Further studies on the epoxidation of propylene in a bipolar trickle bed

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Further studies on the epoxidation of propylene via electrogenerated hypobromite in a trickle bed have been carried out with the aim of increasing the space–time yield. Factors which have been studied in more detail include electrode material, applied voltage, sense of polarity, cell packing arrangements, electrolyte flow rate and sodium bromide concentration. By suitable choice of conditions a significant increase in space–time yield can be obtained, up to a limit set by the depletion of propylene, without a large increase in energy consumption.

1. Introduction

The *in situ* synthesis of propylene oxide via electrogenerated hypobromite is now well known [1, 2]. The great advantage of this method over the traditional hypochlorite route [3] or the electrochemical generation of propylene chlorohydrin [4] is the elimination of the final saponification step which produces large quantities of dilute calcium chloride solution which presents an effluent treatment problem [3].

The production of propylene oxide with high selectivity at high product concentrations in the trickle bed has been reported elsewhere [1, 5]. Those results were obtained for the reactor optimized with respect to current efficiency and thus gave low energy consumption. The present work was an attempt to improve the space–time yield of the reactor by studying the effects of electrolyte flow rate, concentration, cell configurations, electrode polarity and electrode material on the overall reaction.

2. Experimental

The trickle-bed reactor was constructed from a glass tube, 30 cm long by 6.5 cm internal diameter, filled with 14 layers of twenty 12.5 mm Raschig rings (Morganite CY115 carbon) with perforated carbon plates as feeder electrodes. Each layer was separated by a polyester mesh spacer less than 1 mm thick. As the current feeder electrodes were 19 cm apart the electrochemical reactor volume was 6.31×10^{-3} m^3. The dead space above the top feeder electrode was packed with ceramic Raschig rings to facilitate propylene absorption and to help define the flow before it entered the reactor proper. The propylene gas and electrolyte flows were cocurrent. The reactor was plumbed into a flow system consisting of a pump, flow meter, heat exchanger and reservoir, with sampling points and provision for pH and temperature measurement. Electrolyte temperature was kept between 5 and 8° C for each experimental run while the pH equilibrated rapidly to between 10 and 11 without any external control.

Analysis was performed using a Perkin-Elmer F17 gas chromatograph with 2 m columns of Carbowax 20M (10%) on Chromosorb WAW DMCS (80–100 mesh), temperature programmed from 30–60° C at 20° min^{-1}. The concentration of sodium bromate was measured by iodometric titration.

The effect of electrode material on the generation of bromine was investigated by measuring the current–potential profiles for a number of different electrode samples in an H-cell. A Ministat precision potentiostat was used to apply the potential and that of the anode was measured against a saturated calomel electrode protected by a Luggin capillary and tap using a Schlumberger 4440 voltmeter. Current was measured directly
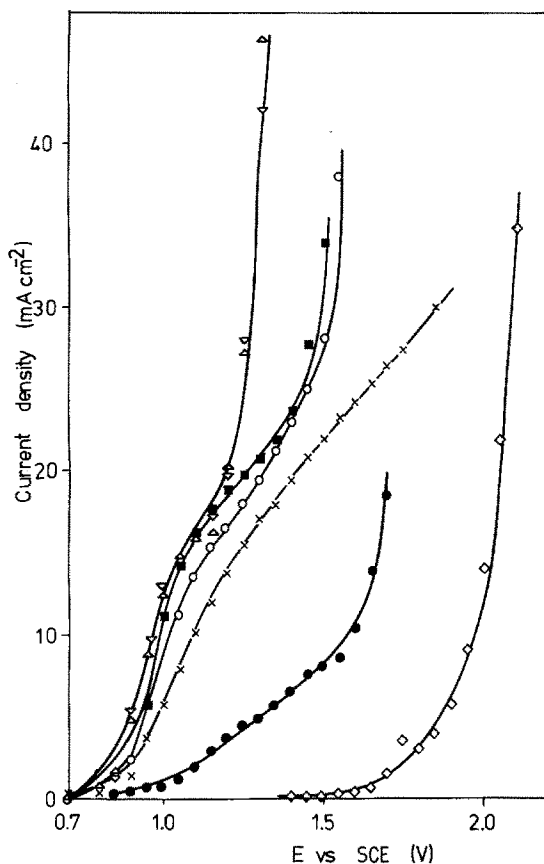
Fig. 1. Potential–current curves for bromine evolution in alkaline 1% NaBr solution for various electrode materials: ×, lead dioxide; ●, platinized titanium; △, ruthenated carbon; ○, graphite; ■, carbon; ▽, ruthenated titanium; ◇, glassy carbon.

with a Sinclair DM2 multimeter. The ruthenated titanium and ruthenated carbon electrodes were made by painting a solution of $RuCl_3$ (1 g) in isopropanol (8 cm^3) on to the substrate and oxidizing in air at $350°$ C for 10 minutes. Many experiments showed that the number of applications and different annealing times did not have a significant effect on electrode activity.

