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Current density optimization in electrochemical synthesis

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Current density in an industrial electrosynthesis process carried out in a single flow electrolyser with planar electrodes has been optimized using a model which includes the main electrochemical and economic parameters, as well as process kinetics. Results obtained using different optimization criteria have been compared. Sample calculations have been made for the cathodic reduction of oxalic acid.

Nomenclature

A	total working electrode area, monopolar connection (m^2)
a	proportionality factor considering depreciation, interest on capital etc. (yr^{-1})
c	total concentration of glyoxylic and oxalic acids ($kmol\,m^{-3}$)
c_A, c_B, c_H	concentration of oxalic acid, glyoxylic acid and hydrogen ions respectively ($kmol\,m^{-3}$)
c_{As}, c_{Bs}, c_{Hs}	surface concentration of oxalic acid, glyoxylic acid and hydrogen ions respectively ($kmol\,m^{-3}$)
C_f	fixed part of the investment cost (\$)
C_i	total investment (\$)
c_w	investment cost per 1 A of current load ($\$\,A^{-1}$)
C_l	labour cost ($\$\,yr^{-1}$)
C_o	operating cost ($\$\,yr^{-1}$)
C_s	constant part of the operating cost, fixed cost ($\$\,yr^{-1}$)
D	total profit ($\$\,yr^{-1}$)
E	electrode potential (V *vs* SCE)
F	Faraday constant ($F = 96485\,C\,mol^{-1}$)
f	factor given in Equation 17 (dimensionless)
ΔH_r	the enthalpy of rth reaction ($J\,mol^{-1}$)
i	total current density ($A\,m^{-2}$)
i_{min}, i_{max}	limiting values of current density, given in Equation 31 ($A\,m^{-2}$)
i_{opt}	optimal value of current density ($A\,m^{-2}$)
i_p	effective current density of product generation ($A\,m^{-2}$)
i_r	partial current density of rth reaction ($A\,m^{-2}$)
i_s	effective current density of reactant consumption ($A\,m^{-2}$)
i_v	symbol for current density used in Table 1 ($A\,m^{-2}$)
J_p, J_s	parameters given in Equations 33 and 34 ($A\,m^{-2}$)
k_f, k_w	parameters given in Equation 39 (W)
k_A, k_B, k_H	mass transport coefficients of reactant A, product B and hydrogen ions respectively ($m\,s^{-1}$)
m'	a proportionality factor in Equation 15 ($W\,m^{-2}$)
m	factor given in Equation 20 ($W\,m^{-2}$)
N	return on investment, ROI (yr^{-1})
N'	incremental return on investment (yr^{-1})
P	production rate ($kmol\,yr^{-1}$)
p	parameter given in Equation 31 ($A\,m^{-2}$)
q	parameter given in Equation 31 ($A^2\,m^{-4}$)
R	total resistance of electrolytic cell, including both ohmic and polarization components (Ω)
r	maintenance cost as a fraction of total investment (yr^{-1})
s_e	cost of energy ($\$\,kWh^{-1}$)
s_m	cost of raw materials ($\$\,kmol^{-1}$)
s_p	selling price of a product ($\$\,kmol^{-1}$)
U	total cell voltage (V)
U_0	a part of cell voltage independent of current density (V)
U_1	voltage parameter given in Equation 19 (V)
U_2	voltage parameter given in Equation 29 (V)
U_f	voltage parameter given in Equation 43 (V)
u_f	parameter used in Equation 47 (dimensionless)
U_w	voltage parameter given in Equation 42 (V)
u_w	parameter used in Equation 46 (dimensionless)
U_N	voltage parameter given in Table 1 (V)
U_p	parameter given in Equation 23, represents the relation between the prices of product and of energy (V)
U_s	parameter given in Equation 24, represents the relation between the prices of raw materials and of energy (V)
U_t	thermoneutral voltage (V)
V	value of a product ($\$\,yr^{-1}$)

