Scale-up studies of the electrolytic reduction of oxalic to glyoxylic acid

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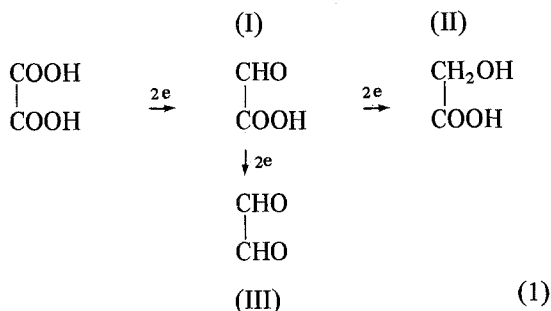
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The work examines a possible process for the electrolytic reduction of oxalic acid to glyoxylic acid. The reaction is investigated in filter press type cells varying from small bench scale to pilot plant size and it is shown that the product can be produced with current efficiencies better than 70% and chemical yields better than 90%. It is demonstrated that the cell product containing 8–10 wt% of glyoxylic acid can be concentrated to the commercial specification of a 50 wt% aqueous solution.

1. Introduction

The work described here was concerned with some of the engineering aspects of developing and scaling-up a process [1] for the electrochemical production of glyoxylic acid (I) by the reduction of oxalic acid. According to the overall scheme

$$
\begin{array}{ccccc}
 & (I) & & (II) & \\
COOH & & CHO & & CH_2OH \\
| & \xrightarrow{2e} & | & \xrightarrow{2e} & | \\
COOH & & COOH & & COOH \\
 & & \downarrow 2e & & \\
 & & CHO & & \\
 & & | & & \\
 & & CHO & & \\
 & & (III) & & (1)
\end{array}
$$

the product can be further reduced to glycollic acid (II) or alternatively to glyoxal (III). Glyoxylic acid is used as an intermediate in the perfumery, pharmaceutical and fine chemical industries and is normally sold as a 50 wt% aqueous solution.

After obtaining preliminary results with small, glass H-cells, filterpress modules of 0·01–0·04 m² in cross-section were used. This work led to experimentation using a pilot plant containing four filterpress modules 0·24 m² in cross-section.

The absence of a supporting electrolyte means that an uncontaminated product may be obtained directly from the electrolytic cell, removing the need for a product purification step and hence reducing the overall production cost.

2. Experimental

2.1. Cells

2.1.1. Small glass cells. Most of the polarization data were obtained with a divided H-type cell of 60 cm³ catholyte capacity and some preliminary preparative runs were performed with a similar cell but with a 200 cm³ catholyte capacity and a cationic ion exchange membrane (Ionac MC-3470 membranes supplied by Ionac Chemical Co., New Jersey, USA) in place of a glass frit.

2.1.2. Small filter press modules. These were made in polypropylene, a typical frame being shown in Fig. 1. Detachable baffles provide a serpentine flow which creates a high degree of turbulence at a relatively low pressure drop. Additionally, as shown schematically in Fig. 2, the baffles provide support for the cationic ion exchange membrane. The numbers in brackets on Fig. 1 refer to the dimensions of the pilot plant module.
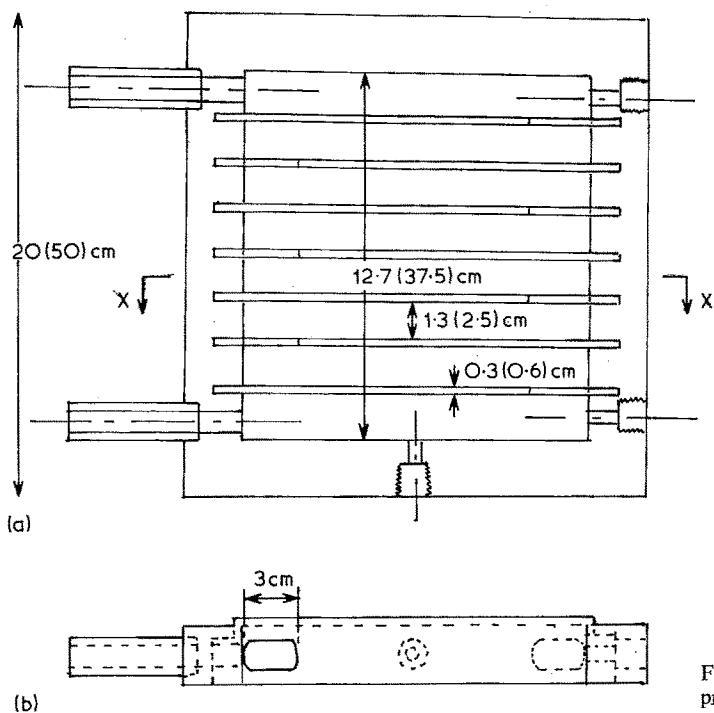
Fig. 1. Schematic drawing of small scale filter press module.

