathodic wave corresponding to $[I^+]$ reduction. As the process appears to be diffusion controlled, the pulsating parameter settings should have an important effect on the pilot performance. The current–potential plots have allowed us to establish the optimal pH and potential (1.1 V vs SCE) at which the electrolysis should be carried out.

4.2. *Pilot plant operation*

The electrolyses were controlled by means of a Heinzinger PTN 32–40 power supply. The total liquid volume circulating in the whole installation was $0.035\,\mathrm{m}^3$. Products were analysed by gas chromatography on a Chrompack 50 m polar column; split injector 200 °C; FID 240 °C, oven 130 °C, 16 psi.

The usual concentrations employed on pilot plant electrolyses were: 0.05 M KI, 0.1 M NaCl, 5% volume *ter*-butanol. Sodium chloride was used as supporting electrolyte, and *ter*-butanol was added to increase the cyclohexanol solubility in water. The initial cyclohexanol concentration was found to be an important operating variable and was set at values between 0.05 and 0.2 M.

Empirical results from a preliminary factorial design study at laboratory scale have shown that the volumetric flow rate has no influence on the conversion rate or overall selectivity [3]. This observation is confirmed by the experimental results obtained from pilot plant electrolyses. Flow rate in all these experiments was kept constant, providing a steady flow velocity of $3.3 \times 10^{-4}\,\mathrm{m\,s^{-1}}$.

In the first seconds of electrolysis the solution takes on a brownish yellow colour. At the same time hydrogen evolution begins and the pH slowly rises. Iodine continues to be generated; within a few minutes the electrolyte becomes dark red and pH reaches a stable value (iodine is reduced at the cathode). Electrolyses were carried out at constant current. For all the reported experiments cell voltage was constant (between 4 and 4.5 V) as well as the anodic potential which, in every case, had values of 1.0 to 1.2 V vs SCE. The catalytic behaviour of the couple $I^-/[I^+]$ allows operation at constant current, cell voltage and working electrode potential [23].

5. Process modelling

As a first approximation, pulsating parameters and flow velocity are set so that the Strouhal number value is equal to or greater than 4. In these hydrodynamic conditions the system can be considered as a continuous stirred tank reactor [24]. In this case all the electrolyte is recirculated after dilution in the reservoir (Fig. 7).

Mass balances for cyclohexanol over the reservoir and the reaction zone, considering first order kinetics, can be written as follows:

(i) Reaction zone (CSTR). C_f and C_e are the cyclohexanol concentrations in the feed and in the exit of the reactor, respectively; K is the apparent reaction rate coefficient; V_1 and V_2 are the reactor and reservoir volumes and Q is the volumetric flow rate.

$$V_1\frac{\mathrm{d}C_\mathrm{e}}{\mathrm{d}t} + (Q + KV_1)C_\mathrm{e} = QC_\mathrm{f} \qquad (10)$$

accumulation + exit + reaction = feed

(ii) Reservoir. Here C_f is the concentration in the exit of the tank, after dilution.

$$V_2\frac{\mathrm{d}C_\mathrm{f}}{\mathrm{d}t} + QC_\mathrm{f} = QC_\mathrm{e} \qquad (11)$$

accumulation + exit = feed

Analytic solution of these equations leads to

$$(C_\mathrm{e})_t = \frac{(C_\mathrm{f})_t}{1+K\tau_1} + \frac{C_0K\tau_1}{1+K\tau_1}\exp\left[-\left(\frac{1+K\tau_1}{\tau_1}\right)t\right] \qquad (12)$$

$$(C_\mathrm{f})_t = \frac{C_0K\tau_1^2}{K\tau_1^2-(1+K\tau_1)^2\tau_2}\exp\left[-\left(\frac{1+K\tau_2}{\tau_1}\right)t\right] - \frac{C_0(1+K\tau_1)^2\tau_2}{K\tau_1^2-(1+K\tau_1)^2\tau_2}\exp\left[-\left(\frac{K\tau_2}{(1+K\tau_1)\tau_2}\right)t\right] \qquad (13)$$

where C_0 is the initial cyclohexanol concentration and τ_1 and τ_2 are the residence times in the reactor and reservoir, respectively. $[I^+]$ is continuously generated and its concentration is assumed to be constant during reactor operation, so that the chemical reaction rate based on cyclohexanol consumption can be expressed by a first order kinetic equation in which the intermediate concentration is included in the rate constant K.

