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The economic evaluation of the electrochemical o-nitrotoluene/o,o-azoxytoluene reduction process

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o-Tolidine, obtained by the reduction of o-nitrotoluene, is used in the production of azo-dyestuffs. The electrochemical reduction of nitrotoluene has to take place in two steps. A continuous process is proposed for the first step, i.e., the electrochemical reduction of o-nitrotoluene to o,o-azoxytoluene in an alkaline ethanol–water solution. Azoxytoluene is separated from the catholyte by crystallization and filtration. The solution, obtained after the isolation of azoxytoluene is regenerated by distillation.

A general method is outlined to calculate the overall production costs for the proposed process since it is representative of electroorganic processes with two consecutive separation processes.

The method is illustrated by the calculation of the costs of an azoxytoluene production of 5 kg h^{-1} as a function of the catholyte composition and the chemical yield. An economic optimization is performed to design the process at the minimum costs. The calculations show that the optimum electrolysis conditions are strongly influenced by the additional processes.

Nomenclature

a	relative decrease in x_N in the electrochemical reactor $a = \Delta x_{N,r}/\bar{x}_{N,r}$
a_b	constant in Equation 30
a_s	constant in Equation 3
A_e	total electrode surface (m^2)
A_{min}	minimal total surface of cathodes (m^2)
b_s	constant in Equation 3
c	costs per m^2 surface (Dfl m^{-2}) subscripts: a anode c cathode m membrane
c_p	specific heat (kJ kg^{-1} K^{-1}) subscripts: c catholyte E washing ethanol
C	cost per kg azoxytoluene (Dfl kg^{-1}) subscripts: b by-product removal en energy inv investment A, f total azoxytoluene formation p of pumps v of vessels W water removal A, i azoxytoluene isolation
C'	total costs (Dfl) subscripts: inv investment r of the reactor
d_c	distance between cathode and membrane (m)
D	diffusion coefficient of nitrotoluene in the catholyte (m^2 s^{-1})
E_b	cell voltage (V)
E_r	reversible voltage (V)
f	price of electric energy (Dfl kWh^{-1})
F	Faraday constant
H	cathode width (m)
$\Delta H_{A,c}$	crystallization enthalpy of azoxytoluene (kJ kg^{-1})
i	current density (A m^{-2}) subscripts: l limiting opt optimum
$\bar{k}$	average mass transport coefficient (m s^{-1})
L	length of cathode (m)
M	molecular weight (kg $kmol^{-1}$) subscripts: A azoxytoluene N nitrotoluene W water
n	number of electrolysis cells
N	mass flow rate of solution (kg s^{-1}) subscripts: A azoxytoluene

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	B by-products
	E ethanol
	N nitrotoluene
	W water
	br from by-product removal to reactor (Fig. 2)
	rr from outlet of reactor to inlet of reactor (Fig. 2)
N'	mass flow rate of ethanol–water solution (kg s^{-1})
	subscripts: df from distillation to filtration (Fig. 3)
	dr from distillation to reaction (Fig. 3)
P_e	electrolysis power (kW)
Q	amount of heat (kW)
	subscripts: c removed from the solution
	E removed from the washing ethanol
	l lost to the environment
r	interest rate on the capital market (fraction/year)
Re	Reynolds number (–)
Sc	Schmidt number (–)
$\overline{Sh}$	average Sherwood number (–)
	subscripts: l in laminar flow
	t in turbulent flow
t_d	depreciation time (year)
t_p	production time per year (s year^{-1})
T	temperature (K)
ΔT	change in temperature (K)
	subscripts: c in the crystallizer
	E in the washing ethanol cooler
x	concentration (weight fraction)
	subscripts: A azoxytoluene
	B by-products
	N nitrotoluene
	W water
	max maximum
	1,2. . .6 these numbers indicate on the location in the flow circuit (Figs. 2 and 3)
$\bar{x}$	average concentration (weight fraction)
	subscripts: N nitrotoluene
	r in the reactor
	c in the crystallizer
Δx	change in concentration (weight fraction)
	subscripts: A azoxytoluene
	N nitrotoluene
	r in the reactor
	c in the crystallizer
z	number of electrons involved (kmol eq. kmol^{-1})
	subscripts: A at the formation of one molecule of azoxytoluene
	N at the reduction of one molecule of nitrotoluene
μ_c	dynamic viscosity of the catholyte (N s m^{-2})
η_i	current efficiency (–)
η_s	chemical yield on mass basis (–)
η_a	anodic polarization (V)
η_c	cathodic polarization (V)
η_Ω	ohmic potential drop (V)
	subscripts: a between anode and membrane
	c between cathode and membrane
	m across the membrane
ρ_c	density of the catholyte (kg m^{-3})

