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Electro-oxidation of benzene in a fixed bed reactor

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A fixed bed electrochemical reactor was used in the laboratory to oxidize benzene to quinone. The reactor consisted of a 3 mm thick bed of 1 mm lead shot, 0.5 m long by 0.05 m wide, sandwiched between a lead feeder plate and an asbestos diaphragm which was compressed against a stainless steel cathode plate. A dispersion of benzene in aqueous sulphuric acid was passed through the reactor and the rates of production of quinone, hydroquinone, carbon dioxide, oxygen and hydrogen, together with the cell voltage and pressure drop, were obtained for a range of operating conditions.

Concentrations of quinone in the benzene product varied from 0.04 to 0.31 M and current efficiencies for quinone were in the range 22 to 55%. In a single pass of 1 M acid and benzene through the reactor at 25° C the quinone efficiency fell from 53% to 39% as the average superficial current density increased from 0.4 to 2.0 kA m^{-2}. At an average superficial current density of 2.0 kA m^{-2} the quinone efficiency decreased with an increase in process temperature (25 to 50° C), but increased with increases in acid concentration (1 to 4 M), acid flow (0.5 to 1.0 cm^3 s^{-1}), benzene flow (0.05 to 10 cm^3 s^{-1}) and co-current nitrogen gas flow (0 to 32 cm^3 s^{-1} at STP). Recycling the 4 M sulphuric acid at 25° C raised the concentration of quinone in the product benzene but decreased the net current efficiency for quinone. Corresponding changes were observed in the cell voltage and in the current efficiencies for hydroquinone, carbon dioxide and oxygen. The results are discussed in terms of the process stoichiometry, electrode kinetics and mass transfer for three-phase flow in a fixed bed reactor.

Nomenclature

A	Acid flow
a_l	Liquid/liquid specific interfacial area
a_s	Liquid/solid specific interfacial area
B	Benzene flow
d_{32}	Sauter mean drop diameter
d_p	Particle diameter
E	Current efficiency
F	Faraday number
I	Total current
i_L	Superficial transfer-limited current density
K	Liquid/liquid distribution coefficient
k_c	Liquid/liquid mass transfer coefficient in continuous phase
k_s	Liquid/solid mass transfer coefficient
L_c	Superficial liquid load – continuous phase
L_d	Superficial liquid load – disperse phase
Q_A	Quinone concentration in aqueous phase
V^0	Standard electrode potential
z	Number of electrons per equivalent

1. Introduction

The electro-oxidation of benzene dispersed in aqueous sulphuric acid has been examined by various workers as a source of *p*-benzoquinone. Much of this previous work has been summarized by Clarke *et al.* [1], together with the results of their own experimental study of the kinetics of electro-oxidation of benzene on anodized lead. Factors known to promote the current efficiency for quinone in this process are the correct choice of anode material, acid concentration, process temperature and (possibly) an oxidation catalyst, with a low current density and rapid mass transfer between benzene, acid and electrode [2].

These principles have been employed in patented systems and processes proposed for quinone production. A key feature of this technology is the use of an extended surface lead or lead dioxide anode, such as a mesh [3], finned plate [4] or crenellated plate [5] across which a

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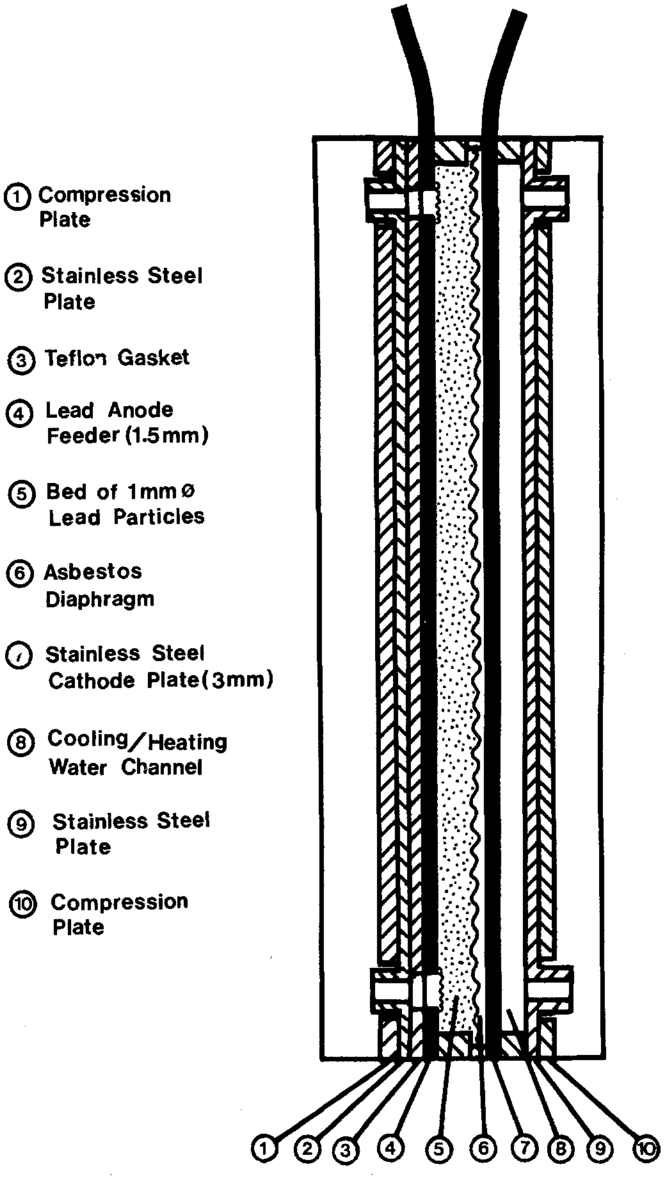

