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Recycle reactor models for complex electrochemical/chemical reaction systems

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The performance of complex electrochemical reaction sequences in recycle plug flow reactors is mathematically modelled. The reactions include successive electron transfers (EE reactions), chemical reaction interposed between successive electron transfers (ECE reactions), simultaneous electron transfers and simultaneous electron transfer and chemical reaction. Both potentiostatic and galvanostatic operations are considered and the effects of important parameters such as mass transport coefficient, recycle ratio and chemical reaction rate in the recycle loop are highlighted. This is done by considering two important electro-organic synthesis reactions, the production of *p*-aminophenol and the reduction of oxalic acid to glyoxylic acid.

Nomenclature

a	activity factor
C_{ji}	concentration of species j at reactor inlet
C_{j}	bulk concentration of species j
$C_{\mathrm{j}}^{\mathrm{S}}$	surface concentration of species j
$C_{\mathrm{j}}^{\mathrm{e}}$	concentration of component j returned to reactor inlet stream
$C_{\mathrm{j}\rho}$	concentration from reactor outlet
C_{je}	equilibrium concentration
E	electrode potential
F	Faraday number
i_{n}	partial current density of step n
i_{T}	total current density
k	deactivation rate constant
$k_{\mathrm{f}}n$	forward electrochemical rate constant of step n
$k_{\mathrm{b}}n$	backward electrochemical rate constant of step n
k_{f}	forward chemical reaction rate constant
k_{r}	reverse chemical reaction rate constant
k_{Lj}	mass transfer coefficient for species j
k_{a}	forward adsorption rate constant
k_{d}	reverse adsorption rate constant
L	reactor length
r	recycle ratio
t	reaction time
u	velocity
Q	flow rate
x	reactor dimension
α_n	constant describing potential dependency of reverse reaction rate constant
β_n	constant describing potential dependency of forward reaction rate constant
Γ_{j}	surface concentration of adsorbed species j

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σ electrode area per unit length
τ residence time of fluid in recycle loop

1. Introduction

The majority of continuous industrial electrolytic reactors, unlike their chemical and catalytic counterparts, operate in a mode of operation where the product steam from the reactor is recycled back to the reactor inlet to achieve an overall high conversion of reactant even though the conversion per pass is small. When flow characteristics in the reactor approach plug flow this system is referred to as a 'plug flow recycle reactor'. This type of reactor has been studied to some extent in chemical reaction engineering [1], but in electrosynthesis little work has appeared in the literature except for simple reactions [2]. The purpose of this communication is to present fundamental mathematical models which describe steady-state recycle behaviour for a number of reaction sequences. Series reactions with chemical reaction and adsorption steps are considered for both potentiostatic and galvanostatic operations. In the latter case, the analysis is restricted to systems with simplified rate forms to allow solutions to be obtained in useful analytical forms.

Parallel reactions and a series parallel reaction sequence involving electrochemical and chemical reactions are also considered. The latter is used to represent the production of *p*-aminophenol in which the importance of mass transport in the reactor and chemical reaction in the recycle loop are illustrated.

2. Mathematical analysis

2.1. *Reactor model and assumptions*

The model system is that of a plug flow recycle reactor shown in Fig. 1. In this system a fraction of the reactor product stream is recycled back to the reactor inlet to achieve a high overall conversion of reactant. The model, however, can also be applied to the following types of operation, single-pass plug flow (zero recycle), continuous stirred tank (infinite recycle), batch and recycle batch (operating in real time and not residence time). It is assumed that electrode potential variation in the reactor is negligible because of the low conversions per pass typical of recycle operation.

The other main assumptions made in the analysis are as follows, other assumptions will be noted where applicable.

(a) reactor operation is in the steady-state and hence start-up criteria have been satisfied
(b) constant volume conditions prevail
(c) isothermal operation
(d) ideal flow characteristics either plug flow or well-mixed
(e) migration effects are negligible and only a single electrode is considered in the reactor
(f) mass transport is represented by a mass transfer coefficient for each species
(g) reactions are first order and electrochemical kinetics are of the Butler–Volmer type

2.2. *The ECE reaction: potentiostatic operation*

For an ECE type of reaction mechanism

$$A + n_1 e \underset{k_{b1}}{\overset{k_{f1}}{\rightleftharpoons}} B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + n_1 e \underset{k_{b2}}{\overset{k_{f2}}{\rightleftharpoons}} D$$

the currents associated with the two electrochemical steps can be written, following Haines, McConvey and Scott [3], as:

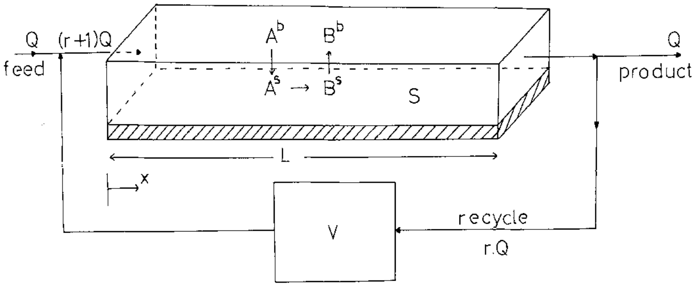


Fig. 1. Plug flow recycle reactor. S: electrode surface, V: recycle holding tank. A and B represent reactant and product in bulk (b) and on the surface (s).