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v'	proportionality factor in Equation 6 ($\$\,\mathrm{m}^{-2}$)
v	parameter given in Equation 25, represents the relation between the investment cost and the price of energy ($\mathrm{W\,m}^{-2}$)
W	total amount of energy required ($\mathrm{kWh\,yr}^{-1}$)
W_{el}	energy of direct current ($\mathrm{kWh\,yr}^{-1}$)
W_{m}	energy required for circulation or stirring of the electrolyte ($\mathrm{kWh\,yr}^{-1}$)
W_{t}	energy required to maintain constant temperature of electrolyte and electrodes ($\mathrm{kWh\,yr}^{-1}$)
z_{r}	the number of electrons exchanged in rth reaction, subscript 1 refers to the main reaction (dimensionless)
α	the mole fraction of glyoxylic acid in acid mixture (dimensionless)
ϵ_{i}	current efficiency (dimensionless)
ϵ_{m}	efficiency of circulation pumps or stirrers, dimensionless
ϵ_{r}	efficiency of transformer-rectifier system including transmission losses (dimensionless)
ϵ_{s}	chemical yield (dimensionless)
ϵ_{t}	efficiency of heating/cooling system, dimensionless
κ	specific conductivity of oxalic and glyoxylic acid solution ($\Omega^{-1}\,\mathrm{m}^{-1}$)
$\nu_{\mathrm{Ar}}, \nu_{\mathrm{Br}}$	a stoichiometric number of a reactant A or a product B, respectively in the rth reaction (dimensionless)
ρ	parameter ($= RA$), characterizing total resistance of the electrolyser ($\Omega\,\mathrm{m}^2$)
τ	working time in a year ($10^3\,\mathrm{h\,yr}^{-1}$)
Φ	parameter given in Equation 22 ($\mathrm{W\,m}^{-2}$)

1. Introduction

Before a new synthetic method, tested on the laboratory scale, can be utilized in industry economic analysis is necessary to evaluate costs and gains and to determine optimal reactor size and the most economic mode of operation. In the present study, a methodology for such an analysis, regarding specific features of electrochemical processes is presented. The most critical parameter is current density and this variable must be optimized in the first place.

2. Selection of optimization criteria

As a basic optimization criterion the total profit, D, can be adopted; this is the difference between product value, V, and total product cost, consisting of operating cost, C_{o}, and investment related cost, aC_{i}, [1]:

$$D = V - C_{\mathrm{o}} - aC_{\mathrm{i}} \qquad (1)$$

Most general criteria used for optimization of complex systems in chemical technology are of an economic nature rather than purely technological. Instead of profit, comparative criteria can be used, for example [2]:

(i) return on investment (ROI)

$$N = \frac{D}{C_{\mathrm{i}}} \qquad (2)$$

(ii) incremental return on investment

$$N' = \frac{\mathrm{d}D}{\mathrm{d}C_{\mathrm{i}}} \qquad (3)$$

The choice between those criteria is to an extent arbitrary. This is because different methods can be used to estimate the effectiveness of investment. Comparison of literature from different countries shows that criteria similar to D have been used in Russia [1] and those like N and N' are considered to be more appropriate in the West [2].

3. Simple cost model

Optimization criteria consist of components which can be related to process parameters by a simple cost model as introduced by Ibl [3, 5].

Assuming, for simplicity, that there is only one commercial electrolysis product

$$V = s_{\mathrm{p}}P \qquad (4)$$

the operating cost, C_{o}, can be represented as a sum of four components

$$C_{\mathrm{o}} = \frac{s_{\mathrm{m}}P}{\epsilon_{\mathrm{s}}} + s_{\mathrm{e}}W + rC_{\mathrm{i}} + C_{\mathrm{w}} \qquad (5)$$

The first term includes the cost of raw and auxiliary materials, as well as the indirect cost, and is proportional to the production rate P. The second term represents the cost of energy W. The next term is a maintenance cost approximately proportional to the plant size and, thus, to the investment cost C_{i}. The last term, the labour cost C_{w}, is assumed to be constant over a fairly wide range of production rate.

The investment cost, C_{i}, is represented by a linear function of electrochemical reactor size and, thus, electrode area, A [3]

$$C_{\mathrm{i}} = C_{\mathrm{f}} + v'A \qquad (6)$$

4. Current density and energy consumption

A main electrochemical process

$$\nu_{\mathrm{A1}}A + z_1 e \longrightarrow \nu_{\mathrm{B1}}B \qquad (7)$$

is considered with $k - 1$ side reactions, in which the reactant A and the product B may also be involved. The overall process takes place in a flow electrolyser with planar electrodes. There is one pair of electrodes or electrodes of the same kind are connected in parallel. The electrolyte solution is well mixed.