Fig. 1. Section of experimental fixed bed reactor (Ø = particle diameter).

dispersion of benzene in sulphuric acid flows at high velocity.

Fixed bed electrodes seem good candidates for benzene oxidation but they do not appear to have been studied in connection with this type of electro-organic process. The work reported below was done to establish the characteristics of a fixed bed electrochemical reactor with multiphase flow, employed in the oxidation of benzene in aqueous sulphuric acid to obtain *p*-benzoquinone.

2. Experimental apparatus and procedure

The reactor used in this study consisted of a sandwich of lead particles between a lead anode feeder plate, a woven asbestos diaphragm and a stainless steel cathode plate. The electrode bed was 500 mm high x 50 mm wide x 3 mm thick and it consisted of spherical lead particles 0.9 – 1.1 mm diameter. Fig. 1 shows the cross-section of the reactor and Fig. 2 is a flow diagram of the experimental apparatus.

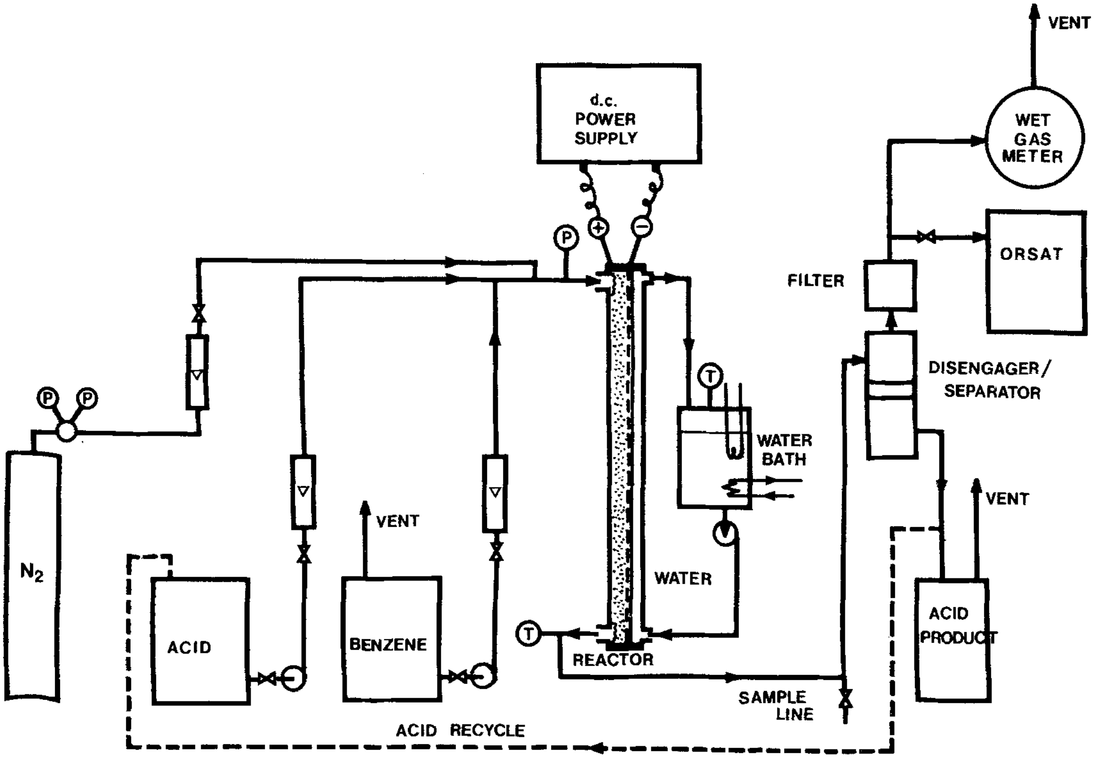

Fig. 2. Apparatus flow diagram.

In the experiments a flow of aqueous sulphuric acid at about 20° C was combined at a tee with a flow of benzene and the mixture passed downward through the anode bed. In some cases a co-current nitrogen flow was introduced with the acid/ benzene mixture at another tee just downstream of the acid/benzene mixing point.

Direct current was passed through the protruding ends of the electrode plates and the temperature of the exit stream was controlled by a countercurrent flow of thermostated water across the back of the cathode. The mixture leaving the cell was passed to a gas disengaging vessel from which the liquids overflowed to disposal or recycle and the gas was delivered to a wet test meter.