$$\frac{i_1}{n_1F} = k_f1C_A^S - k_b1C_B^S \tag{1}$$

$$\frac{i_1}{n_1F} = k_{LA}(C_A - C_A^S) \tag{2}$$

$$\frac{i_2}{n_2F} = k_f2C_C^S - k_b2C_D^S \tag{3}$$

$$\frac{i_2}{n_2F} = k_{LD}(C_D^S - C_D) \tag{4}$$

where C_j and C_j^S refer to species concentration in the bulk and at the surface, and k_{Lj} the corresponding mass transfer coefficients. The rate constants can be defined by expressions of the type:

$$k_f1 = k_1 \exp(\beta_1 E) \qquad k_b1 = k_1 \exp(-\alpha_1 E)$$

where k_1, β_1, α_1, etc. in the simplest situations merely represent experimentally determined parameters.

Combining Equations 1–3 with Equation 4 to eliminate surface concentrations gives

$$\frac{i_1}{n_1F} = \frac{k_f1C_A - k_b1C_B}{1 + (k_f1/k_{LA}) + (k_b1/k_{LB})} \tag{5}$$

$$\frac{i_2}{n_2F} = \frac{k_f2C_C - k_b2C_D}{1 + (k_f2/k_{LC}) + (k_b2/k_{LD})} \tag{6}$$

The equations for the model reactor system with recycle ratio r, volumetric flow rate Q, velocity u and electrode area: unit length σ are

$$\frac{dC_A}{dx} = \frac{-\sigma}{(r+1)Q}\frac{i_1}{n_1F} \tag{7}$$

$$\frac{dC_B}{dx} = \frac{\sigma}{(r+1)Q}\frac{i_1}{n_1F} - \frac{(k_fC_B - k_rC_C)}{(r+1)u} \tag{8}$$

$$\frac{dC_C}{dx} = \frac{(k_fC_B - k_rC_C)}{(r+1)u} - \frac{\sigma}{(r+1)Q}\frac{i_2}{n_2F} \tag{9}$$

$$\frac{dC_D}{dx} = \frac{\sigma}{(r+1)Q}\frac{i_2}{n_2F} \tag{10}$$

Substituting Equations 5 and 6, the above simultaneous first order model equations can be written in matrix form as

$$\begin{bmatrix} D+p_1 & -p_2 & 0 & 0 \\ -p_1 & D+p_2+p_3 & p_4 & 0 \\ 0 & -p_3 & D+p_4+p_5 & -p_6 \\ 0 & 0 & -p_5 & D+p_6 \end{bmatrix} \begin{bmatrix} C_{\mathrm{A}} \\ C_{\mathrm{B}} \\ C_{\mathrm{C}} \\ C_{\mathrm{D}} \end{bmatrix} = 0 \tag{11}$$

where $p_1 = k_{\mathrm{f}}1\sigma/(r+1)\mathrm{Q}Y1, p_2 = k_{\mathrm{b}}1\sigma/(r+1)\mathrm{Q}Y1, p_3 = k_{\mathrm{f}}/(r+1)u, p_4 = k_{\mathrm{r}}/(r+1)u, p_5 = k_{\mathrm{f}}2\sigma/(r+1)\mathrm{Q}Y2$ and $p_6 = k_{\mathrm{b}}2\sigma/(r+1)\mathrm{Q}Y2$, and where $Y2 = 1 + (k_{\mathrm{f}}2/k_{\mathrm{LC}}) + (k_{\mathrm{b}}2/k_{\mathrm{LD}})$ and $Y1 = 1 + (k_{\mathrm{f}}1/k_{\mathrm{LA}}) + (k_{\mathrm{b}}1/k_{\mathrm{LB}})$. The reaction scheme involves a homogeneous chemical reaction taking place mainly in the bulk solution and, therefore, further reaction could take place in the recycle loop. The conversion of the intermediate reaction B to C in this loop will depend on the flow characteristics, i.e. whether plug flow exists or a holding tank (CSTR) is in the line. The concentrations of B and C returned to the inlet and mixed with fresh feed are given by:

(a) for plug flow,

$$\frac{C_{\mathrm{B}}^{\mathrm{e}} - C_{\mathrm{B}\rho}}{C_{\mathrm{B}} - C_{\mathrm{B}\rho}} = 1 - \exp\left[\frac{-k_{\mathrm{f}}\tau(M+1)}{M+1-(C_{\mathrm{Be}}/C_{\mathrm{A0}})}\right] \tag{12}$$

$$C_{\mathrm{C}}^{\mathrm{e}} = C_{\mathrm{B}\rho} + C_{\mathrm{C}\rho} - C_{\mathrm{B}}^{\mathrm{e}} \tag{13}$$

where $M = C_{\mathrm{C}}^{\mathrm{e}}/C_{\mathrm{B}}^{\mathrm{e}}$. $C_{\mathrm{j}}^{\mathrm{e}}, C_{\mathrm{j}\rho}$ and C_{je} are concentrations of component j which are, respectively, returned to the reactor inlet stream, from the reactor outlet and the equilibrium concentration and τ is the residence time of fluid in the recycle loop