2.1.3. Pilot plant cell. The four modules making up the pilot plant cell are constructed from frames identical in design and materials with those shown in Fig. 1, but scaled up to a cross-sectional area of 0.24 m^2. The arrangement of frames and diaphragm is again that of Fig. 2. Fig. 3 provides a slightly simplified flow sheet and to give some indication of overall scale Fig. 4 is a general view of the pilot plant. All runs were carried out batchwise.

Fig. 2. Exploded view of filter press module: E electrodes; C cell frames; D diaphragm; B baffles.

2.2. *Materials*

Cathode materials investigated were lead of different purities, graphite, dimensionally stable cathodes* and a lead/thallium (2·75%) alloy. Six anode materials were studied, namely platinum, lead, lead/antimony and lead/thallium alloys, graphite and a dimensionally stable anode [3] (DSA).

AnalaR oxalic acid was used for small scale experiments, but commercial grade for the pilot plant. Sulphuric acid was AnalaR in all experiments.

2.3. *Analysis*

Glyoxylic acid was determined either volumetrically by means of the bisulphite compound or gravimetrically as the 2 : 4 dinitrophenyl hydrazone. Oxalic acid was determined gravimetrically as the calcium salt, and by-product glyoxal by a method described by Becke and Gross [2]. A spectrophotometric method was used for the detection of glycollic acid and formic acid, the
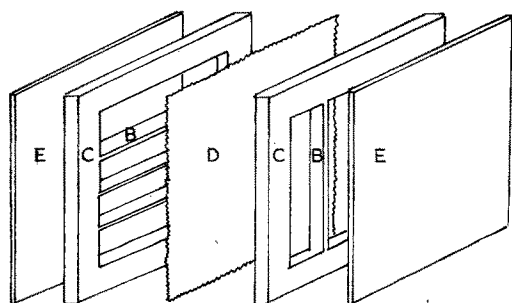
* Dimensionally stable anodes and cathodes were supplied by Permelec S.p.A. Milano, Italy: DSC batch no. BZ381, DSA batch no. BZ379.
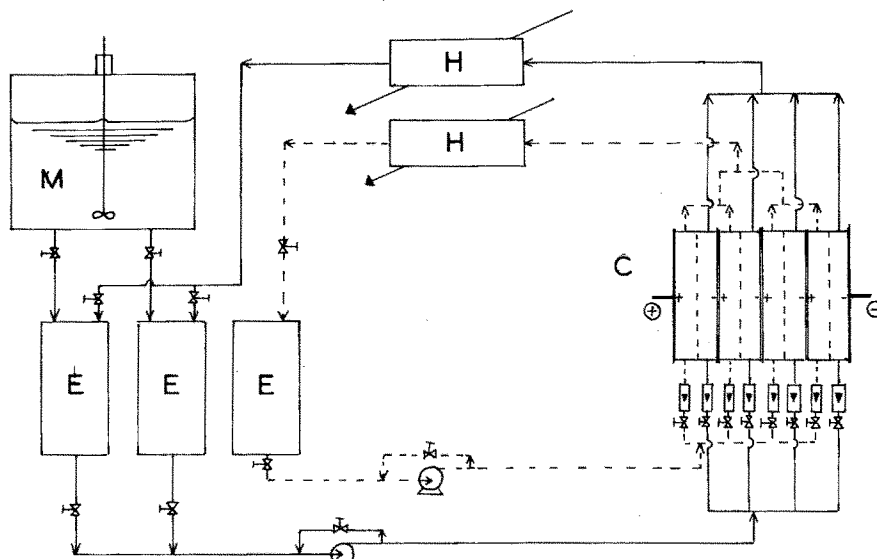
Fig. 3. Simplified flow sheet of pilot plant. —— catholyte flow circuit; – – – anolyte flow circuit; C cell bank, H heat exchanger, M mixing tank, E electrolyte tank.

former by reacting it with 2,7-dihydronaphthalene at 90–100° C [3], the latter by means of 2-thiobarbituric acid [4]. Formaldehyde was looked for qualitatively [5].