1. Introduction

Electrochemical production of o-tolidine (tolidine) from o-nitrotoluene (nitrotoluene) has to take place in at least two separate steps, namely: the reduction of nitrotoluene to o,o-azoxytoluene (azoxytoluene) in alkaline solution and the reduction of azoxytoluene to hydrazotoluene in acidic solution, which is then directly rearranged into tolidine [1]. Tolidine is used as an intermediate for the production of azo-dyestuffs, important pigments for textiles.

Experiments have shown that the azoxytoluene can be produced electrochemically in a continuously operating process involving electrolysis in a divided flow cell, crystallization and filtration to separate azoxytoluene from the catholyte. The process uses a water-ethanol catholyte and a distillation to remove excess water from the catholyte caused by water-formation in the cathode compartment and water transport from the anode into the cathode compartment (Fig. 1).

It is well known that the overall costs of, in particular electro-organic processes are profoundly influenced by product separation costs [2] and by costs of anolyte and catholyte regeneration. The azoxytoluene process is typical of electro-organic

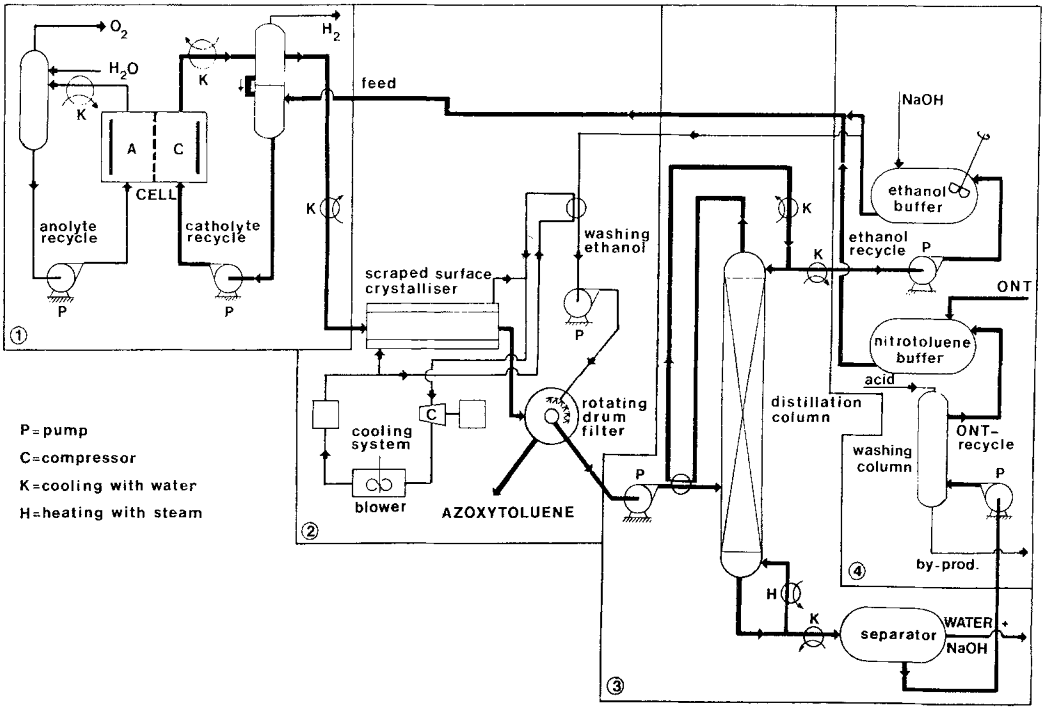

Fig. 1. Simplified flowscheme of the azoxytoluene production process. The numbers indicate the units for azoxytoluene formation (1), the azoxytoluene isolation (2), the water removal (3), and the by-product removal (4).

processes where two different methods of separation are applied simultaneously.