The combined liquid products of the reactor were sampled from a tee between the reactor and disengagement vessel and the product gas was sampled from the line between the disengagement vessel and wet test meter.

The efficiency of the process was found by collecting the product mixture for 1 min and measuring its total quinone content, as well as by separate analyses of both acid and benzene phases for quinone and hydroquinone.

The quinone content of the liquids was determined by iodimetry [6] and the hydroquinone by titration with ceric ammonium sulphate using diphenylamine indicator [6]. The other organic components of the liquid were not determined. Several blank runs (without benzene) established that the generation of other oxidizing species, such as persulphate, was not significant. Orsat analysis gave the carbon dioxide and oxygen content of the product gas and the nitrogen and hydrogen content was calculated through the mass balance.

The reagents were analytical grade sulphuric acid and benzene, commercial nitrogen (99 + $\%N_2$) and filtered tap water whose typical analysis is:

Component	*Concentration* ($mg\,l^{-1}$)
Ca	2
Mg	1
Fe	0.3
Cu	0.05
Conductivity	18 μmho cm^{-1}

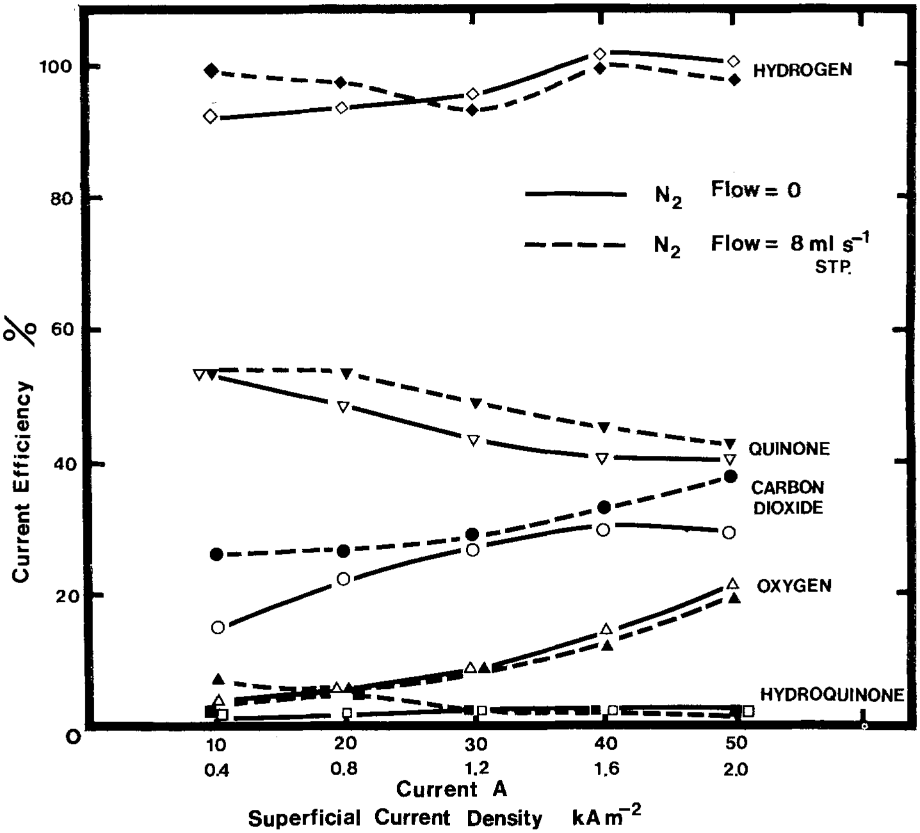

Fig. 3. Effects of current on current efficiencies for benzene oxidation in fixed bed anode. Conditions: single pass, 1 M H_2SO_4, 25° C. Acid flow = 0.92 $cm^3 s^{-1}$, benzene flow = 0.1 $cm^3 s^{-1}$.

The experiments were performed over a period of several days. On start up the reactor was run for about 20 min on acid alone at a superficial current density of 2000 A m^{-2} before introduction of the benzene. For each run the operating conditions then were held steady for about 30 min before sampling and two liquid samples were taken about 5 min apart and analysed to check for steady state of the process. The mean liquid residence time in the reactor for the lowest flows used was about 1 min.

When the reactor was shut down between runs it was purged with water, then with nitrogen and maintained sealed from the air with the power supply disconnected.

3. Results

3.1. *Current density and nitrogen flow*

Fig. 3 shows the current efficiencies for quinone, carbon dioxide, oxygen, hydroquinone and hydrogen obtained from a series of single pass runs at 25° C with 1 M H_2SO_4. The current efficiencies were calculated, respectively, from the stoichiometry of Equations 1, 3, 5, 7 and 8 which are given in Section 4. In these runs the acid and benzene product flows were fixed at 0.92 and 0.1 $cm^3 s^{-1}$, respectively, and the measurements made for nitrogen flows of 0 and 8.3 $cm^3 s^{-1}$ over a range of superficial current densities from 0.4 to 2.0 kA m^{-2}. To maintain the product benzene flow at the higher gas load, the feed benzene flow was increased to compensate the increased rate of benzene evaporation in the reactor. The product gas flow was also corrected for its benzene content on the assumption that it was saturated with benzene at the temperature of the wet-gas meter.