3. Results and discussion

3.1. Polarization curves

Fig. 5 shows a typical set of polarization curves obtained with the small H-cell for 0·5 M oxalic acid. Similar results were obtained with the filter-press cells. Significant reduction of oxalic acid occurs from − 1·1 V (all potentials in this paper are with respect to the SCE), hydrogen evolution being negligible below − 1·2 V. The presence of supporting electrolyte was found to be unnecessary, the required conductivity being provided by the oxalic/glyoxylic acid mixture. From Fig. 5, one can see that glyoxylic acid is not reduced in the potential range shown, this result being attributed to the stabilization of the aldehyde
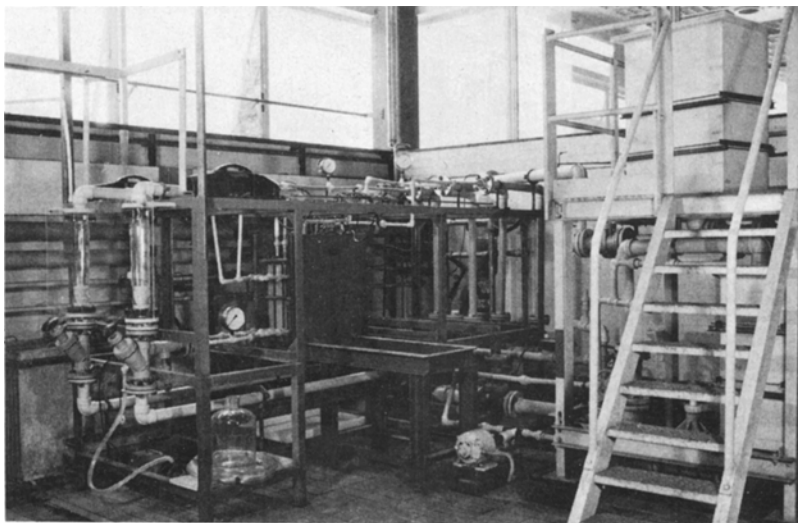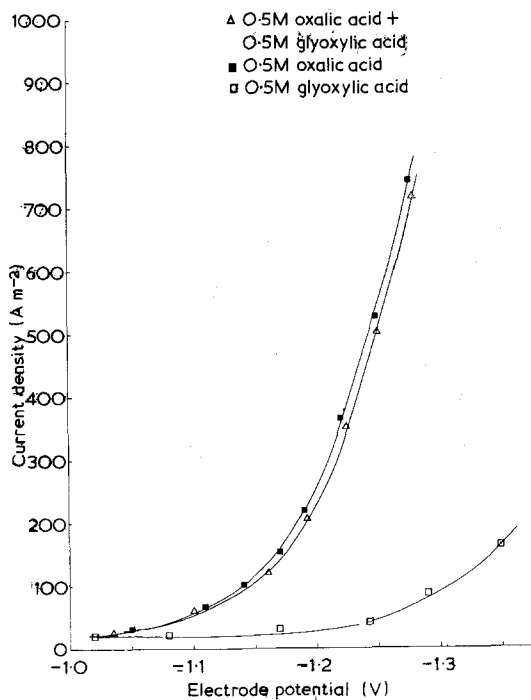

Fig. 4. General view of pilot plant.

Fig. 5. Polarization curves for 99·999% lead cathode.

Fig. 6. Current efficiencies of glyoxylic acid production for various cathode materials, and a DSA, at 8° C and 1000 A m^{-2}.

group by hydration. Using saturated oxalic acid (approx. 1 M) resulted in considerably higher current densities for a given electrode potential and in consequence most preparative runs were performed in a current density range of 1000–2000 A m^{-2}.