The total current density, i, is equal to the sum of the current densities, i_{r}, of all reactions occurring. For the convenience of further considerations the current densities i_p and i_s refer to the generation of product and to the consumption of reactant

$$i_p = \frac{z_1}{\nu_{B1}} \sum_{r=1}^{k} i_r \frac{\nu_{Br}}{z_r} \tag{8}$$

$$i_s = \frac{z_1}{\nu_{A1}} \sum_{r=1}^{k} i_r \frac{\nu_{Ar}}{z_r} \tag{9}$$

Current efficiency ϵ_i and chemical yield ϵ_s may be expressed as

$$\epsilon_i = i_p/i \quad \text{and} \quad \epsilon_s = i_p/i_s \tag{10}$$

Energy consumption is vital in all electrochemical processes. Energy is used not only immediately as direct current driving the electrode reactions (W_{el}) but also to maintain constant temperature of electrolyte and electrodes (most often by cooling $-W_t$) and for circulation or stirring of the electrolyte (W_m). The total amount of energy, W, carried by alternating current is

$$W = W_{el}/\epsilon_r + |W_t|/\epsilon_t + W_m/\epsilon_m \tag{11}$$

The amount of d.c. energy involved can be written as

$$W_{el} = (U_0 i + R i^2 A) A \tau \tag{12}$$

The energy, W_t, which should be supplied to, or withdrawn from, the system to maintain a constant electrolyte temperature may be calculated from the thermal balance on the electrochemical reactor [4]. Assuming that electrolysis is carried out at ambient temperature:

$$W_t = W_{el} - U_t i A \tau \tag{13}$$

where

$$U_t = \frac{1}{iF} \sum_{r=1}^{k} i_r \frac{\Delta H_r}{z_r} \tag{14}$$

is sometimes called the thermoneutral voltage. If enthalpies $\Delta H_r/z_r$ (per 1 mole of electrons) for each reaction do not differ much, then U_t hardly depends on the current density and will be considered constant.

By assuming constant flow velocity, following Ibl and Adam [5], the power required for pumping, W_m, is proportional to the electrode area:

$$W_m = m' A \tau \tag{15}$$

m' being a proportionality factor.

The total energy requirement for the electrolytic process is

$$W = A \tau f (\rho i^2 + U_1 i + m) \tag{16}$$

The following symbols have been used:

$$f = 1/\epsilon_r + 1/\epsilon_t \tag{17}$$

$$\rho = RA \tag{18}$$

$$U_1 = U_0 - \frac{U_t}{1 + \epsilon_t/\epsilon_r} \tag{19}$$

$$m = \frac{m'}{\epsilon_m f} \tag{20}$$

The parameter characterizing the resistance of the electrolyser, ρ, remains nearly constant for electrolytic cells with cross-sectional geometry independent of length (providing that the polarization component is small compared to ohmic drop).

Considering all the previous relations the total profit, D, is given by

$$D = s_e f A \tau \Phi - C_s \tag{21}$$

where

$$\Phi = U_p i_p - U_s i_s - \rho i^2 - U_1 i - m - v \tag{22}$$

New symbols used in this equation have the following meaning:

$$U_p = \frac{s_p \nu_{B1}}{s_e F f z_1} \text{ (in V)} \tag{23}$$

$$U_s = \frac{s_m |\nu_{A1}|}{s_e F f z_1} \text{ (in V)} \tag{24}$$

$$v = \frac{(a + r) v'}{s_e f \tau} \text{ (in W m}^{-2}\text{)} \tag{25}$$

Other components of the operating cost are fairly constant over a relatively narrow range of current density and can be regarded as a fixed cost C_s

$$C_s = (a + r) C_f + C_w \text{ (in \$ yr}^{-1}\text{)} \tag{26}$$

5. Profit as an optimization criterion: additional conditions

The total profit D defined by Equation 1 increases without limits with growing production rate P. To use it as an optimization criterion some limiting conditions must be added in accordance with the actual problem. There are three typical situations when optimization is necessary. For each of them profit, D, can be expressed in a form clearly exhibiting its dependence on current density, the main controlled variable of each electrochemical process, which is responsible for the intensity of the process and, on the other hand, for the amount of energy used:

(i) optimal design for limited rate of production,

$$D = s_e f F P \frac{\Phi}{i_p} - C_s \tag{27}$$

(ii) optimal design for limited consumption of energy,

$$D = s_e W \frac{\Phi}{\rho i^2 + U_1 i + m} - C_s \tag{28}$$

(iii) adaptive procedure for existing electrolyser.

$$D = s_e f A \tau \Phi - C_s \tag{21}$$

For a constant rate of production current density determines the size of the electrolyser. If there is a limitation for energy usage, this condition imposes an interrelation between production rate and electrode area. Finally, if optimization is based on an existing electrolyser, current density determines the rate of production.

6. The range of acceptable solutions of optimization problems

The obvious requirement for any practical process is a positive value of the profit, D. This also requires a positive value of Φ (Equation 18). To determine an interval of current density in which $\Phi > 0$ the following abbreviation is used:

$$U_2 = \frac{U_p i_p - U_s i_s}{i} = (U_p - U_s/\epsilon_s)\epsilon_i \qquad (29)$$

If it is assumed that efficiencies ϵ_i and ϵ_s do not depend on current density, i, Φ is a square trinomial. Equation $\Phi = 0$ has two positive solutions when

$$\frac{U_2 - U_1}{2\sqrt{[\rho(v + m)]}} > 1 \qquad (30a)$$

If this condition is not fulfilled the profit, D, always has a negative value and a given process is economically unacceptable.