3. Results and discussion

The four most suitable substrates were found to be carbon, graphite, ruthenated carbon and ruthenated titanium, as shown in Fig. 1, since the other materials exhibited lower limiting currents, some at higher potentials. Carbon was chosen as the trickle-bed packing due to its wider potential
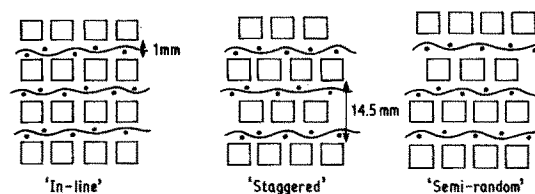

Fig. 2. Possible arrangements of Raschig rings in a trickle-bed reactor.

range at the limiting current compared to the ruthenated materials and its ready availability in the form of Raschig rings. The slight advantage of the ruthenated material with respect to its lower energy consumption was not considered important to the aims of this study.

It was discovered that the arrangement of Raschig rings within the reactor is important. Three basic arrangements are possible, namely 'in-line', 'staggered' and 'semi-random', as shown in Fig. 2. The 'in-line' array proved superior to the 'staggered' both in terms of space–time yield and energy consumption, as shown in the carpet plot (Fig. 3). The difference in reactor performance is probably explained by the more uniform
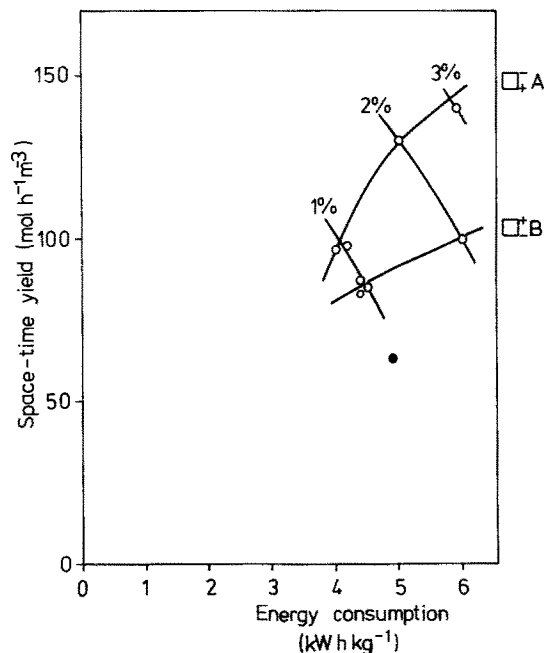

Fig. 3. Effects of polarity and sodium bromide concentration on space–time yield and energy consumption after 60 electrolyte recycles. ○, Electrolyte flow rate = 500 cm^3 min^{-1}, $V = 3.5$ V/layer, 'in-line' configuration. ●, 1% NaBr, $Q_L = 500$ cm^3 min^{-1}, $V = 3.5$ V/layer, 'staggered' configuration, polarity B.

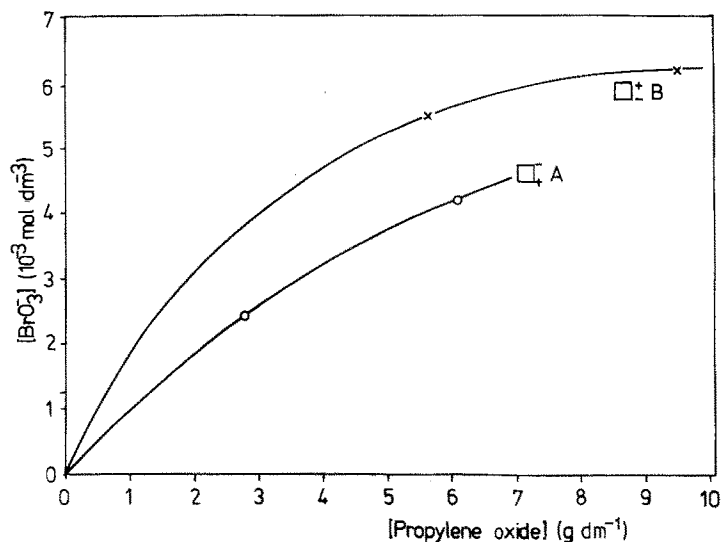Fig. 4. Effect of polarity on sodium bromate production as a function of propylene oxide concentration. 2% NaBr solution, 3.5 V/layer, $Q_L = 500$ cm^3 min^{-1}.