(b) for CSTR,

$$C_{\mathrm{B}}^{\mathrm{e}} = \frac{C_{\mathrm{B}\rho}(1+\tau k_{\mathrm{r}}) + \tau k_{\mathrm{r}} C_{\mathrm{C}\rho}}{(1+\tau k_{\mathrm{f}} + \tau k_{\mathrm{r}})} \tag{14}$$

The residence time of fluid in the connecting pipework may also be important but it is assumed negligible in this instance.

The residence time of the fluid in the recycle stream may be sufficiently high for equilibrium to be achieved, i.e. $C_{\mathrm{B}}^{\mathrm{e}}/C_{\mathrm{C}}^{\mathrm{e}} = k_{\mathrm{r}}/k_{\mathrm{f}} = C_{\mathrm{Be}}/C_{\mathrm{Ce}}$. The concentrations of B and C going to the reactor inlet are

$$C_{\mathrm{Bi}} = \frac{C_{\mathrm{B0}} + rC_{\mathrm{B}}^{\mathrm{e}}}{(r+1)} \tag{15}$$

$$C_{\mathrm{Ci}} = \frac{C_{\mathrm{C0}} + rC_{\mathrm{C}}^{\mathrm{e}}}{(r+1)} \tag{16}$$

where C_{B0} and C_{C0} are the initial concentrations of B and C.

It is now a relatively simple task to obtain expressions for the concentrations of reactant and products as a function of reactor length and to evaluate output concentrations. Further chemical reaction of B to C, however, could occur until equilibrium is achieved. However, rather than deal with unwieldy analytical solutions it is frequently appropriate to consider the reaction scheme as composed of a set of irreversible steps. The solutions to the set of equations can be written as:

$$\frac{C_{\mathrm{A}}}{C_{\mathrm{Ai}}} = \exp(-p_1 x) \tag{17}$$

$$\frac{C_{\mathrm{B}}}{C_{\mathrm{Ai}}} = \frac{p_1}{p_3 - p_1}[\exp(-p_1 x) - \exp(-p_3 x)] + \frac{C_{\mathrm{Bi}}}{C_{\mathrm{Ai}}}\exp(-p_3 x) \tag{18}$$

$$\frac{C_{\mathrm{C}}}{C_{\mathrm{Ai}}} = \frac{p_3 p_1}{p_3 - p_1}\left[\frac{\exp(-p_1 x) - \exp(-p_5 x)}{p_5 - p_1} - \frac{\exp(-p_3 x) - \exp(-p_5 x)}{p_5 - p_3}\right]$$

$$+\frac{p_3 C_{\mathrm{Bi}}}{C_{\mathrm{Ai}}}\left[\frac{\exp(-p_3 x)-\exp(-p_5 x)}{(p_5-p_3)}\right]+\frac{C_{\mathrm{Ci}}}{C_{\mathrm{Ai}}}\exp(-p_5 x) \tag{19}$$

$$C_{\mathrm{D}} = (C_{\mathrm{Di}}+C_{\mathrm{Ci}}+C_{\mathrm{Bi}}+C_{\mathrm{Ai}})-(C_{\mathrm{A}}+C_{\mathrm{B}}+C_{\mathrm{C}}) \tag{20}$$

Equation 20 is the material balance for the cell operation.

The concentration C_{Ai}, etc., to the reactor inlet are given by expressions of the type

$$C_{\mathrm{Ai}} = \frac{C_{\mathrm{A0}}+rC_{\mathrm{A}}^{\mathrm{e}}}{(r+1)} \tag{21}$$

One of the main assumptions in this analysis, i.e. chemical reaction occurring in the bulk electrolyte, warrants some discussion. Generally the occurrence of chemical reaction is an integral feature of electrochemical reactions, be it either the addition of hydrogen ion or the removal of a water molecule. In such instances reaction is usually very fast (instantaneous and not rate determining) and reactions of the type A → B are considered to be governed by an electron transfer step. For chemical reaction to occur in the bulk electrolyte implies the reaction is slow and mass transfer carries species across the diffusion layer before significant reaction takes place. This is a case considered in one of the following examples. Alternatively, the chemical reaction could be with a species present mainly in the bulk, say in the treatment of two-phase electrolytes where, for example, the second reacting species is a dissolved gas, or when the second reacting species originates from the counter electrode. In such cases the reaction may again be fast.