The condition (Relation 30a) may be difficult to check as it requires a lot of process data. Fortunately, it is possible to simplify this condition. The resulting approximate inequality reads as follows:

$$\frac{(s_p - s_m/\epsilon_s)\epsilon_i}{33.4 z_1 (U s_e (a + r) c_i)^{1/2}} > 1 \qquad (30b)$$

This relation permits the elimination of some processes at an early stage of investigation. For a process which fulfils Condition 30a there is an interval $i_{\min} < i < i_{\max}$, in which $\Phi > 0$. Limiting values are

$$i_{\min} = p - \sqrt{(p^2 - q)} \quad i_{\max} = p + \sqrt{(p^2 - q)} \qquad (31)$$

where $p = (U_2 - U_1)/2\rho$ and $q = (v + m)/\rho$.

As the fixed cost, C_s, exceeds zero the condition $\Phi > 0$ is not sufficient to ensure that $D > 0$. A sufficiently large production rate is also necessary. Figure 1 illustrates this graphically. This plot is made for the case of constant production rate; however in other cases the plots are similar.

7. Optimization equations

By differentiating Equations 21, 27 or 28 with respect to the current density, i, and equating the derivative to zero we obtain optimization equations for appropriate situations and, thus, the optimal current density.

7.1. *Constant rate of production*

The optimization equation takes the form:

$$\rho i^2(1 - 2i_p/J_p) + U_1 i(1 - i_p/J_p) + v + m + U_s(i_s - J_s i_p/J_p) = 0 \qquad (32)$$

The parameters J_p and J_s in this equation are given by

$$J_p = i\,\frac{\mathrm{d}i_p}{\mathrm{d}i} \qquad (33)$$

$$J_s = i\,\frac{\mathrm{d}i_s}{\mathrm{d}i} \qquad (34)$$

7.2. *Limited amount of energy*

Differentiating expression 28:

$$(U_p J_p - U_s J_s)(\rho i^2 + U_1 i + m) - (U_p i_p - U_s i_s - v)(2\rho i^2 + U_1 i) = 0 \qquad (35)$$

7.3. *Constant size of the electrolytic cell*

In this case the optimization equation reads:

$$U_p J_p - U_s J_s - U_1 i - 2\rho i^2 = 0 \qquad (36)$$

In the simplest case that efficiencies ϵ_i and ϵ_s are independent of the current density, analytical solutions of

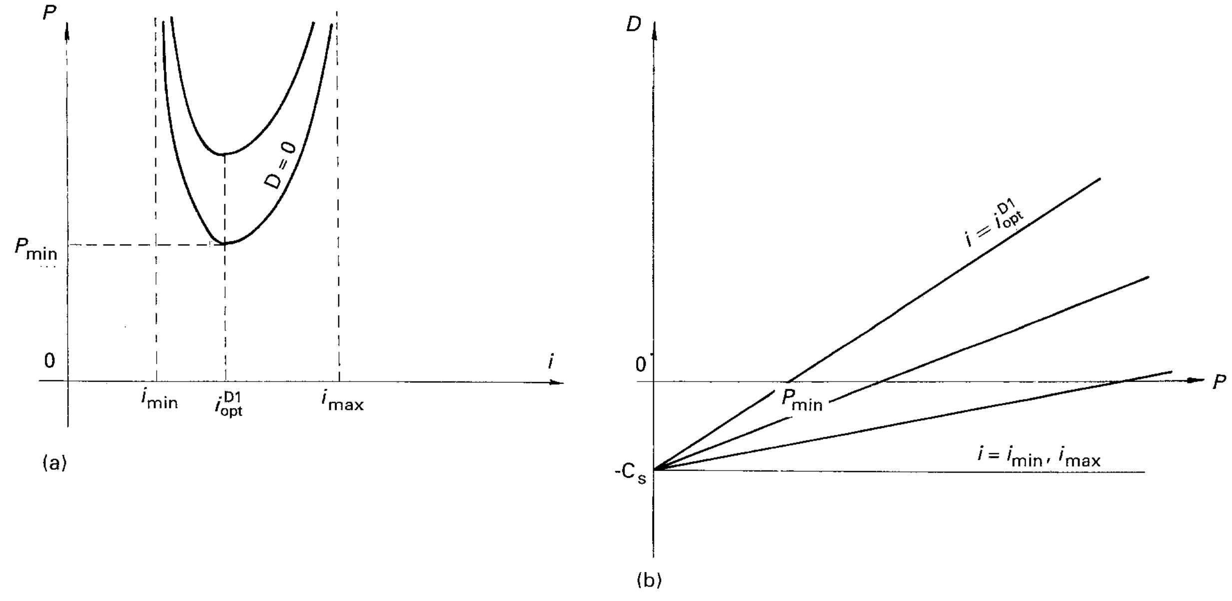

Fig. 1. The area of acceptable solutions of optimization problems with total profit, D, taken as a criterion. (a) Lines of equal profit in terms of current density, i, against production rate, P. (b) Profit, D, as a function of production rate, P, for different values of current density, i.