This apparent rate constant (K) is a function of the amplitude and frequency of the pulsation, current density and initial concentration of cyclohexanol,

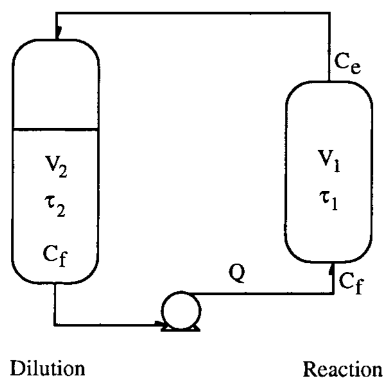


Fig. 7. Process modelling scheme.

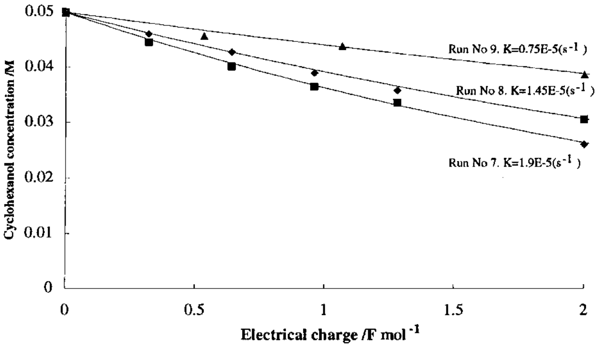


Fig. 8. Alcohol consumption for a 2 F mol^{-1} electrical charge.

since all these parameters have an effect over the concentration of the mediator and its diffusion. The value of K was found from experimental data fitting (Fig. 8). The installation volumes and the applied flow rate correspond to $\tau_1 = 60$ s and $\tau_2 = 300$ s at the steady flow velocity imposed in pilot plant operation.

6. Results and discussion

Table 1 summarizes the operating conditions for this series of runs on the pilot plant. The corresponding results are given in Table 2.

Comparison between run number 9 (without pulsation) and all the other experiments, shows that conversion rate and ketone yield are significantly enhanced by the application of pulsation. Figure 8 shows the cyclohexanol concentration profiles for experimental runs 7, 8 and 9 (points) as well as those calculated by means of the process model (continuous lines), as a function of the current passed through the electrolyte for a charge of 2 F mol^{-1}.

K, calculated from experimental data, is a measure of the cyclohexanol consumption, and shows the same behaviour as the conversion rate ($X = (C_0 - C_e)/C_0$) (Fig. 9). In the following discussion we use K, rather than conversion rate, since the value of K is directly proportional to [I$^+$] concentration. The values of K are related to its value without pulsation (K_0).

Increasing the amplitude results in an increase in K and in the ketone yield (runs 6 and 8). Amplitude seems to be the only parameter having an effect over the ketone yield, which reaches values around 60% in every case. Experiments done with a 0.1 m amplitude (runs 5 and 6) are the only ones showing a product yield higher than 60%. Current density presents the same effect over K as amplitude (runs 5 and 6). Increasing frequency (runs 7 and 8), or initial cyclohexanol concentration (runs 1, 2 and 4) yields poor results for K.

Experimental data fitting produces the following results for K and ketone yield (Y) as a function of amplitude, frequency, current density and initial concentration of cyclohexanol. Equations 14 and 15 are valid for parameters in the range shown in Table 1.

Table 1. Operating conditions of pilot plant electrolyses

Run	*Amplitude* /m	*Frequency* /s^{-1}	*Current density* /A m^{-2}	*Sr*	C_0 /M
1	0.02	1.15	50	438	0.2
2	0.02	1.15	65	438	0.1
3	0.02	0.17	50	65	0.1
4	0.02	1.15	50	438	0.05
5	0.1	0.5	50	952	0.05
6	0.1	0.5	25	952	0.05
7	0.02	0.17	25	65	0.05
8	0.02	0.5	25	190	0.05
9	0	0	25	0	0.05

Table 2. Results from 24 h pilot plant operation

Run	*Conversion*	*Ketone yield*	*Selectivity*	*Current passed* /F mol^{-1}	*Initial/Final* pH	10^5 K s^{-1}
1	0.67	0.59	0.88	2.56	6.0/7.0	1.15
2	0.72	0.59	0.82	3.33	5.5/6.0	1.3
3	0.75	0.60	0.77	5.10	7.0/7.1	1.5
4	0.74	0.57	0.78	10.25	7.2/7.2	1.78
5	0.81	0.63	0.78	10.25	7.2/7.5	1.74
6	0.78	0.66	0.85	5.10	7.0/7.3	1.6
7	0.80	0.59	0.73	5.10	7.3/7.5	1.9
8	0.72	0.60	0.88	5.10	6.7/7.0	1.45
9	0.48	0.38	0.80	5.10	7.0/7.1	0.75*

* In literature it is considered that, for hydrodynamic conditions yielding $Sr \leq 4$, the problem is that of a plug flow reactor, and not a CSTR [23]. Our installation does not behave as a plug flow reactor, since there is no concentration profile along the axial direction of the flow in the electrodes zone. The case without pulsation will be treated as a CSTR.