The intermediate region between very fast and slow chemical reactions will in general need a more realistic model representation than that described in this article. Chemical reaction will occur in the bulk electrolyte and in the diffusion layer, simultaneously with mass transport. The analysis then relies on the solution of the familiar plug flow reactor radial diffusion model with chemical reaction:

$$D\frac{\partial^2 C}{\partial y^2}-\frac{\partial C}{\partial \tau_{\mathrm{r}}}-R = 0 \tag{22}$$

where y is the coordinate direction perpendicular to the surface, τ_{r} is the residence time of electrolyte in the reactor and R is the rate of chemical reaction and is a function of the x coordinate direction. This in itself may be an oversimplification of the system behaviour. Although the treatment of this problem is beyond the scope of this article, it is currently in preparation.

2.3. *The EE type reaction with adsorption*

The reaction scheme is

$$\mathrm{A}+n_1 e \underset{k_{\mathrm{b}1}}{\overset{k_{\mathrm{f}1}}{\rightleftharpoons}} \mathrm{B} \underset{k_{\mathrm{d}}}{\overset{k_{\mathrm{a}}}{\rightleftharpoons}} \mathrm{B}_{\mathrm{ads}}+n_2 e \underset{k_{\mathrm{b}2}}{\overset{k_{\mathrm{f}2}}{\rightleftharpoons}} \mathrm{C}$$

The reaction currents can be written as before as

$$\frac{i_1}{n_1 F} = k_{\mathrm{f}}1C_{\mathrm{A}}^{\mathrm{S}}-k_{\mathrm{b}}1C_{\mathrm{B}}^{\mathrm{S}} \tag{23}$$

$$\frac{i_2}{n_2 F} = k_{\mathrm{f}}2\Gamma_{\beta}-k_{\mathrm{b}}2C_{\mathrm{C}}^{\mathrm{S}} \tag{24}$$

$$\frac{i_1}{n_1 F} = k_{\mathrm{LA}}(C_{\mathrm{A}}-C_{\mathrm{A}}^{\mathrm{S}}) \tag{25}$$

$$\frac{i_2}{n_2 F} = k_{\mathrm{LC}}(C_{\mathrm{C}}^{\mathrm{S}}-C_{\mathrm{C}}) \tag{26}$$

$$\frac{i_1}{n_1F} = k_{\mathrm{LB}}(C_{\mathrm{B}}^{\mathrm{S}} - C_{\mathrm{B}}) + k_{\mathrm{a}}C_{\mathrm{B}}^{\mathrm{S}} - k_{\mathrm{d}}\Gamma_{\beta} \tag{27}$$

$$\frac{i_2}{n_2F} = k_{\mathrm{a}}C_{\mathrm{B}}^{\mathrm{S}} - k_{\mathrm{d}}\Gamma_{\beta} \tag{28}$$

where Γ_{β} is the surface concentration of adsorbed B.

Combining these equations to eliminate surface concentrations and substituting in the reactor model equations yields a set of three differential equations similar in form to Equation 11. As in the ECE mechanism it is less cumbersome to consider reactor behaviour in terms of approximate Tafel-type kinetics. The recycle reactor model equations then become

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}x} = \frac{-\sigma}{(r+1)Q}\frac{i_1}{n_1F} = \frac{-\sigma}{(r+1)Q}\frac{k_{\mathrm{f}}1C_{\mathrm{A}}}{Y1} \tag{29}$$

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}x} = \frac{\sigma}{(r+1)Q}\left\{\frac{\left[k_{\mathrm{LB}}\left(1+\dfrac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\right)\dfrac{i_1}{n_1F} - k_{\mathrm{LB}}C_{\mathrm{B}}\right]}{\left[1+\dfrac{k_{\mathrm{LB}}}{k_{\mathrm{a}}}\left(1+\dfrac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\right)\right]}\right\} \tag{30}$$

$$\mathrm{d}C_{\mathrm{C}} = -(\mathrm{d}C_{\mathrm{A}} + \mathrm{d}C_{\mathrm{B}}) \tag{31}$$

The solution of Equation 29 is as that for Equation 17 previously.

Combining Equations 29 and 30 we obtain

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}C_{\mathrm{A}}} = \left\{k_{\mathrm{LB}}Y1/k_{\mathrm{f}}1\left[1+\frac{k_{\mathrm{LB}}}{k_{\mathrm{a}}}\left(1+\frac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\right)\right]\right\}\left[\frac{C_{\mathrm{B}}}{C_{\mathrm{A}}} - \left(1+\frac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\right)\right] \tag{32}$$

The solution of Equation 32 is

$$\frac{C_{\mathrm{B}}}{C_{\mathrm{Ai}}} = \frac{\rho_6}{1-\rho_7}\left[\left(\frac{C_{\mathrm{A}}}{C_{\mathrm{Ai}}}\right)^{\rho_5} - \frac{C_{\mathrm{A}}}{C_{\mathrm{Ai}}}\right] + \frac{C_{\mathrm{Bi}}}{C_{\mathrm{Ai}}}\left(\frac{C_{\mathrm{A}}}{C_{\mathrm{Ai}}}\right)^{\rho_5} \qquad (\rho_7 \neq 1) \tag{33}$$

where

$$\rho_6 = 1+\frac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\Big/\left[\frac{1}{k_{\mathrm{LB}}}+\frac{1}{k_{\mathrm{a}}}\left(1+\frac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\right)\right] \quad \text{and} \quad \rho_7 = Y1k_{\mathrm{LB}}\Big/k_{\mathrm{f}}1\left[1+\frac{k_{\mathrm{LB}}}{k_{\mathrm{a}}}\left(1+\frac{k_{\mathrm{d}}}{k_{\mathrm{f}}2}\right)\right]$$

2.4. *Galvanostatic operation*

In the treatments that follow it is assumed that the region of potential operation does not encompass solvent decomposition.