Table 1. Optimal current densities calculated with the assumption that efficiencies ϵ_i and ϵ_s were independent of the current density

Limiting condition	*Optimization criteria*	
	Profit	*Return on investment*
Constant rate of production	$i_{opt}^{D1} = \sqrt{[(v+m)/\rho]}$	$i_{opt}^{N1} = -i_v + \sqrt{[i_v^2 + (i_v U_N + m)/\rho]}$ where $i_v = v/U_f \epsilon_i \quad U_N = U_2 - U_1 - U_w \epsilon_i$
$P = 1350\,\text{kmol yr}^{-1}$	$i_{opt}^{D1} = 963\,\text{A m}^{-2}$, $A = 15.7\,\text{m}^2$	$i_{opt}^{N1} = 1174\,\text{A m}^{-2}$, $A = 12.8\,\text{m}^2$
Limited amount of energy	$i_{opt}^{D2} = i_v + \sqrt{[i_v^2 + (i_v U_1 + m)/\rho]}$ where $i_v = v/U_2$	$i_{opt}^{N2} = -i_v + \sqrt{[i_v^2 + (i_v U_N + m)/\rho]}$ where $i_v = v(1+u_w)/u_f U_2 \qquad U_N = U_2/(1+u_w) - U_1$
$W = 1 \times 10^6\,\text{kWh yr}^{-1}$	$i_{opt}^{D2} = 649\,\text{A m}^{-2}$, $\text{A} = 13.9\,\text{m}^2$ $P = 811\,\text{kmol yr}^{-1}$	$i_{opt}^{N2} = 648\,\text{A m}^{-2}$, $\text{A} = 14.0\,\text{m}^2$ $P = 812\,\text{kmol yr}^{-1}$
Constant size of the electrolytic cell	$i_{opt}^{D3} = i_{opt}^{N3} = \dfrac{U_2 - U_1}{2\rho}$	
$A = 10\,\text{m}^2$	$i_{opt}^{D3} = i_{opt}^{N3} = 1755\,\text{A m}^{-2}$, $P = 1572\,\text{kmol yr}^{-1}$	

Sample data: $s_m/s_e = 1.97\,\text{kWh mol}^{-1}$, $s_p/s_e = 6.94\,\text{kWh mol}^{-1}$, $a + r = 0.3\,\text{yr}^{-1}$, $v'/s_e = 3.12 \times 10^5\,\text{kWh m}^{-2}$, $f = 3.11$, $\tau = 8.0 \times 10^3\,\text{h yr}^{-1}$, $m = 257\,\text{W m}^{-2}$, $v = 3762\,\text{W m}^{-2}$, $\rho = 4.33 \times 10^{-3}\,\Omega\,\text{m}^2$, $U_0 = 2.15\,\text{V}$, $U_1 = 1.23\,\text{V}$, $U_s = 11.8\,\text{V}$, $U_p = 41.6\,\text{V}$, $U_t = 1.43\,\text{V}$, $\epsilon_s = 0.83$, $\epsilon_i = 0.6$, $U_2 = 16.43\,\text{V}$, $C_f/s_e = 3.12 \times 10^6\,\text{kWh}$, $C_w/s_e = 4.69 \times 10^5\,\text{kWh yr}^{-1}$

Equations 32, 35 and 36 can be obtained. These solutions have been collected in Table 1.

Generally, however, numerical procedures must be applied. The flowchart for such a procedure is very simple; the only problem is to know how the total current density distributes between partial electrode reactions. In other words the dependence of i_p and i_s on i must be known and then $\mathrm{d}i_p/\mathrm{d}i$ and $\mathrm{d}i_s/\mathrm{d}i$ calculated.

According to Condition 30a the following inequality is valid:

$$i_{min} < i_{opt}^{D2} < i_{opt}^{D1} < i_{opt}^{D3} < i_{max} \tag{37}$$

Optimal current density for the case (i) does not depend on the price of product; for the case (ii) it is independent of the price of energy and for the case (iii) it is independent of the investment cost.