potential distribution possible down the length of the bed with the 'in-line' array and the sensitivity of the overall reaction to the contacting pattern [1]. Significantly, the very high current efficiencies reported by Ehdaie [1, 6] were obtained in highly ordered beds. The major source of iR drop is in the solution across the mesh separator and in the case of the 'in-line' array this drop is always across 1 mm gaps, whereas in the 'staggered' array the distance between adjacent electrode faces varies from 1 to 14.5 mm (Fig. 2). This effect would be more pronounced in trickle beds packed with thin-walled Raschig rings than in beds consisting of perforated carbon discs made by a mechanical process, which would be easier to align.

As the ratio of vessel diameter to Raschig ring diameter was only 5.2, rather than 10 or greater, which is desirable, the results quoted may not be typical of larger beds. Except at a few local sites when a Raschig ring was immediately adjacent to the wall, however, no evidence of a film flowing down the glass vessel wall was observed.

The effects of bed polarity and sodium bromide concentration are also shown in Fig. 3. Space–time yields and energy consumption were found to be better in beds when the top face of the Raschig ring layers was cathodic. This is surprising in the light of previous work [1, 6] which showed the opposite case to be true. This is due in part to the smaller amount of bromate by-product produced with polarity A, shown in

Fig. 4. Since the oxidation of bromide to bromate (either chemically or electrochemically) consumes at least three times as many electrons as the oxidation of bromide to bromine, the reduction of excess bromine actually minimizes the electrical loss. Of course, if the chemical consumption of bromine in the primary reaction is fast enough
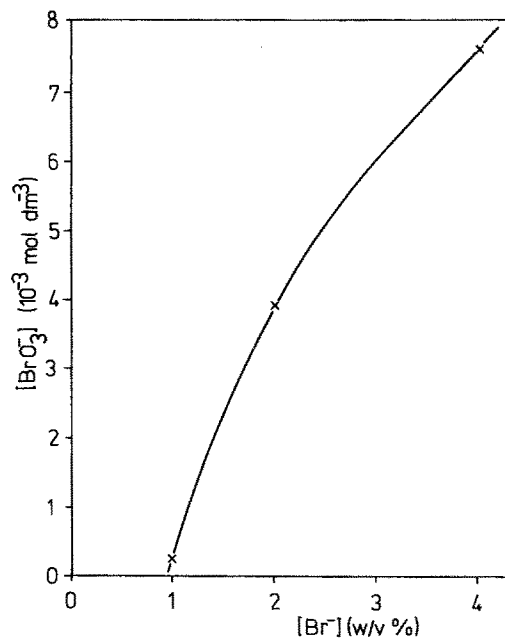
Fig. 5. Production of sodium bromate as a function of sodium bromide concentration for a propylene oxide concentration of 5.37 g dm^{-3}. Polarity A, 3.5 V/layer, $Q_L = 500$ cm^3 min^{-1}.
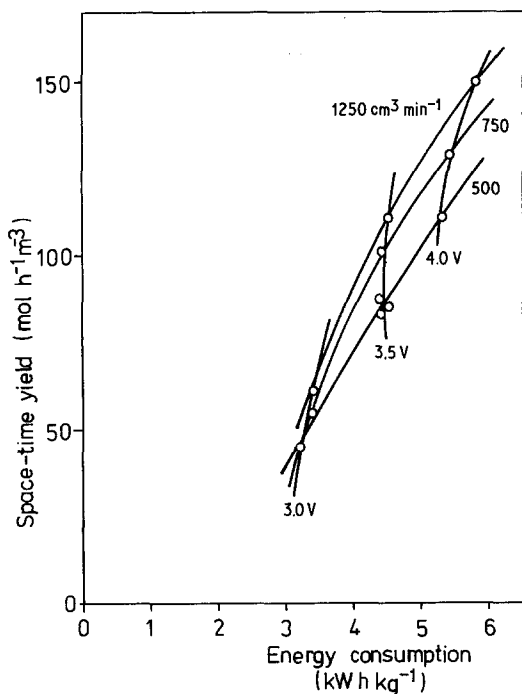
Fig. 6. Effect of electrolyte flow rate and cell voltage on space–time yield and energy consumption after 60 electrolyte recycles. $\circ$, 'In-line', 3.5 V/layer, $Q_L = 500$ cm^3 min^{-1}, 1% NaBr, polarity B.