For the same set of runs the concentrations of quinone and hydroquinone measured in the acid and benzene phases are shown in Table 1. These product solutions had a yellow-brown colour which became darker on standing.

Table 1. Concentrations of quinone and hydroquinone in product solutions. Conditions: as for Fig. 3

Current (A)	*Cell voltage*	*Acid flow* ($cm^3\ s^{-1}$)	*Feed nitrogen flow* ($cm^3\ s^{-1}$ STP)	*Product benzene flow* ($cm^3\ s^{-1}$)	*Quinone in benzene* (M ± 0.003)	*Quinone in acid* (M ± 0.003)	*Hydroquinone in benzene* (M)	*Hydroquinone in acid* (M ± 0.001)	*Feed pressure* (bar)
10	2.70	0.92	0	0.1	0.04	0.006	≃ 0	0.005	0.61
20	3.17	0.92	0	0.1	0.08	0.009	≃ 0	0.003	0.85
30	3.62	0.92	0	0.1	0.11	0.011	≃ 0	0.003	1.02
40	3.85	0.92	0	0.1	0.13	0.014	≃ 0	0.009	1.12
50	4.03	0.92	0	0.1	0.15	0.017	≃ 0	0.011	1.29
10	2.71	0.92	8.3	0.1	0.04	0.004	≃ 0	0.001	0.92
20	3.15	0.92	8.3	0.1	0.09	0.010	≃ 0	0.006	1.50
30	3.56	0.92	8.3	0.1	0.12	0.014	≃ 0	0.003	1.77
40	3.85	0.92	8.3	0.1	0.14	0.015	≃ 0	0.010	1.57
50	4.10	0.92	8.3	0.1	0.16	0.018	≃ 0	0.009	1.77

Table 2. Effects of acid, N_2 and benzene loads on current efficiencies and quinone production. Current = 50 A, exit temperature = 25° C, 1 M H_2SO_4, single pass flows

Acid flow ($cm^3\ s^{-1}$)	N_2 *flow* ($cm^3\ s^{-1}$)	*Benzene flow* ($cm^3\ s^{-1}$)	*Current efficiency (%)*				*Quinone concentration* (M)		*Cell voltage*	*Feed pressure* (bar)
			Quinone	CO_2	O_2	*Hydroquinone*	*Acid*	*Benzene*		
0.5	0	0.05	27 (± 3)	50 (± 3)	22 (± 1)	1 (± 0.5)	0.021 (± 0.003)	0.19 (± 0.01)	4.00	0.5
		0.10	27	44	23	1	0.016	0.14	4.06	0.7
	32	0.05	32	49	23	1	0.026	0.24	3.90	1.2
		0.10	30	48	21	1	0.020	0.16	4.06	1.2
1.0	0	0.05	34	37	21	2	0.018	0.16	3.99	1.2
		0.10	39	28	21	2	0.017	0.15	4.03	1.3
	32	0.05	37	43	19	2	0.017	0.17	3.86	2.0
		0.10	43	47	22	3	0.018	0.16	4.03	2.0

3.2. *Acid, benzene and nitrogen flows*

The results of a factorial experiment on the effects of the acid, benzene and nitrogen loads on the single pass process efficiencies are shown in Table 2. As in Fig. 3 the current efficiency measured for hydrogen is close to 100 in all of these runs.

3.3. *Acid concentration, temperature and nitrogen flow*

Table 3 summarizes the results of a factorial experiment on the effects of the feed acid concentration, reactor outlet temperature and nitrogen load on the process efficiency and product quinone concentrations. Again, the current efficiency for hydrogen measured in these runs was around 100%.

Here it was observed that the product solutions (particularly the acid phase) at 50° C were considerably darker than those at 25° C.

3.4. *Acid recycle*

The effect of recycling all the product acid to the reactor, with fresh benzene feed, is summarized in Table 4.

In the experiments with acid recycle, the product solutions became considerably darker than those from single-pass runs, a scum accumulated at the benzene/acid interface in the separator, a brown/black precipitate appeared in the recycling acid and the pressure drop through the reactor gradually increased. Owing to these problems the reactor had to be shut down after about 4 h continuous operation.

4. Discussion

The stoichiometry of the predominant processes which may occur in the reactor is summarized in Equations 1 – 8.