8. Return on investment as an optimization criterion

Return on investment can be expressed in terms of process data in the following way:

$$N = \frac{s_e f \tau A \Phi - C_s}{C_f + v' A} \tag{38a}$$

or after rearrangement

$$N = (a + r)\frac{A\Phi - k_f - k_w}{k_f + vA} \tag{38b}$$

New symbols used in this formula are:

$$k_f = (a + r)(C_f / s_e f \tau) \tag{39a}$$

$$k_w = C_w / s_e f \tau \tag{39b}$$

For big and modern facilities, in which C_f and C_w are relatively small the following approximation can be used:

$$N \approx \frac{a + r}{v}\Phi \tag{40}$$

Differentiation of this criterion leads to Equation 36 as in the case of constant electrolyser size and criterion D. So the optimal current density is independent of the investment cost, determined by v, and of the electrode area A. If C_f and C_w cannot be neglected, analysis should include three cases as before:

8.1. *Constant rate of production*

Suitable rearrangement of Equation 38a leads to

$$N = (a + r)\frac{\Phi - (U_w + U_f) i_p}{v + U_f i_p} \tag{41}$$

where

$$U_l = \frac{C_w \nu_{B1}}{P s_e F f z_1} = \frac{\tau \nu_{B1}}{P F z_1} k_w \quad \text{(in V)} \tag{42}$$

$$U_f = (a + r)\frac{C_f \nu_{B1}}{P s_e F f z_1} = \frac{\tau \nu_{B1}}{P F z_1} k_f \quad \text{(in V)} \tag{43}$$

Graphical representation of Equation 41 is shown in Fig. 2. Differentiation of Equation 41 results in an optimization equation.

$$\begin{aligned} &(U_s i_s + \rho i^2 + U_1 i + m) U_f J_p \\ &-(U_s J_s + 2\rho i^2 + U_1 i)(v + U_f i_p) \\ &+(U_p - U_w) v J_p = 0 \end{aligned} \tag{44}$$

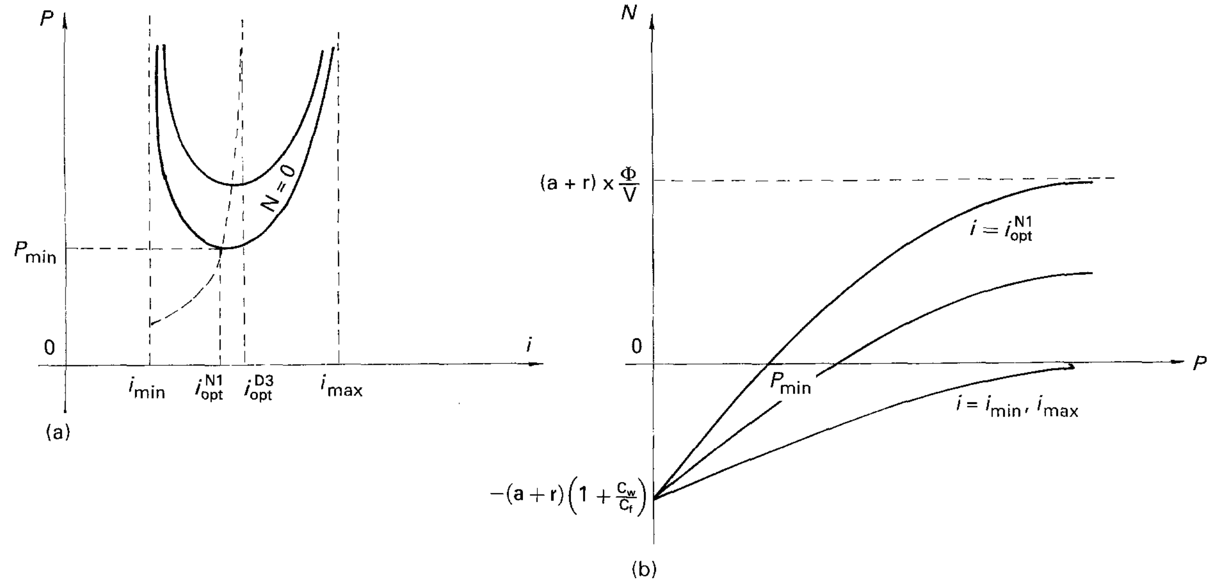

Fig. 2. The area of acceptable solutions of optimization problems with return on investment (ROI) taken as a criterion. (a) Lines of equal ROI in terms of current density, *i*, against production rate, *P*. (b) ROI as a function of production rate, *P*, for different values of current density, *i*.