In this study a method is outlined for calculating the overall costs of the azoxytoluene production in small quantities. This method is illustrated by the calculation of the costs of an azoxytoluene production of 5 $\mathrm{kg\,h^{-1}}$.

2. Electrolytic conditions

The process design is strongly affected by both the electrochemical process and the additional separation processes. In particular, the electrolyte, the raw materials, the main product and, eventually, by-products are of great interest for selecting the type of electrochemical reactor and the additional processes.

2.1. *The electrolytic cell*

The electrochemical reduction of nitrotoluene to azoxytoluene takes place according to [3]

$$2\,\mathrm{RNO_2} + 6\mathrm{H^+} + 6\,\mathrm{e} \rightarrow \mathrm{R} - \underset{\underset{\mathrm{O}}{\downarrow}}{\mathrm{N}} = \mathrm{N} - \mathrm{R} + 3\mathrm{H_2O}$$

where $\mathrm{R} = \mathrm{CH_3C_6H_5}$.

This reduction has to be performed in a divided cell to prevent electrochemical oxidation of reduced organic material. The electrode compartments of the cell are separated by a cation-exchange membrane of the Nafion type.

2.2. *Catholyte and anolyte*

The catholyte is a one phase mixture of water and ethanol chosen because of a higher chemical yield of azoxytoluene in a water–ethanol solution than in a highly concentrated aqueous McKee-salt solution [1].

To prevent the formation of two immiscible liquid phases the concentration of water in the catholyte may not exceed a maximum. It has been found that at temperatures up to 313 K this maximum depends on the concentration of nitrotoluene (x_N) and on the temperature. The logarithm of the maximum concentration of water in the catholyte ($x_{\mathrm{W,max}}$) is found to be

$$\log x_{\mathrm{W,max}} = -1.38 + 0.004\,T - 2.86\,x_\mathrm{N} \tag{1}$$

The solubility of azoxytoluene in the catholyte is determined as a function of the nitrotoluene concentration at temperatures between 275 K and 291 K for ethanol–water solutions (vol %/vol % = 90 : 10) containing no NaOH, and 0.5 mol dm^{-3} NaOH.

It has been found that the relation between the maximum concentration of azoxytoluene ($x_{\mathrm{A,max}}$), the concentration of nitrotoluene and the temperature is given by

$$\log \frac{x_{\mathrm{A,max}}}{1 - x_{\mathrm{A,max}}} = -14.74 + 0.0492\,T + (0.094\,T - 21.52)\,\frac{x_{\mathrm{N}}}{1 - x_{\mathrm{N}}} \tag{2}$$

The presence of NaOH has no influence upon the solubility of azoxytoluene in the catholyte. Since the solubility of azoxytoluene at temperatures below 273 K is much more influenced by the amount of nitrotoluene and the temperature than by the water–ethanol ratio, relation 2 is used to calculate $x_{\mathrm{A,max}}$ at all ratio's in the economic evaluation. A solution of 2 mol dm^{-3} H_2SO_4 serves as the anolyte.

2.3. *Chemical yield and current efficiency*

As well as azoxytoluene, by-products are formed. These by-products are water and probably aromatic amines. The chemical yield (η_s) of azoxytoluene is defined by the ratio of the azoxytoluene production and the nitrotoluene consumption on a weight basis (this implies that the maximum theoretical yield is 0.82). The chemical yield depends on many factors, in particular, the nitrotoluene and azoxytoluene concentrations in the reactor [1].

From the experimental results [1] it follows that a chemical yield of 0.82 is attainable at low current densities ($i \ll i_1$), nitrotoluene concentrations higher than 0.2 mol dm^{-3} and at azoxytoluene concentrations lower than 0.1 mol dm^{-3}.

No extensive research about the effect of these parameters on the azoxytoluene yield is performed. It has been found that η_s decreases with increasing x_A/x_N ratio, especially at $x_A/x_N > 1$ [1].