At the anode

$$\underset{\text{benzene}}{C_6H_6} + 2H_2O \xrightarrow{1.5\ V} \underset{\text{benzoquinone}}{C_6H_4O_2} + 6H^+ + 6e \qquad (1)$$

$$\underset{\text{benzoquinone}}{C_6H_4O_2} + 6H_2O \rightarrow \underset{\text{maleic acid}}{C_4H_4O_4} + 12H^+ + 2CO_2 + 12e \qquad (2)$$

$$\underset{\text{benzene}}{C_6H_6} + 8H_2O \rightarrow \underset{\text{maleic acid}}{C_4H_4O_4} + 18H^+ + 2CO_2 + 18e \qquad (3)$$

$$\underset{\text{maleic acid}}{C_4H_4O_4} + 4H_2O \rightarrow 12H^+ + 4CO_2 + 12e \qquad (4)$$

$$2H_2O \xrightarrow{1.23\ V} O_2 + 4H^+ + 4e \qquad (5)$$

$$\underset{\text{hydroquinone}}{C_6H_6O_2} \xrightarrow{0.70\ V} \underset{\text{benzoquinone}}{C_6H_4O_2} + 2H^+ + 2e \qquad (6)$$

At the cathode

$$2H^+ + 2e \xrightarrow{0.00\ V} H_2 \qquad (7)$$

$$\underset{\text{benzoquinone}}{C_6H_4O_2} + 2H^+ + 2e \xrightarrow{0.70\ V} \underset{\text{hydroquinone}}{C_6H_6O_2} \qquad (8)$$

There are probably other electrode reactions involving the oxidation and reduction of organic species, as well as homogeneous reactions such as the decomposition, sulphonation and polymerisation of quinone, hydroquinone or maleic acid [2], but these reactions are not elaborated in the literature.

4.1. *Effect of current density*

Quinone is generated in the anode in competition with carbon dioxide (or maleic acid) and oxygen, while it is converted to hydroquinone at the cathode. If the process follows the above stoichiometry, the sum of the current efficiences for quinone, carbon dioxide and hydroquinone should be 1.0. Over the 25 experimental runs this sum varies between 0.79 and 1.14 with a mean of 0.94 ± 0.04 to 95% confidence, which is significantly different from 1.0. Presumably there are other reactions occurring whose products are not determined, which account for up to about 20% of the current. The fraction of the current used to oxidize hydroquinone (Reaction 6) is not measurable directly, but the high efficiency of hydrogen generation at the cathode implies that only up to about 5% of the current can be used in shunting quinone between Reactions 6 and 8.

Since both pathways 1 + 2 and 1 + 3 give the same total current for quinone plus carbon dioxide these data do not indicate the predominant

Table 3. Effect of acid concentration, exit temperature and N_2 load on current efficiencies and quinone production. Current = 50 A, acid flow = 1 cm^3 s^{-1}, exit benzene flow = 0.05 cm^3 s^{-1} single pass

Acid concentration (M)	*Temperature* (° C)	*N_2 flow* (cm^3 s^{-1} STP)	*Current efficiency (%)*				*Quinone concentration (M)*		*Cell voltage*	*Feed pressure* (bar)
			Quinone	*CO_2*	*O_2*	*Hydroquinone*	*Acid*	*Benzene*		
1	25	0	34 (± 3)	37 (± 3)	21 (± 1)	2 (± 0.5)	0.18 (± 0.003)	0.16 (± 0.01)	4.00	0.5
		32	37	43	19	2	0.017	0.17	3.90	1.2
	50	0	30	47	13	3	0.015	0.14	3.80	0.9
		32	33	42	16	3	0.021	0.16	3.73	1.6
4	25	0	53	21	8	2	0.029	0.21	3.41	1.5
		32	55	29	10	2	0.034	0.26	3.44	2.2
	50	0	43	40	5	4	0.020	0.16	3.49	1.5
		32	49	26	9	4	0.028	0.17	3.30	2.3

Table 4. Effect of acid recycle on current efficiencies and quinone production. Current = 50 A, acid flow = 1 cm^3 s^{-1}, exit benzene flow = 0.05 cm^3 s^{-1}, 4 M H_2SO_4, temperature = 25° C

Acid flow	*N_2 flow* (cm^3 s^{-1} STP)	*Current efficiency (%)*			*Quinone concentration* (M)		*Hydroquinone in acid* (M)	*Cell voltage*	*Feed pressure* (bar)
		Quinone	*CO_2*	*O_2*	*Acid*	*Benzene*			
Single pass	0	53 (± 3)	21 (± 3)	8 (± 1)	0.029 (± 0.003)	0.21 (± 0.01)	0.005 (± 0.001)	3.41	1.5
	32	55	29	10	0.034	0.26	0.005	3.44	2.2
100% recycle	0	22	68	15	0.040	0.29	0.009	3.22	1.8
	32	24	86	4	0.049	0.31	0.012	3.25	1.7