8.2. *Constant energy consumption*

ROI can be expressed in this case by

$$N = (a + r)\frac{\Phi - (u_w + u_f)(\rho i^2 + U_1 i + m)}{v + u_f(\rho i^2 + U_1 i + m)} \tag{45}$$

where

$$u_1 = \frac{C_w}{s_e E} = \frac{f\tau}{E} k_w \tag{46}$$

and

$$u_f = (a + r)\frac{C_f}{s_e E} = \frac{f\tau}{E} k_f \tag{47}$$

Graphical representation of Equation 45 is similar to that of Equation 41. The optimization equation takes the form:

$$\begin{aligned}(U_p J_p - U_s J_s)(\rho i^2 + U_1 i + m + (v/u_f)) \\ -[U_p i_p - U_s i_s - (1 + u_w)(v/u_f)](2\rho i^2 + U_1 i) = 0\end{aligned} \tag{48}$$

8.3. *Constant size of the cell*

With a constant value of the investment cost C_i both criteria *D* and *N* lead to identical results. The optimization equation takes the form of Equation 36.

9. Incremental return on investment as an optimization criterion

Adoption of the incremental ROI N' as an optimization criterion is reasonable when an existing facility is to be modernized and enlarged. Reconstruction is advisable if N' is greater than the value of *N* obtainable hitherto. With enlargement of the facility one of the following additional conditions should be considered:

(i) the production rate, *P*, from the enlarged facility should remain unchanged, i.e. the current density should be reduced;

(ii) energy consumption should remain constant, this also requires reduction in the current density;

(iii) current density remains unchanged: at optimum level considering profit, *D*, the rate of production will be greater.

9.1. *Constant rate of production*

Considering relations between production *P* and i_p leads to

$$N' = \frac{a + r}{v}\left[\Phi + i_p\left(U_s\frac{di_s}{di_p} - U_p + (2\rho i + U_1)\frac{di}{di_p}\right)\right] \tag{49}$$

With ϵ_i and ϵ_s constant Equation 49 simplifies to

$$N' = \frac{a + r}{v}(\rho i^2 - m - v) \tag{50}$$

Criterion N' takes positive values for $i > i_{opt}^{D1}$ and the condition $N' > N$ is fulfilled for $i > i_{opt}^{N1}$.

9.2. *Constant energy consumption*

Suitable rearrangement of the Equation 3 leads, in this case, to

$$\begin{aligned}N' = \frac{a + r}{v}\Bigg[U_p i_p - U_s i_s - v - (U_p J_p - U_s J_s) \\ \times\left(\frac{\rho i^2 + U_1 i + m}{2\rho i^2 + U_1 i}\right)\Bigg]\end{aligned} \tag{51}$$

If efficiencies ϵ_i and ϵ_s do not depend on current density Equation 51 simplifies to

$$N' = (a+r)\left(\frac{U_2}{v}\frac{\rho i^2 - m}{2\rho i + U_1} - 1\right) \qquad (52)$$

The criterion N' takes positive values if $i > i_{\text{opt}}^{\text{D2}}$, and condition $N' > N$ is met for $i > i_{\text{opt}}^{\text{N2}}$.

9.3. *Constant current density*

For constant current density the criterion N' has a very simple form:

$$N' = \frac{a+r}{v}\Phi \qquad (53)$$

In this case criterion N' is independent of the cell size. The right-hand sides of Equations 40 and 53 are identical; this means that criterion N increases asymptotically to the value of N' with the cell size. Condition $N' > N$ is satisfied in the entire interval $i_{\min} < i < i_{\max}$. ROI depends only slightly on the cell size, but distinctly on the current density.

10. Sample optimization problem: oxalic acid reduction

One of the methods of synthesis of ethylvanilin includes the step of coupling glyoxylic acid and 2-ethoxyphenol. Conveniently, in this reaction, glyoxylic acid may be used as ~0.8 M solution, which can be prepared electrochemically by the reduction of oxalic acid. Catholyte from the electrochemical reactor can be used without any further processing. In contrast to the manufacturing of commercial glyoxylic acid, no evaporation is needed and the process to be optimized consists of the electrochemical step only.