Initial experiments involving a platinum anode showed that transport of platinum to the cathode was sufficient to cause considerable hydrogen evolution, thereby highlighting the need for complete absence of any low hydrogen overvoltage metals.

3.2. Preparative runs with the H-cell and small filter press cell

Preliminary runs with the H-cell indicated that current efficiencies and chemical yields of better than 90% could be obtained using a cathode made of 99·999% lead at current densities up to 2000 A m^{-2}. Somewhat lower current efficiencies were achieved using less pure lead.

Turning now to the later work with the small filter press modules, some typical results showing the effect of cathode materials on current efficiency at a current density of 1000 A m^{-2} are
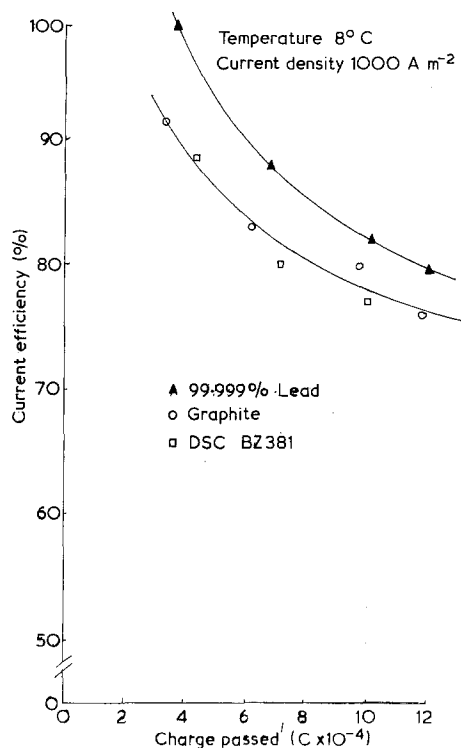
given in Fig. 6. The advantage of 99·999% lead is evident. Most of the loss in current efficiency is due to hydrogen evolution which increases with electrolysis time, even if the concentration of oxalic acid is kept at the saturation level. Separate experiments starting with considerable amounts of glyoxylic acid, say 10 wt%, and a fresh cathode indicated that hydrogen evolution was not connected with the product concentration. Fig. 7 shows the effect of electrolysis time on current efficiencies using 99·999% lead and dimensionally stable anodes. It can be seen that the current efficiency falls from a value well above 90% to just over 60% in fifteen hours. On investigating this effect with the small glass cell it was found that hydrogen evolution increased with time in a manner expected on the basis of the data shown in Fig. 7, but stopping the electrolysis for a few hours restored the current efficiency to its original high value. With filter press type cells periodic cleaning of the cathode with nitric acid improved current efficiencies but did not restore them to their original values. This is a similar problem to that encountered with the platinum anode and the
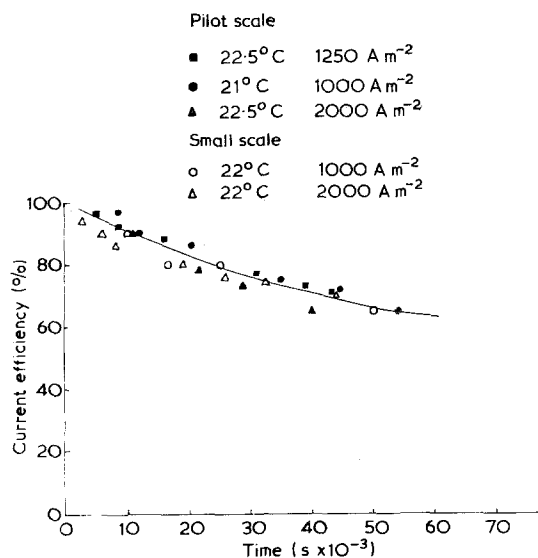
Fig. 7. Current efficiency of glyoxylic acid production as a function of electrolysis time for a 99·999% lead cathode and a DSA.

Fig. 8. Variation of current efficiency with temperature. Cathode 99·999% lead.

conclusion is that trace amounts of low hydrogen overvoltage metals must gradually be adsorbed onto active cathodic sites.