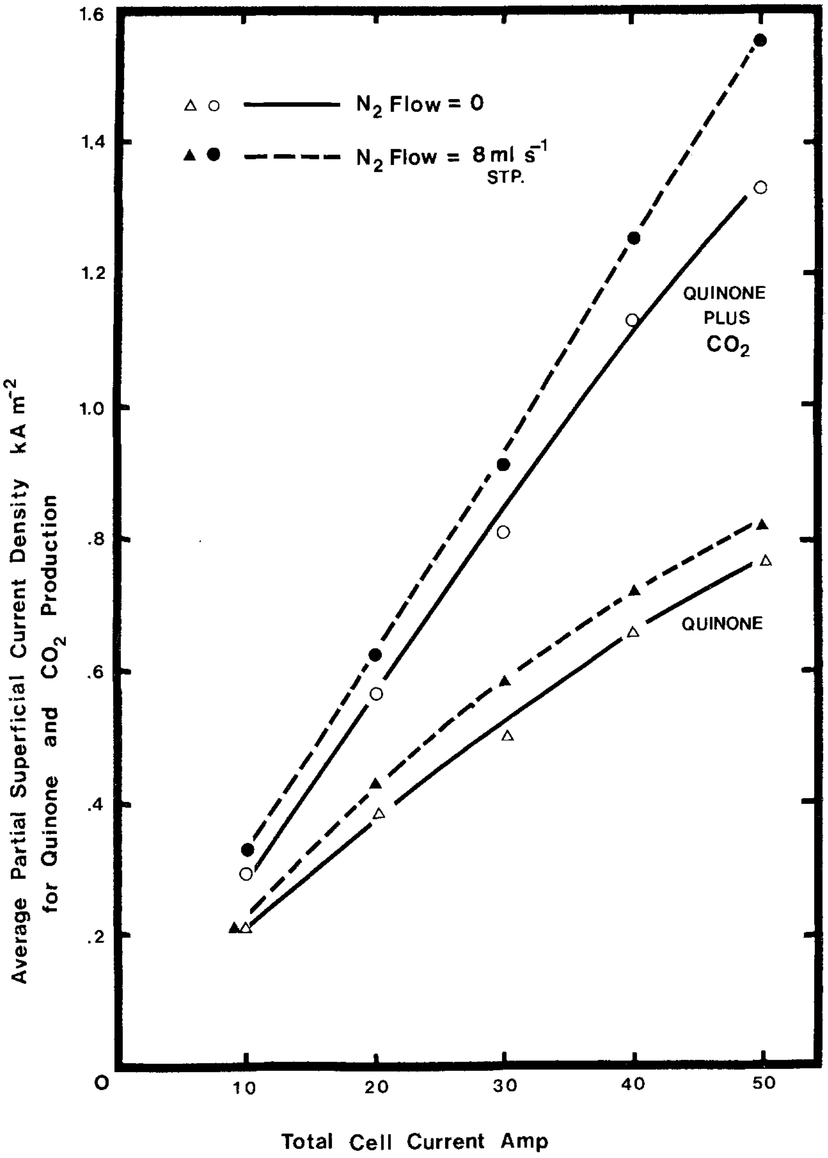

Fig. 4. Partial currents for quinone and carbon dioxide generation in fixed bed anode. Conditions: as for Fig. 3.

source of carbon dioxide. However, the trend of increasing the sum of the anode current efficiencies with increasing current density (in Fig. 3) may correspond to a shift in the distribution of anode reactions to favour reactions such as Reaction 4.

The curves of partial current efficiencies in Fig. 4 show the expected trend with increasing current density and agree qualitatively with the data of Clarke *et al.* [1].

Quantitatively, the difference between these results and those of Clarke *et al.* could be due to the effect of the electrode potential distribution in the fixed-bed anode. For example, a current of 50 A to the fixed-bed, which corresponds to an average real current density on the particle surfaces of 185 A m^{-2} would cause an average potential gradient through the anode bed in 1 M H_2SO_4 of about 0.1 V mm^{-1} with consequent drastic variations in the local current efficiencies through the bed.

Further the benzoquinone and maleic acid concentration (not stated in Clarke's work) and the conditions of mass transfer may also contribute to the different current efficiencies observed between these results and those of Clarke *et al.*

The high current efficiency for hydrogen and low efficiency for hydroquinone indicate that the diaphragm is performing its function of suppressing the convection of quinone in the aqueous phase to the cathode. Over the 25 runs performed in this work the sum of the current efficiencies for hydrogen and hydroquinone varied from 0.88 to 1.16, with a mean of 0.99 ± 0.05 to 95% confidence.

4.2. *Effects of other variables*

The results of the analysis of variance of the data in Tables 2 and 3 are summarized in Table 5. Table 5 shows those single variables and linear interactions which the analysis indicates to have a significant effect on the process efficiency in the range of the experiments. The effect is considered significant if the statistical significance level is 0.05 or lower.

4.2.1. Acid concentration and temperature. With respect to acid concentration and process temperature these results parallel those of previous investigators. The solubility of benzene in sulphuric acid at 25° C falls from about 1.5×10^{-2} M to 0.9×10^{-2} M as the acid concentration rises from 1 to 4 M [7]. Despite this there is a positive effect of the increased acid concentration on the current efficiency for quinone. This effect may be partly due to the higher electrolyte conductivity which allows a more uniform potential distribution through the anode bed. The corresponding decreases in current efficiency for carbon dioxide and for oxygen would also be a consequence of the improved potential distribution.

An increase in process temperature also raises the electrolyte conductivity, but is not sufficient to balance the negative effects of temperature upon the decomposition and/or secondary oxidation of quinone, the latter being evidenced by the increased current efficiency for carbon dioxide. The strong effect of temperature on quinone efficiency is an indication that the secondary electro-oxidation of quinone proceeds under activation control.