Electrochemical reduction of oxalic to glyoxylic acid can be performed on lead or mercury cathodes. To demonstrate results of a sample optimization the reduction of oxalic acid on a mercury cathode has been chosen as an example. Kinetic data have been taken from [6]. The main reaction is

$$\begin{array}{ccc} \text{COOH} & & \text{CH(OH)}_2 \\ | & +2\text{H}^+ + 2\text{e}^- \longrightarrow & | \\ \text{COOH} & & \text{COOH} \\ & & \\ \text{A} & & \text{B} \end{array} \qquad (54)$$

$$i_1/2F = 1.31 \times 10^{-13} c_{\text{As}} c_{\text{Hs}}^2 \exp(-20E)$$

Apart from the main Reaction 54 two side reactions occur, one involving reactant and product consumption (55) and the second (56) hydrogen evolution:

$$\text{A} + \text{B} + 2\text{H}^+ + 2\text{e}^- \longrightarrow \text{by products} \qquad (55)$$

$$i_2/2F = 3.54 \times 10^{-14} c_{\text{As}} c_{\text{Bs}} c_{\text{Hs}}^2 \exp(-20E)$$

$$\text{H}^+ + \text{e}^- \longrightarrow \tfrac{1}{2}\text{H}_2 \qquad (56)$$

$$i_3/F = 6.82 \times 10^{-10} c_{\text{Hs}} \exp(-12E)$$

Mass transport has been considered by the equations

$$i_s = i_1 + i_2 = 2k_A F(c_A - c_{As}) \qquad (57)$$

$$i_p = i_1 - i_2 = 2k_B F(c_{Bs} - c_B) \qquad (58)$$

$$i_3 = k_H F(c_H - c_{Hs}) \qquad (59)$$

For the solution of optimization equations it is also necessary to know the concentration dependence of the resistance of the catholyte. Data were determined experimentally. For the specific conductivity, κ, of oxalic and glyoxylic acid solution with total concentration of 0.25–1.0 kmol m^{-3} at a temperature 293 ± 0.2 K the following regression equation was obtained [7]:

$$\kappa = (13.359 - 11.652\alpha + 8.126\alpha^2 - 9.049\alpha^3)(c)^{1/3}$$
$$- 4.599 + 4.379\alpha - 4.177\alpha^2 + 4.229\alpha^3 \qquad (60)$$

where κ is in $\Omega^{-1}\,\text{m}^{-1}$ units. The standard deviation calculated with this formula was $0.031\,\Omega^{-1}\,\text{m}^{-1}$.

Sample data are collected in Table 1. Additionally $c_A = 0.64$ kmol m^{-3}, $c_B = 0.30$ kmol m^{-3}. Taking profit as the criterion and solving Equations 32, 35 and 36 the following results are obtained:

constant rate of production, $P = 1350$ kmol yr^{-1}
$i_{\text{opt}}^{\text{D1}} = 1040$ A m^{-2}, $A = 14.4$ m^2
limited amount of energy, $W = 1 \times 10^6$ kWh yr^{-1}
$i_{\text{opt}}^{\text{D2}} = 746$ A m^{-2}, $A = 11.2$ m^2, $P = 730$ kmol yr^{-1}
size of the cell, $A = 10$ m^2
$i_{\text{opt}}^{\text{D3}} = 1871$ A m^{-2}, $P = 1753$ kmol yr^{-1}.

These values of optimal current density are higher than those from Table 1 calculated from simplified equations.

Figure 3 shows the dependence of optimal current density and energy consumption vs. conversion and parameter $v + m$. This graph has been plotted in dimensionless coordinates relating current density to the value of $i_{\text{opt}}^{\text{D1}}$, and energy consumption to the limiting value Z_j^0 obtainable for $c_B \longrightarrow 0$.

At low fractional conversion the optimum current density is approximately constant, only slightly

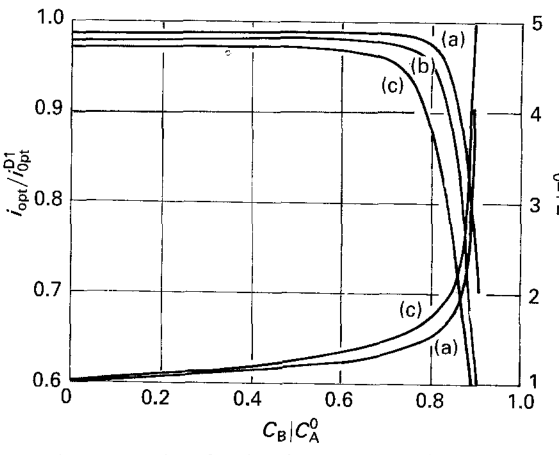

Fig. 3. The impact of the fractional conversion and parameter $v + m$ on optimum current density and specific energy consumption for oxalic acid reduction. $(v + m)$ values: (a) 1.5, (b) 6, and (c) 24 kW m^{-2}.

lower than i_{opt}^{D1}, the value expected for constant current efficiency and chemical yield. In fact, in the process under consideration, this assumption is satisfied with good accuracy for low product concentration. The higher the value of the parameter $v + m$, defined by the relation of investment and energy costs, the more visible is the effect of current efficiency changes with fractional conversion on the optimal current density. A similar but less distinct impact of this parameter can be observed in the case of energy consumption.

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