B. Electrochem 4(2) February 1988, pp 149-151

FLOW REACTOR FOR THE ELECTRO-OXIDATION OF GLUCOSE

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[Received: 1987 July; Accepted: 1987 December]

The electro-oxidation of glucose to calcium gluconate has been investigated in an undivided bipolar flow reactor with narrow inter-electrode gaps. The process conditions such as current density, electrolyte concentration, temperature and rate of flow have been optimised and a detailed material balance has been carried out. A comparative evaluation of the flow reactor with rotating electrode cell has been made on the basis of energy consumption for the process.

Key words: Electro-oxidation of glucose, bipolar flow cell, calcium gluconate

INTRODUCTION

The electro-oxidation of glucose to calcium gluconate (CaGl) in laboratory and semicommercial scales has already been investigated exhaustively by a number of workers [1-3]. The basic aspects of the indirect oxidation have been studied and oxidation of bromide ions was reported to be the potential determining reaction [4,5]. The electro-oxidation of glucose using rotating graphite anode has been extensively studied and the attainment of high current densities with high current and chemical yields and low bromide losses has been reported [6-8]. The process conditions have been optimised and detailed material balance studies have been carried out [9]. A 500 ampere cell was designed and operated using the rotating electrode technique and the process has been commercialised. The operating cell voltage in the 500 ampere cell was 9-11 volts and the power consumption for electrolysis was of the order of 2.4 - 2.6 kwh/kg of calcium gluconate [10].

The present studies have been carried out in an undivided flow reactor with narrow inter-electrode gaps to optimise the conditions of flow electrolysis for maximising product yield and minimising bromide loss. The study also covers a comparative evaluation of the designs of bipolar flow cell (BFC) and rotating electrode cell (REC) on the basis of energy consumption.

EXPERIMENTAL

The BFC used in the present studies comprised of a stack of graphite disc electrodes packed inside a PVC housing, as shown in Fig. 1. The electrical connection was given to the two end electrodes in the stack were separated by insulating spacers suitably positioned and the interelectrode gap was 1.0 to 2.0 mm. The electrolyte was circulated from bottom to top and flowed through the opening provided on the electrodes.

The flow reactor was operated in the batch recycle mode with total recirculation of electrolyte. All chemicals were of technical grade. The electrolyte was prepared in a jacketed vessel and circulated through the flow reactor by a centrifugal pump. The flow rate was measured by means of a rotameter. The individual elements in the Flow Reactor System were connected by rubber tubing. The DC power supply was provided by a rectifier [0-75V-25A].

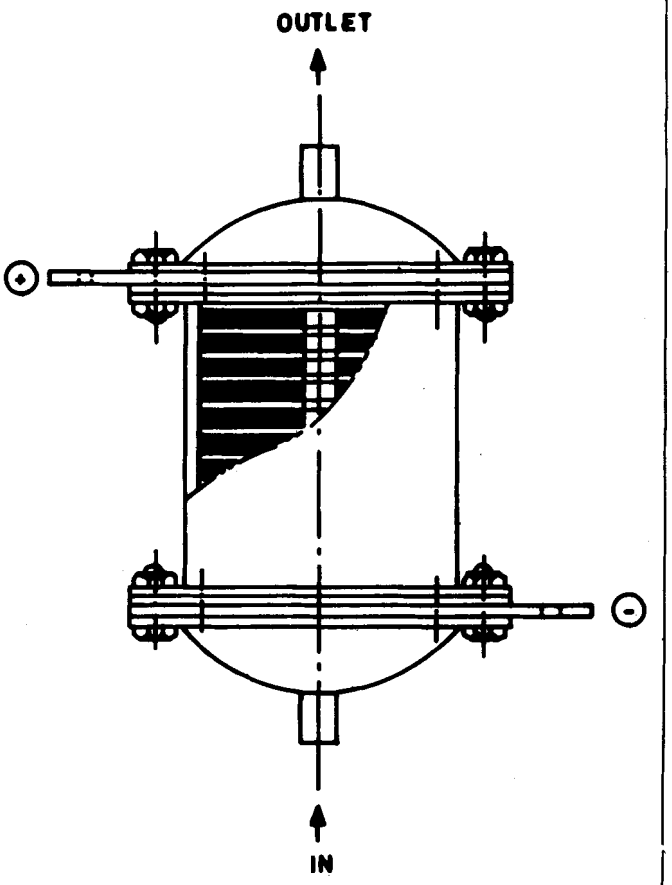

Fig. 1: Bipolar flow cell

The electrolysis was conducted for theoretical time based on 2F per mole of glucose charged. The build up of calcium gluconate was estimated by periodical chemical analysis of calcium ion content in electrolyte. Current efficiency values were computed periodically based on the analysis of calcium content.