2.4.1. Series electrochemical (EE) reaction. The reaction scheme is

$$\mathrm{A} \xrightarrow{k_{\mathrm{f}}1} \mathrm{B} \xrightarrow{k_{\mathrm{f}}2} \mathrm{C}$$

For recycle reaction operation we can write

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}x} = -\delta\frac{i_1}{n_1F} \tag{34}$$

and

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}x} = \delta\left(\frac{i_1}{n_1F} - \frac{i_2}{n_2F}\right) \tag{35}$$

where $\delta = \sigma/(r+1)Q$ and the total current density is given by

$$i_T = i_1 + i_2 \tag{36}$$

Combining Equations 34 and 35 we obtain

$$\left(1 + \frac{n_1}{n_2}\right)\frac{dC_A}{dx} + \frac{dC_B}{dx} = -\delta\frac{i_T}{n_2F} \tag{37}$$

which yields on integration

$$\left(1 + \frac{n_1}{n_2}\right)(C_A - C_{Ai}) + (C_B - C_{Bi}) = \frac{-\delta i_T x}{n_2F} \tag{38}$$

With the assumption that $\beta_2 = \beta_1$ (equal Tafel slopes) which is frequently found in practice we can divide Equation 35 by Equation 34 to give

$$\frac{dC_B}{dC_A} = -1 + \frac{k_2 n_1}{k_1 n_2}\frac{C_B}{C_A} \tag{39}$$

which has the known solutions [1]

$$\frac{C_B}{C_{Ai}} = \frac{1}{1-(n_1k_2/n_2k_1)}\left[\left(\frac{C_A}{C_{Ai}}\right)^{(n_1k_2/n_2k_1)} - \frac{C_A}{C_{Ai}}\right] + \frac{C_{Bi}}{C_{Ai}}\left(\frac{C_A}{C_{Ai}}\right)^{(n_1k_2/n_2k_1)} \qquad (n_1k_2 \neq n_2k_1) \tag{40}$$

and

$$\frac{C_B}{C_{Ai}} = \frac{C_A}{C_{Ai}}\left[\frac{C_{Bi}}{C_{Ai}} - \ln\left(\frac{C_A}{C_{Ai}}\right)\right] \qquad (n_1k_2 = n_2k_1) \tag{41}$$

In fact the variation of product distribution in systems with unequal Tafel slopes varies little from this case for a large range of parameters. Details of this and other related work is currently in preparation [3].

2.4.2. ECE reaction. The reaction scheme is of the type considered in Section 2.2. with the additional assumption that the first electrochemical reaction is at its limiting current. We can, therefore, write the total current as

$$i_T = n_1 F k_{LA} C_A + i_2 \tag{42}$$

The variation of C_A in the reactor is given by

$$\frac{C_A}{C_{Ai}} = \exp(-k_{LA}\delta x) \tag{43}$$

which when combined with Equation 8 for irreversible reactions gives

$$\frac{dC_B}{dx} = \delta k_{LA} C_{Ai} \exp(-k_{LA}\delta x) - \frac{k_f C_b}{(r+1)u} \tag{44}$$

with the general solution

$$\frac{C_B}{C_{Ai}} = \frac{\delta k_{LA}}{\{[k_f/(r+1)u] - \delta k_{LA}\}}\left[\exp(-\delta k_{LA}x) - \exp\left(\frac{-k_f x}{(r+1)u}\right)\right] + \frac{C_{Bi}}{C_{Ai}}\exp\left[\frac{-k_f x}{(r+1)u}\right] \tag{45}$$

Combining Equation 10 with Equation 43 and integrating gives the concentration of D as

$$C_D - C_{Di} = \frac{\delta i_T x}{n_2F} - \frac{n_1 C_{Ai}}{n_2}[1 - \exp(-k_{LA}\delta x)] \tag{46}$$

Additionally, Equation 20 applies.

The inlet concentration of B and C are influenced by chemical reaction in the recycle loop and are given by

(a) for plug flow

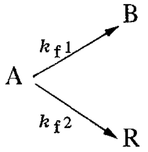
$$\frac{C_B^e}{C_{B\rho}} = \exp(-k_f\tau) \tag{47}$$

(b) for a CSTR

$$\frac{C_B^e}{C_{B\rho}} = \frac{1}{1 + k_f\tau} \tag{48}$$

with $C_C^e = (C_{B\rho} - C_B^e) + C_{C\rho}$ and $C_{Bi} = (C_{B\rho} + rC_B^e)/(r + 1)$ and similarly for C_{Ci}.