Of the anode materials investigated, lead/antimony, lead thallium, graphite and dimensionally stable anodes gave identical current efficiencies with time indicating that the degree of cathode contamination (if any) due to their presence in the cell was similar. A DSA was finally chosen since all other materials suffered from severe corrosion problems.

According to the literature [6] the temperature of the electrolyte should not exceed 10° C in order to minimize formation of glycollic acid. Fig. 8 shows results obtained with the H-cell on the effect of temperature on the formation of hydrogen and glycollic acid. It can be seen that although hydrogen evolution does increase somewhat above 10° C glycollic acid formation does not rise appreciably until 20° C is reached. Similar results were obtained with filter press cells. On the basis of these results 20° C was selected as the temperature of operation for the pilot plant although there is scope for further electrolyses at lower temperatures.

Since the current efficiency of glyoxylic acid formation appears to be effectively constant [7] for catholyte flow rates in the range of Reynolds numbers, (Re), of 9000–19 000 a value of 14 000 was selected for all runs with the bench filter press
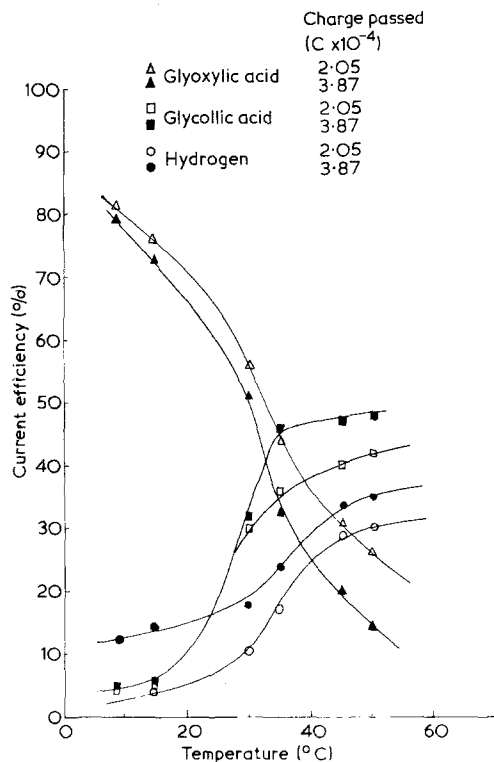
cells and the pilot plant modules. For this purpose (Re) is defined as:

$$(Re) = (v\rho d_e)/\mu \qquad (2)$$

where v is the average velocity of the catholyte between the baffles, ρ and μ are its density and viscosity respectively and d_e is an equivalent diameter given by:

$$d_e = 4A/P = 2ws/(w + s) \qquad (3)$$

where A is the cross-sectional area for the serpentine flow, P the corresponding perimeter, w the width of a baffle and s the separation between them.

3.3. Preparative runs with the pilot plant

Fig. 7 shows current efficiencies obtained with the pilot plant as a function of time. Again there is the same downward trend due to contamination of the cathode observed with the smaller cells and it is interesting to note that the current efficiency did not change significantly on scale-up. Unfortunately a really satisfactory washing procedure with nitric acid has not yet been developed and this sets an

upper conversion limit of 8–10 wt% of glyoxylic acid. Under these conditions current efficiencies exceeded 70%. A typical analysis of a completed batch was glyoxylic acid 8·05 wt%, glycollic acid 0·43 wt% in a saturated solution of oxalic acid, with amounts of glyoxal being negligible.

3.4. *Separation of the product*

To separate the product, the completed batch was submitted to a two stage evaporation in a climbing film evaporator accompanied by crystallization and filtration of the oxalic acid before and after the second evaporation stage. The final product was a 50 wt% aqueous solution of glyoxylic acid, containing less than 2 wt% of oxalic acid. For a number of purposes the presence of the latter is not deleterious, but experiments showed that the oxalic acid could be oxidized to CO_2 by passing the catholyte through an anode compartment in a divided cell. This procedure does, however, result in the destruction of about 2% of the glyoxylic acid.

4. Conclusion

It has been shown that glyoxylic acid can be pro-

duced with current efficiencies of better than 70% and chemical yields better than 90% in a filter press type pilot plant cell. In addition it has been demonstrated that for this reaction results obtained with small cells are reproduced on a pilot plant scale.

Acknowledgements

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