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RESULTS AND DISCUSSION

The flow reactor studies were conducted to examine the effect of flow rate and current density on current efficiency and bromide loss. For collecting data for process optimisation studies and also to make a comparative evaluation of the reactor performance with the REC the energy consumption was evaluated during the course of electrolysis under different flow conditions.

Effect of flow rate

The reaction rate in an electrochemical flow reactor is controlled by the electrolyte flow rate. The effect of flow rate on current efficiency and bromide loss was studied by conducting experiments at varying flow rates keeping current density constant. Typical results are indicated in Table I.

TABLE-I : Effect of flow rate on current efficiency and bromide loss at constant current density for the electro-oxidation of glucose

Volume of electrolyte: 15 litres; glucose: 3.0 kg, NaBr: 0.3 kg, $CaCO_3$: 1.2 kg; temperature: 307 - 313 K; C.D. 3.75 A dm^{-2}; theoretical time

No	Flow rate ($l.min^{-2}$)	CaGl formed (g)	NaBr at the end of electrolysis (g)	C.E (%)	Bromide loss (%)
1	7.5	2538	228	74.8	24
2	12.5	2576	236	75.9	21.3
3	25.0	2423	240	71.4	20
4	45.0	2464	218	72.6	27.3

It is seen that bromide loss is higher at very low as well as very high flow rates while the variation in current efficiency values are marginal at medium flow rate. Higher bromide losses at low flow rates may be attributed to ineffective mixing at the electrode surface while at very high flow rates it may be due to the loss of free bromine or formation of by-products [11].

Effect of current density

The effect of current density on current efficiency and bromide loss at constant flow rates is indicated in Table II. It is seen that current efficiency decreases and bromide loss increases with increasing current densities. The variation of energy consumption with flow rate at constant current density was computed during the course of electrolysis and the same is shown in Fig. 2. It is seen that the energy consumption increases sharply at high product concentration due to the depletion of glucose with consequent fall in current efficiency. Power consumption is high at low flow rates while the variation is not much at medium to high flow rates. Variation of energy consumption with current density is shown in Fig. 3. Here also power consumption increases towards the end of electrolysis i.e. at high product concentration. The variation is not pronounced while operating lower current densities. The

TABLE-II: Effect of current density on current efficiency and bromide loss for the electro-oxidation of glucose at constant flow rate

Flow rate: 25 $l.min^{-1}$; other conditions: Same as Table I

S. No	Current density (A. dm^{-2})	Current (A)	CaGl formed (g)	NaBr at the end of electrolysis (g)	C.E. (%)	Bromide loss (%)
1	2	8	2664	264	78.5	12
2	3	12	2609	261	76.9	13
3	3.75	15	2440	246	72	18
4	5	20	2308	234	68	22

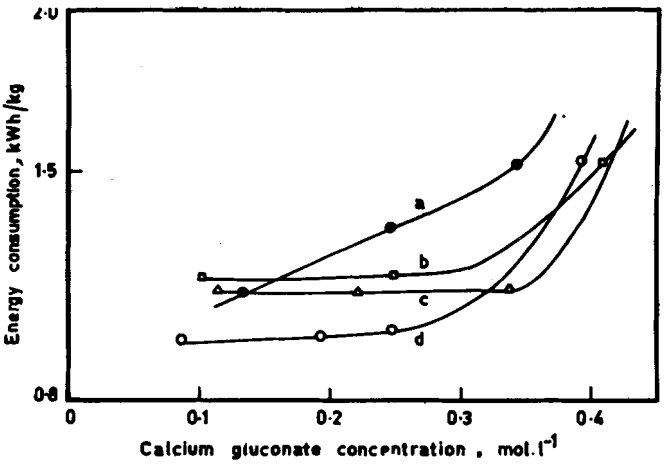

Fig. 2: Variation of energy consumption with calcium gluconate during electrolysis at different flow rates at constant current density. (3.75A.dm^{-2}): (a) / l.min^{-1} (b) 15 l.min^{-1} (c) 25 l.min^{-1} (d) 45 l.min^{-1}