From the reaction scheme for the reduction of nitrotoluene [3] and assuming by-products are formed by reduction of azoxytoluene, it can be deduced that at constant electrolyte flow conditions and cathode potential, the azoxytoluene yield is:

$$\eta_s = a_s - b_s \frac{x_A}{x_N} \tag{3}$$

This relation is supported by the experimental results if $a_s = 0.82$ and $b_s = 0.04$.

It has been found that a current efficiency (η_i) for the azoxytoluene formation of about 85% can be attained at maximum chemical yield [1]. This means that 15% of the current is used for hydrogen production. The formation of hydrogen is not included in the calculation of the process costs.

Moreover, it is assumed, that the formation of one molecule of azoxytoluene needs two electrons and the molecular weight of the by-products is equal to the molecular weight of azoxytoluene. It can be shown that the current efficiency for the azoxytoluene formation is:

$$\eta_i = 3\,\eta_s/(3.28 - \eta_s) \tag{4}$$

2.4. *Cell voltage*

The cell voltage (E_b) depends on many factors, including the nature of the electrode materials, anolyte and catholyte compositions, type of membrane, the distances between membrane and the electrodes and the current density. Generally,

$$E_b = E_r + \eta_a + \eta_c + \eta_\Omega \tag{5}$$

In the following, approximations are given for these contributions to the cell voltage.

Taking into account a difference of about 14 pH-units between anolyte and catholyte and considering the current density/potential curve for the reduction of nitrotoluene at platinum [3], it is assumed that $E_r = 1.8$ V.

Only the reduction of nitrotoluene is taken into account at calculating the overpotential of the cathode. It can be deduced theoretically that η_c increases with $\log \bar{k}i/(i_1 - i)$. From experimental data it can be derived that

$$\eta_c = 0.5 + 0.1 \log (\bar{k}i/(i_1 - i))$$

For oxygen evolution at the anode it is given

$$\eta_a = 0.5 + 0.1 \log i.$$

The ohmic resistance of the catholyte depends strongly on the weight fraction of water in the catholyte (x_W). It has been found, that for an alkaline water-ethanol solution and a distance between the membrane and the cathode of 2 mm, the ohmic potential drop across the catholyte is

$$\eta_{\Omega,\mathrm{c}} = 3\,i\,10^{-(1.4\,x_\mathrm{W}+3)}.$$

The ohmic potential drop across the anolyte, with a specific resistance of 110 Ωm and a distance between membrane and anode of 4 mm, is given by $\eta_{\Omega,\mathrm{a}} = 4.4 \times 10^{-5}\,i\,\mathrm{V}$. The ohmic potential drop across the Nafion 495-membrane is given by $\eta_{\Omega,\mathrm{m}} = 1.2 \times 10^{-4}\,i\,\mathrm{V}$. Summation of these contributions gives the overall cell voltage:

$$E_\mathrm{b} = 2.8 + 0.1 \log \frac{\bar{k} i}{i_1 - i} + 0.1 \log i$$

$$+ 3\,i\,10^{-(1.4 x_\mathrm{W}+3)} + 1.64 \times 10^{-4}\,i \qquad (6)$$

2.5. *The increase of the water content of the catholyte*

According to the electrode reaction for the reduction of nitroluene, three molecules of water are formed per molecule of azoxytoluene. It is assumed that no water is formed during the formation of other by-products.

The transport of H$^+$-ions and water through the membrane are inter-connected. Based on literature data [4], it is assumed that 2.5 molecules of water per H$^+$-ion are transported from the anolyte to the catholyte. It is also assumed that this transport is independent of the composition of both electrolytes. It can be derived that

$$N_\mathrm{W} = 18 \frac{M_\mathrm{W}}{M_\mathrm{A}} \frac{N_\mathrm{A}}{\eta_\mathrm{s}}. \qquad (7)$$

3. The economic evaluation of the process

The process scheme (Fig. 1) is divided into four parts which are evaluated separately. These parts concern the azoxytoluene formation, the azoxytoluene isolation, the catholyte regeneration and some additional units. The parts are interconnected by the mass balance for the catholyte components.