2.4.3. Parallel electrochemical reactions. For a reaction scheme of the type



we can write the partial current densities as [4]

$$\frac{i_1}{n_1F} = C_A\bigg/\left(\frac{1}{k_{LA}} + \frac{1}{k_f1} + \frac{k_f2}{k_f1k_{LA}}\right) \tag{49}$$

and

$$\frac{i_1}{n_1} = \frac{k_f1}{k_f2}\frac{i_2}{n_2} \tag{50}$$

The reactor design equation for Component A becomes

$$\frac{dC_A}{dx} = -\delta\left[\left(1 + \frac{k_f2}{k_f1}\right)\bigg/\left(1 + \frac{n_2}{n_1}\frac{k_f2}{k_f1}\right)\right]\frac{i_T}{n_1F} \tag{51}$$

which clearly gives a linear decrease in concentration along the reactor when $n_2 = n_1$. The ratio of k_f2 to k_f1 (and hence Tafel slopes) dictates the relative production of B and R along the reactor and hence must be assessed. If Equation 49 is differentiated and combined with Equation 51 we obtain

$$\frac{k_f2}{k_f1}\left\{\frac{(\beta_2 - \beta_1)[1 - (n_2/n_1)]}{k_{LA}} - \frac{n_2}{n_1}\frac{\beta_2}{k_f1} - \frac{\beta_1}{k_f2}\right\}\bigg/\left(1 + \frac{k_f2}{k_f1}\right)\left(1 + \frac{n_2}{n_1}\frac{k_f2}{k_f1}\right)dE = -\delta\,dx \tag{52}$$

For certain integer ratios of β_2/β_1 frequently found in practice Equation 52 has a relatively straightforward analytical solution and generally can be formed as an infinite series. The simple case when $\beta_2 = \beta_1$ gives

$$C_{Ai} - C_A = \left[\left(1 + \frac{k_2}{k_1}\right)\bigg/\left(1 + \frac{n_2}{n_1}\frac{k_2}{k_1}\right)\right]\frac{\delta i_T x}{n_1F} \tag{53}$$

and

$$(C_B/C_R) = (k_1/k_2) \tag{54}$$

3. Predicted reactor behaviour for a variety of reaction schemes

3.1. *An ECE scheme during potentiostatic operation*

Consider an ECE reaction sequence in which the chemical reaction is fast. Typical performance characteristics are presented in Fig. 2 for a value of $k_f1 = 3 \times 10^{-6}$ m s^{-1} and $k_f1/k_f2 = 5$. This data has taken account of the increase in mass transfer rate at higher recycle rate by assuming the mass transfer coefficient is proportional to $(r + 1)^{0.8}$, i.e. the Dittus–Boelter equation applies. The data shows concentrations of C going through a maximum at a particular value of $\sigma L/Q$ (i.e. electrode length), and the

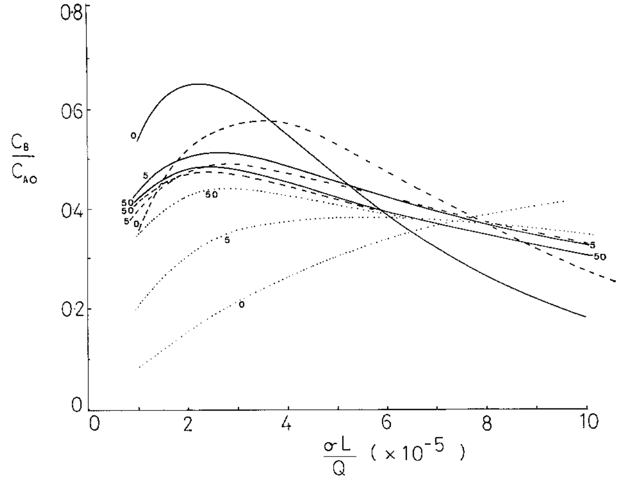
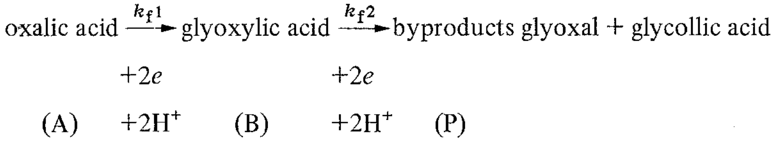


Fig. 2. Variation of yield for an ECE reaction. The effect of recycle ratio r (values on figure) and mass transfer coefficient, $k_L = 10^{-4}$: solid lines (——); $k_L = 10^{-5}$; dashed lines (– – –); $k_L = 10^{-6}$; dotted lines (. . . . .).

effect of recycle is typically to reduce yields of C. Under approximately mixed mass transfer and kinetic control (dashed lines) the effect of an increase in recycle is not as detrimental as in kinetic control due to an enhancement in mass transfer rate. This effect is more pronounced in approximately mass transfer control (dotted lines) where increases of recycle increases the yield of C.