electro-oxidation of glucose involves three steps viz. electrogeneration of bromine, chemical in situ oxidation of glucose with subsequent regeneration of bromide and the transport of bromide to the electrode surface for bromine regeneration. Current efficiency is high and bromide losses are low when these three rates are evenly balanced.

Optimisation of process parameters such as flow rate, current density will be done based on total minimum cost and will be reported separately.

Comparative evaluation of B F C and R E C

Rotating electrode cells of 500 ampere capacity are being used at present for commercial production of calcium gluconate in the

TABLE III: Comparative features of REC and BPC for the oxidation of glucose

No	Parameters	REC	BPC
1	Operating current density ($A.dm^{-2}$)	8-10	3-5
2	Cell voltage (V)	10-11	4-5 per gap
3	Current efficiency (%)	80-90	70-75
4	Energy consumption (kWh/kg)	2.6-2.8	1.2-1.4
5	Space time yield (kg/hr.l)	0.01	0.096
6	Electrode area per unit volume (cm^{-1})	0.04	0.7
7	Bromide loss (%)	15-25	20-30

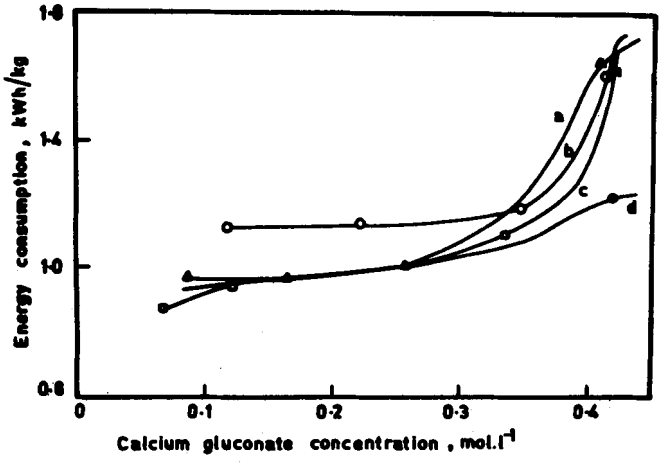

Fig. 3: Variation of energy consumption with calcium gluconate concentration during electrolysis at different current densities at constant flow rate (25 l.min^{-1}): (a) 3.75 A.dm^{-2} (b) 5 A.dm^{-2} (c) 3A.dm^{-2} (d) 2A.dm^{-2}

country. Comparative features of the above design and the present flow reactor design are tabulated in Table III based on the present studies for BFC and reported values for the REC [11].

It is seen from the data that the energy consumption for electrolysis is lower by nearly 50% with the use of BFC. This is due to the lower cell voltage of 4-5 volts per gap achieved due to narrow inter-electrode gaps. The lower values of operating current densities with the BFC are more than compensated by its very high ratio of electrode area per unit volume as compared to REC design. It is also seen from the Table that space time yield (kg/hr, litre of cell volume) which is a measure of the production capacity of the cell is nearly ten times higher with BFC thereby requiring less investment for the same production capacities. However the bromide loss is marginally higher with BFC and current efficiency values are also marginally lower. The investment cost of the BFC is likely to be much lower as compared to the REC on account of the simplicity of the design.

CONCLUSION

A narrow gap BFC design has been developed for the electro-oxidation of glucose to calcium gluconate. The effect of electrolysis parameters such as flow rate and current density on current efficiency, bromide loss and energy consumption has been studied. A comparative evaluation of the design with the earlier REC indicates that energy consumption is lower by 50% with the use of the new cell design. Space time yield values are also higher with the new cell design.

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