4.2.2. Acid, benzene and nitrogen flow. The influence of the fluid flows on process efficiency can be resolved in terms of effects on mass transfer and the extent of secondary electrode reactions.

For a given current efficiency the equilibrium concentration of quinone in the acid leaving the reactor is given by,

$$Q_A = \frac{zFEI}{A + KB} \tag{9}$$

At 25° C the value of K, the distribution coefficient of quinone between benzene and

Table 5. Significance of the effects of operating variables on process efficiencies, quinone production and cell voltage

Independent variable		*Dependent variable*						
		Current efficiency				*Quinone concentration*		*Cell voltage*
		Quinone	*CO_2*	*O_2*	*Hydroquinone*	*Acid*	*Benzene*	
Acid concentration	(*C*)	* (+)	* (–)	* (–)	* (+)	* (+)	* (+)	* (–)
Temperature	(*T*)	* (–)	* (+)		* (+)		* (–)	* (–)
Acid flow	(*A*)	* (+)	* (–)		* (+)	* (–)		* (–)
Benzene flow	(*B*)	* (+)				* (–)	* (–)	* (+)
Nitrogen flow	(*G*)	* (+)	* (+)					* (–)
$C \times T$					*			
$C \times G$								
$T \times G$			*					
$A \times B$		*				*	*	
$A \times G$								
$B \times G$								*

* Statistical significance level = 0.05 or lower. (+), (–) Indicate that increasing the independent variable (increases) (decreases) the dependent variable.

1 M H_2SO_4, is determined from the experimental data as 8.9 ± 0.4 M/M. Thus an increase in either the acid or benzene flow lowers the concentration of quinone in the acid phase and should suppress its secondary oxidation and reduction. The fall in current efficiency for carbon dioxide with increased acid flow may be a reflection of this effect.

The data of Clarke *et al.* [1] indicates that at the superficial current densities used here, the current efficiencies in the process are influenced by the capacity of the system for benzene transport to the anode surface.

The capacity for benzene transport in the fixed bed reactor depends upon the mass-transfer coefficients and areas of the liquid/liquid and liquid/solid interfaces. These parameters are determined by the acid, benzene and gas loads on the anode bed. The mass-transfer coefficient between acid and anode may also be influenced by evolution of gas (CO_2 and O_2) on the anode surface.

Rates of mass transfer between two immiscible liquids in co-current three-phase flow through fixed beds are not documented in the literature. The capacity coefficient for transfer of isobutanol to water in two-phase (liquid/liquid) co-current flow through a fixed bed of 3 mm glass spheres is correlated by Leacock and Churchill [8] as,

$$k_c a_1 = 3.2 \times 10^{-3} (L_c L_d)^{0.75} \qquad (10)$$

and subsequent work by Duffy and Kadlec [9] gives a relation between the Sauter mean dispersed phase drop diameter and packing particle diameter in which,

$$d_{32} \propto d_p^{0.2} \qquad (11)$$

Leacock and Churchill reported $k_c a_1$ values up to 0.9 s^{-1} but for the highest flow used in the electrochemical reactor, Equations 10 and 11 predict $k_c a_1 = 1.2 \times 10^{-2} \text{ s}^{-1}$. Assuming the whole bed to be electroactive, this gives a liquid/liquid transfer-limited superficial current density for benzene oxidation in the fixed bed anode of 0.31 kA m^{-2}. This result is low since the transfer-limited current for benzene oxidation must be at least equal to the partial current for quinone production, which is shown in Fig. 4 up to 0.78 kA m^{-2}. In fact, the current density for benzene oxidation may be up to 1.5 kA m^{-2} if the rate of carbon dioxide generation is taken into account.

Co-current flow of inert gas in fixed bed reactors is known to increase liquid to solid mass transfer coefficients [10]. In the case of three-phase flow (gas/benzene/acid) through fixed beds the flow of gas also probably enhances liquid to liquid mass transfer.

Observations in a transparent apparatus revealed a considerable improvement in the dispersion of the organic phase when co-current gas was introduced with the flow of two immiscible liquids through a fixed bed of glass beads. No information on such a system is contained in the literature but liquid/liquid extraction in air-agitated open and baffled columns has been examined by Fernandes and Sharma [11], who passed air upwards, countercurrent to a flow of *n*-hexyl formate and 1 M sodium sulphate in water. They found that with a phase volume ratio of 0.06 (organic/aqueous) the capacity coefficient for liquid/liquid mass transfer in the open column rose from $2.7 \times 10^{-2} \text{ s}^{-1}$ to $5.1 \times 10^{-2} \text{ s}^{-1}$ as the superficial air velocity increased from 0.05 to 0.3 m s^{-1}. The liquid/liquid interfacial area was also increased by raising the phase volume ratio and by the presence of horizontal baffles in the column. In the present case the rate of liquid to liquid transfer of benzene and of quinone must be enhanced by the flow of carbon dioxide, oxygen and nitrogen in the anode bed, but the magnitude of this effect cannot be calculated from existing information.