3.2. *An EE scheme during galvanostatic operation*

To illustrate the predicted behaviour of a series electrochemical reaction scheme during galvanostatic operation the production of glyoxylic acid in aqueous solution is considered. The reaction scheme is



$$\begin{array}{ccccc} \text{oxalic acid} & \xrightarrow{k_{f1}} & \text{glyoxylic acid} & \xrightarrow{k_{f2}} & \text{byproducts glyoxal + glycollic acid} \\ & +2e & & +2e & \\ (\mathrm{A}) & +2\mathrm{H}^+ & (\mathrm{B}) & +2\mathrm{H}^+ & (\mathrm{P}) \end{array}$$

The condition of operation for this example are as follows and have been taken from Goodridge *et al.* [5]:

(a) the Reynolds number in a parallel plate cell is in excess of 10 000 to minimize mass transport limitations

(b) Tafel slopes for both reaction steps are equal and a ratio of $k_1/k_2 = 8$ is assumed

(c) an initial concentration of oxalic acid is taken as 10^3 mol m^{-3}.

This reaction has been the subject of a number of studies [5, 6] and one of the more recent [5] has shown the electrode behaviour to be affected by contamination resulting in significant levels of hydrogen reduction. By a suitable choice of electrolyte additive it is, however, possible to offset this contamination to a considerable degree. In either case, with or without additive, recycle reactor operation is now always a dynamic problem.

Before employing the model equations in this example it is worth making some observations on the system. As electrode activity varies during operation its response to organic reaction continually decreases with time. This decrease in glyoxylic acid production rate will make the desired steady-state recycle operation impossible, as to maintain a fixed product output either flow rate, recycle or cell current will need adjusting continuously. Other strategies are possible such as simultaneous electrode reactivation.

The effect of deactivation on the model equations for operation is (following Scott [7], where an activity factor $a = 1 - kt$ is introduced into the model equations) such that the equivalent form of

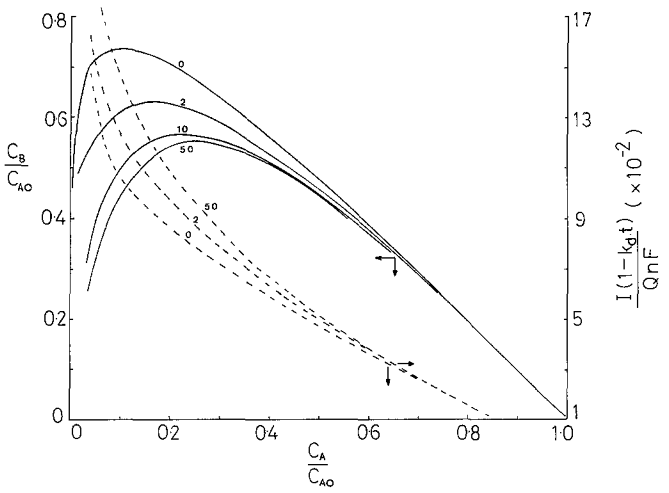


Fig. 3. The effect of recycle ratio on glyoxylic acid production; yield vs reactant concentration characteristics for glyoxylic acid production. Yield of B: solid lines (——) with recycle ratio *r* indicated. Dashed lines (– – –) equivalent cell current.

Equation 38 becomes

$$C_B - C_{Bi} + 2(C_A - C_{Ai}) = -\frac{\delta i_T L}{nF}(1-kt) \tag{55}$$

where L is the reactor length.

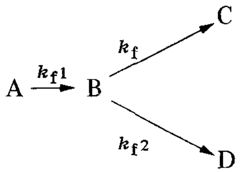
This assumes that deactivation does not vary along the reactor, all reactions are deactivated according to the same mechanism and that start-up does not significantly deactivate the system (if it did then the activity factor could be written as $a = a_0 - kt$).

This equation implies that to maintain a set production rate the current density of operation should be increased continuously during operation to maintain $i_T(1-kt)$ at a constant value. For glyoxylic acid production at a temperature of 20° C (without additives), the value of k is approximately 1.5×10^{-5} s^{-1} implying a maximum electrode life of approximately 19 h which clearly will not permit continuous operation unless an additive is used to suppress deactivation.

Typical performance data for glyoxylic acid production is given in Fig. 3 in the form of glyoxylic acid concentration (C_B) vs oxalic acid concentration (C_A) for several recycle ratios. The expected trend of C_B going through a maximum as the conversion of A increases is seen. The value of this maximum decreases with recycle ratio and will approach the performance characteristics of a continuous stirred tank reactor. Also shown in Fig. 3 are the equivalent cell currents (shown as $I(1-kt)/QnF$) required to achieve these product concentrations. These currents are higher at larger recycle ratios which is indicative of lower efficiency.