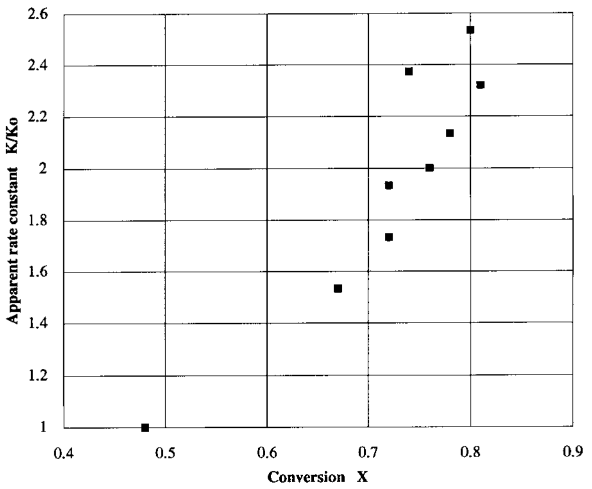


Fig. 9. Apparent reaction rate constant as a function of conversion rate. $K_0 = 7.5 \times 10^{-6}\ \mathrm{s}^{-1}$ is the constant calculated without pulsated flow (experimental run number 9).

$$K = 3.2575(a) + 0.1751(f) + 0.2684(j) - 3.1646(C_0) + 1.3819 \tag{14}$$

$$Y = 1.4518(a) + 0.0653(f) - 0.0254(j) + 0.1736(C_0) + 0.4824 \tag{15}$$

These equations confirm that apparent reaction rate and ketone yield are mostly sensitive to amplitude and cyclohexanol concentration. Frequency and current density have a weak influence over the electrolysis performance. Since the objective of this work is to obtain the maximum product yield as a priority, with the highest possible conversion rate, a rough optimization guide is to work with high amplitude settings, thus increasing the transport rate of the intermediate between electrode and solution.

If there is an interaction between $[\mathrm{I}^+]$ and cyclohexanol, increasing the alcohol concentration leads to a reduction of the free $[\mathrm{I}^+]$ concentration. This explains why the K value decreases while reactant concentration increases. More intermediate $[\mathrm{I}^+]$ is generated when current density increases, and slightly higher values of K are obtained. The influence of current density is weak as the limiting variable in this case is the initial iodide concentration, which was kept constant for all experiments.

7. Conclusions and perspectives

The electrosynthesis of cyclohexanone has been investigated in a pulsed pilot plant reactor in which platinized titanium electrodes were installed. Analytica studies of the reacting system allowed establishment of general operating conditions for pH and working electrode potential. Monitoring the pH during pilot plant operation showed that it increases slightly in 24 h electrolyses; no further control of this variable is required. The identity of the intermediate species is not known with certainty; however, the presence of cyclohexanol seems to stabilize this intermediate in a neutral solution.

Since the process is diffusion controlled, the parameters of the pulsating movement have a strong influence on the reactor performance. Frequency must be set at low values, while high values of amplitude provide the best results for cyclohexanone yield. A high initial alcohol concentration increases the overall product yield, but it reduces the chemical reaction rate constant. Increasing current density improves the electrolysis result, only if the initial iodide concentration is set in accordance with the applied current. The pilot plant runs yielded satisfactory conversions and selectivities for an industrial process.

The model established for this process allowed the apparent reaction rate to be found for each pilot plant run. This model can be used as a tool for the study of other first order kinetic schemes to be tested in the reactor.

The $\mathrm{I}^-/[\mathrm{I}^+]$ catalytic couple is not highly selective and can be applied to the oxidation of more interesting secondary alcohols. Primary alcohols can be oxidized to esters by this method. It would be interesting to apply the technique to the synthesis of esters using liquid–liquid dispersions as reacting media, where the organic phase droplets could work simultaneously as a reactant reservoir and as a product extraction method.

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