Rates of mass transfer from liquid to solid in trickle beds are better served by established data and can be predicted from correlations such as those summarized in a review by Charpentier [12]. For the case of an acid phase saturated with benzene and uniform activity for benzene oxidation through the anode, the liquid to solid mass transfer-limited superficial current densities for benzene, with co-current gas flow, have been estimated by the method outlined in [13] and are summarized in Table 6. Table 6 also shows estimates of the liquid hold-up and voltage drop in the electrolyte across the bed in the direction of current for a superficial current density of 2 kA m^{-2}, where the real current density on the particle surface is assumed uniform throughout the bed.

If the carbon dioxide formed in the process comes predominantly from Reactions 2 or 3 the sum of the partial currents for generation of quinone and of carbon dioxide is equivalent to the

Table 6. Liquid to solid mass transfer for benzene oxidation in trickle-bed reactor. Current = 50 A, exit temperature = 25° C, 1 M H_2SO_4, single pass flows

Fluid flow				*Active bed thickness (assumed)*	*Experimental partial superficial CD for quinone plus carbon dioxide*	*Predicted limiting superficial CD for benzene oxidation*		*Liquid hold up*	*ΔV across anode bed at 2 kA m^{-2}*
Acid ($cm^3 s^{-1}$)	*Gas* ($cm^3 s^{-1}$ STP)		*Benzene* ($cm^3 s^{-1}$)						
	In	*Out*		(mm)	(kA m^{-2})	$k_s a_s$ (s^{-1})	i_L (kA m^{-2})		(V)
0.5	0	8	0.1	3	1,42	0.18	4.9	0.48	0.30
	32	40	0.1	3	1.56	0.25	6.3	0.36	0.41
1.0	0	8	0.1	3	1.34	0.21	5.3	0.60	0.23
	32	40	0.1	3	1.80	0.27	7.4	0.46	0.31

rate of benzene oxidation. A plot of the sum of partial currents for quinone and carbon dioxide in Fig. 4 indicates that for superficial current densities up to 2 kA m^{-2} the rate of benzene oxidation was not limited by mass transfer in this reactor. However, the numbers in Table 6 show the average rate of benzene oxidation approaches 30% of the liquid to solid mass transfer-limited value, while the potential drop across the bed is sufficient to give at least a 50-fold variation in real current density on the electrode particles under pure activation control (assuming an electrochemical charge transfer coefficient of 0.5). In the anode bed near the counter electrode the mass transfer constraint promotes oxidation of quinone over its generation. This effect suppresses the current efficiency for quinone production and is particularly injurious in view of the conclusion of Clarke *et al.* [1] that the electro-oxidation of benzene to quinone is second order with respect to benzene concentration. Thus the positive effect of co-current gas flow on quinone efficiency can be rationalized in terms of the corresponding enhancement of benzene transfer to the anode surface. This is reflected in the fact that co-current nitrogen flow actually *lowers* the cell resistance.

There are no useful data in the literature on the kinetics of electro-oxidation of *p*-benzoquinone. However, it appears from the present results that quinone oxidation is dominated by electrode kinetics, since the concentration of quinone in the acid product easily exceeds the saturation concentration of benzene in the acid.

4.2.3. Acid recycle. Table 4 shows that acid recycle causes large losses in the current efficiency for quinone production. The immediate effect of recycling acid is to raise the concentrations of quinone and hydroquinone in the acid in the reactor. This results in increased losses of current efficiency in Reactions 2, 6 and 8, the former being clearly indicated by the increased current efficiency for carbon dioxide with acid recycle.

The depolarizing effect of quinone and hydroquinone on the electrodes is also seen in the decrease of cell voltage with acid recycle. Acid recycle would be essential to any practical application of this process for the production of benzoquinone. The negative effects of acid recycle could be reduced by increasing the benzene/acid ratio to give a more dilute product stream but the problems caused by acid recycle would be a major obstacle to the commercial use of this process.

5. Conclusion

The fixed bed reactor is a useful device for electro-organic processing. Together with high specific electrode area, the flow of organic and aqueous phases through a fixed bed provides effective mass transfer, which is enhanced by a co-current flow of inert gas.

In the case of electro-oxidation of benzene, dispersed in aqueous sulphuric acid, on a fixed bed of 1 mm lead particles, the current efficiency for quinone production depended on superficial current density, temperature, acid concentration, acid flow and benzene flow and was increased by a co-current flow of nitrogen gas. The current efficiency for quinone was probably determined by a balance between the rates of oxidation of benzene to quinone and of quinone to products such as maleic acid and carbon dioxide. At the highest average superficial current density of 2 kA m^{-2} the rate of benzene oxidation was strongly influenced by the rate of benzene transfer to the anode surface. The oxidation of quinone was apparently activation controlled, with the quinone concentration in the aqueous phase governed by the acid to benzene ratio in the reactor feed.

Recycling acid to the reactor lowered the current efficiency for quinone and caused operating problems which would compromise the commercial development of this process.

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