3.3. *An electrochemical/chemical reaction scheme during potentiostatic operation*

As an example system consider a reaction scheme of the form



which is representative of the reduction of nitrobenzene (A) in acidic media [8] to N-phenylhydroxylamine (B) which either undergoes protonation to form *p*-aminophenol (C) or is reduced electrochemically to aniline (D). It is known that mass transport has a considerable influence on the production of p-aminophenol in that higher rates improve selectivity. The chemical reaction in this step is known to be slow. Under potentiostatic conditions the following expression for the variation of C_B during recycle operation can be shown to be given by

$$\frac{C_B}{C_{Ai}} = \frac{p_1}{Y2(p_3 + p_5 - p_1)} \left(e^{-p_1 x} - e^{-(p_3+p_5)x}\right) + \frac{C_{Bi}}{C_{Ai}} e^{-(p_3+p_5)x} \tag{56}$$

The variation of C_A is given by Equation 17 and the variation of product concentration C_C is given by

$$\frac{C_C - C_{Ci}}{C_{Ai}} = \frac{p_3 p_1}{Y2(p_3 + p_5 - p_1)} \left[\frac{(1 - e^{-p_1 x})}{p_1} - \frac{1 - e^{-(p_3+p_5)x}}{p_3 + p_5}\right] + \frac{p_3 C_{Bi}}{C_{Ai}} \left(\frac{1 - e^{-(p_3+p_5)x}}{p_3 + p_5}\right) \tag{57}$$

The following expressions also apply

$$\frac{C_C}{C_{A0}} + \frac{C_D}{C_{A0}} = 1 - \frac{C_A + C_B}{C_{A0}} \tag{58}$$

and

$$C_D = \frac{p_5}{p_3}\left[C_C - rC_B \frac{k_f \tau}{(1 + k_f \tau)}\right] \tag{59}$$

With a holding tank in the recycle line the concentrations of B and hence C and D depend on the extent of reaction in this tank. Consider now the performance of the system with the following operating conditions evaluated [9].

$$k_f 1 = 1.2 \times 10^{-7} \exp \frac{[2.3E]}{170} \mathrm{m\,s^{-1}}$$

$$k_f 2 = 1.7 \times 10^{-8} \exp \frac{[2.3E]}{170} \mathrm{m\,s^{-1}}$$

$$k_f = 3.5 \times 10^{-4}\ \mathrm{s^{-1}}$$

The expression for the variation of mass transfer coefficient with recycle flow rate as described in Section 3.1 has been incorporated.

Typical performance characteristics are presented in Fig. 4. With this system where chemical reaction and electrochemical reaction are competitive the larger residence time of the recycle holding tank enhances chemical product yield and selectivity, as does a higher recycle ratio. Higher rates of mass transport are also beneficial in giving higher selectivities due to the enhanced removal of the intermediate B from the surface.

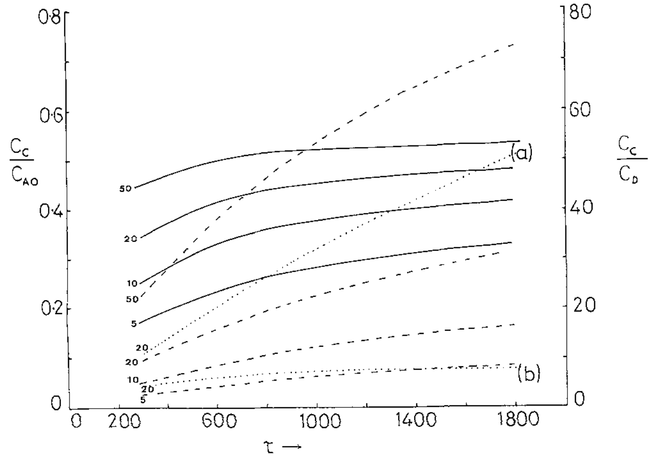


Fig. 4. Variation of yield and selectivity for p-aminophenol as a function of recycle tank holding time and recycle ratio (values indicated on figure) $(\sigma L/Q) = 10^5$. Yield: C_C/C_{A0} (——) solid lines, $k_L = 10^{-6}$; Selectivity: C_C/C_D (– – –) dashed lines, $k_L = 10^{-5}$; C_C/C_D (. . . .) dotted lines; (a) $k_L \to \infty$; (b) $k_L = 10^{-7}$.

4. Conclusions

Several mathematical models of potentiostatic steady-state recycle reactor operation have been developed for electrochemical reaction schemes involving chemical reaction steps. These models can be readily extended to include many combinations of reaction steps and also serve to illustrate the behaviour during galvanostatic operation. Chemical reaction in the recycle loop and mass transport in the reactor have been shown in certain reaction schemes to be an important factor in operation.

The model equations allow the prediction of operating conditions of flow rate, recycle and current to achieve specified production rates and product compositions and can be used to determine the effect of step changes in current, flow rate, etc. The dynamic response of such systems, e.g. during start-up, is outside the scope of this article, but may prove to be an important factor in industrial operation. Although approximate treatment of galvanostatic operation has been considered, an exact treatment is clearly of great importance and will be published later.

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