Fig. 6 shows that it is possible to increase the space–time yield by increasing the applied voltage across the reactor and by increasing the electrolyte flow rate. Current efficiencies and energy consumptions after about 30 minutes ranged from 92% (3.2 kW h kg^{-1}) at 6.5 mA cm^{-2} to 62% (5.8 kW h kg^{-1}) at 29.8 mA cm^{-2}. The major reason for the increase in energy consumption with increasing applied potential was the increased rate of oxygen evolution at the higher potentials (Fig. 1). Increasing the electrolyte flow rate increases the energy consumption slightly due to the thickening of the electrolyte film, leading to an associated increase in non-Faradaic current.

At the upper end of the performance envelope, when the reactor was being driven hard at high potentials and current densities, the rate of propylene oxide production decreased with time and charge passed. This was due to the increased rate of bromine production at the higher current densities, which led to depletion of propylene in solution, thus causing the rate-determining step in the overall reaction to be the rate of propylene absorption into solution. The excess bromine so formed was then free to participate in the various loss reactions to bromate. This was shown to be the case by decreasing the number of Raschig rings to seven, thus reducing the number of cells in series from 15 to 8. The depletion of propylene in solution down the length of the smaller reactor was then not so great and so the system was in better balance, with the result that less bromate was produced for a given concentration of propylene oxide (Fig. 7).

The limitation to the performance of this reactor when driven hard is therefore the concen-

(see below), polarity B would be preferred, as it was in Ehdaie's case [1, 6].

More concentrated sodium bromide solutions increase the rate of propylene oxide production but with an accompanying increase in energy consumption due to the increase in non-Faradaic current associated with increasing solution conductivity. Also the rate of bromate formation is enhanced with increasing bromide concentration which leads to a loss in current efficiency (Fig. 5).
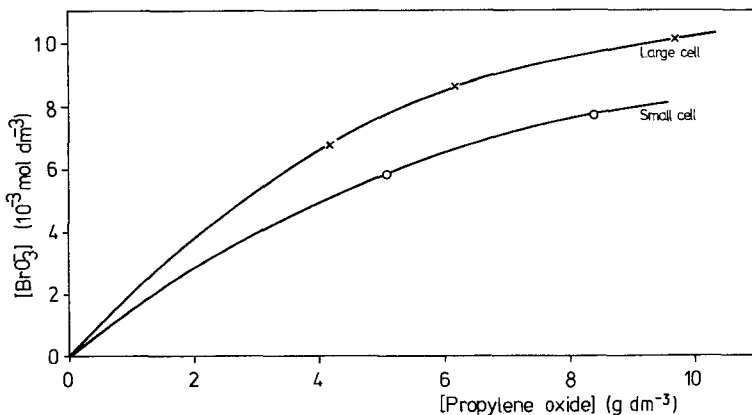

Fig. 7. Effect of length of cell on production of sodium bromate as a function of propylene oxide concentration.

tration of propylene in solution, which is determined by its rate of absorption which needs to be as high as possible. This can be achieved by operating with a pressurised system, as Goodridge *et al.* [2] have in the case of their flooded bed.

Increasing the space–time yield by decreasing the length of individual cell elements and increasing their cross-sectional areas will be reported elsewhere [7].

4. Conclusions

It has been shown that the performance of the bipolar trickle-bed reactor is strongly dependent upon cell polarity, i.e., the contacting pattern, which affects both the main and parasitic reactions, and the spatial arrangement of cell elements, which affects the potential distribution in the bed. The space–time yield for propylene oxide pro-

duction can be increased by at least a factor of three by using higher electrolyte flow rates and applied voltages than used by earlier workers [1, 5] but at the expense of energy consumption. However, when the reactor is driven hard electrochemically, the rate of absorption of propylene from the gas phase becomes a limitation.

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