Integral optimization parameters, deduced from the mass balances, affecting each part of the process, are used to optimize the complete process. These parameters are:

1. the average nitrotoluene concentration in the electrochemical reactor, $\bar{x}_{\mathrm{N,r}}$, in weight fraction;
2. the relative decrease in nitrotoluene concentration in the electrochemical reactor, $a = \Delta x_{\mathrm{N,r}}/\bar{x}_{\mathrm{N,r}}$;
3. the decrease in azoxytoluene concentration due to the isolation, $\Delta x_{\mathrm{A,c}}$, in weight fraction;
4. the chemical yield of the azoxytoluene formation on a weight basis, η_s.

The evaluation starts with the calculation of the mass flows and component concentration being essential for the size of each process part. Hereafter, the total of investment costs and energy costs is calculated as a function of the optimizatio parameters, for each part of the process, at a fixed rate of azoxytoluene production (N_A). Finally, these parameters are optimized to minimize the total process costs. It should be noted that the costs of raw-materials and labour are not included.

3.1. *The overall mass balance*

The mass balances of nitrotoluene, azoxytoluene and the by-products (Fig. 2) are used to calculate the size of all parts of the process that are involved with the reaction, the azoxytoluene isolation and the by-product removal.

The mass balances of water and ethanol (Fig. 3) are used to determine the size of the water removal process. Therefore, these balances are evaluated separately. From the overall mass balances of nitrotoluene, azoxytoluene and by-products (Fig. 2) it follows that:

$$N_\mathrm{N} = N_\mathrm{A}/\eta_\mathrm{s} \qquad (8)$$

and

$$N_\mathrm{B} = N_\mathrm{N} - N_\mathrm{A}. \qquad (9)$$

Since $a = \Delta x_{\mathrm{N,r}}/\bar{x}_{\mathrm{N,r}}$ it can be deduced that x_N on location (1) at the liquid circuit (Fig. 2):

$$x_{\mathrm{N,1}} = \bar{x}_{\mathrm{N,r}}\,(1 - \tfrac{1}{2} a) \qquad (10)$$

From relation (3) and from the mass balances of nitrotoluene and azoxytoluene it is calculated that

$$x_{\mathrm{A,1}} = \frac{\bar{x}_{\mathrm{N,r}}}{b_\mathrm{s}}\,(a_\mathrm{s} - \eta_\mathrm{s}) + \tfrac{1}{2}\,\eta_\mathrm{s}\,a\,\bar{x}_{\mathrm{N,r}} \qquad (11)$$

with the condition

$$\frac{\bar{x}_{\mathrm{N,r}}}{b_\mathrm{s}}\,(a_\mathrm{s} - \eta_\mathrm{s}) - \tfrac{1}{2}\,\eta_\mathrm{s}\,a\,\bar{x}_{\mathrm{N,r}} \geqslant 0;$$

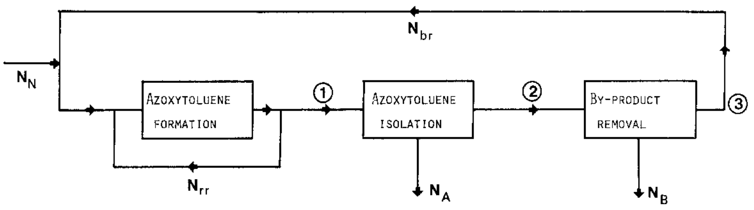

Fig. 2. Scheme of the mass flow rates for nitrotoluene (N_N), azoxytoluene (N_A), the by-products (N_B) and solutions. The index numbers indicate the locations in the process circuit.

and

$$N_{br} = N_A\,(1 - x_{A,1}) - N_B\,\Delta x_{A,c} \tag{12}$$

and

$$N_{rr} = \frac{N_N}{a\,\bar{x}_{N,r}} - N_N - N_{br} \tag{13}$$

These relations are sufficient to design the azoxytoluene formation process. Additionally, the following parameters are necessary to calculate the azoxytoluene isolation and the by-products removal processes:

$$x_{A,2} = x_{A,1} - \Delta x_{A,c} \tag{14}$$

and

$$x_{N,2} = \frac{N_{br} + N_N}{N_{br} + N_B}\,x_{N,1} \tag{15}$$

Assuming a complete removal of by-products ($x_{B,3} = 0$) it follows

$$x_{B,2} = \frac{N_B}{N_B + N_{br}} \tag{16}$$

Before evaluating the mass balances of water and ethanol (Fig. 3) some assumptions have been made:

(a) The mass flow of washing ethanol (N'_{df}) is equal to the mass flow of solution into the filter:

$$N'_{df} = N'_{dr} + N_W \tag{17}$$

(b) Because the amount of azoxytoluene and nitrotoluene in location (3) in Figs. 2 and 3 is low compared with the amount of ethanol and water, a good approximation is:

$$N'_{dr} = N_{br}$$

(c) The total input of water is given by Equation 7.

(d) The allowed maximum water concentration is given by Equation 1.

(e) To obtain a good separation between the water phase and the nitrotoluene phase of the bottom fraction of the distillation, it is assumed that $x_{W,5} \geqslant 0.975$. From this assumption it follows that

$$N_E \leqslant 0.025\,N_W \tag{18}$$

From the mass balance of water and these assumptions, it follows:

$$x_{W,4} = \frac{N_{br} + N_W}{2\,N_{br} + 2\,N_W + N_E}\,(x_{W,\max} + x_{W,6}) \tag{19}$$

and

$$x_{W,6} = \frac{N_{br} + N_W}{N_{br}}\,x_{W,\max} - \frac{N_W + N_E}{N_{br}}\,x_{W,5} \tag{20}$$

3.2. *The costs of the azoxytoluene formation*

The costs of the azoxytoluene formation consist mainly of the investment costs of the reactor, current rectifier, electrolyte coolers, electrolyte recirculation pumps, and of the electrical energy costs.

The overall cost of this part of the process is a function of the current density and the parameters a, $\Delta x_{A,c}$, $\bar{x}_{N,r}$ and η_s. An optimization should be performed to determine for $0 < i \leqslant i_1$

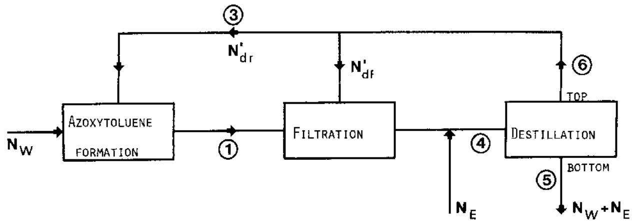

Fig. 3. Scheme of the mass flow rates for water (N_W), ethanol (N_E) and solutions. The numbers indicate the locations in the process circuit.

the optimal current density:

$$i_{\mathrm{opt}} = \mathrm{MIN}\,[C_{\mathrm{inv}}(i) + C_{\mathrm{en}}(i)] \tag{21}$$

First, information has to be gained concerning i_1 being the upper boundary of the current density range.

3.2.1. *The limiting current density.* Current densities higher than the limiting current density (i_1) of the nitrotoluene reduction will cause a considerable decrease in chemical yield. Consequently, we only discuss the process for $i < i_1$. The limiting current density can be calculated from the cell geometry, the mass flow rate relations and the nitrotoluene concentration.

A filter press cell with electrodes of length L and width H and with a distance of d_c between cathode and membrane is used. The cross-section of the cathode compartment is equal to $d_c H$. The reactor consists of n cells.

For an infinitely wide electrode with fully developed flow and a rather small change in the average concentration along the reactor, [5] gives relations for the limiting current and the average Sherwood number for laminar and turbulent flow.

In this paper we calculate the process costs for a small relative decrease in nitrotoluene concentration in an electrochemical reactor being equal to or less than 0.1. For determining the limiting current density i_1, the average concentration of nitrotoluene $\bar{x}_{\mathrm{N,r}}$ is used. Taking into consideration the change in the dimension of concentrations, it follows from [5] that the limiting current density is given by:

$$i_1 = z_{\mathrm{N}} F \frac{\rho_c}{M_{\mathrm{N}}} \frac{\bar{x}_{\mathrm{N,r}}}{1 - \bar{x}_{\mathrm{N,r}}} \overline{Sh} \frac{D}{2\,d_c} \tag{22}$$

The mass transfer rate of nitrotoluene to the cathode is given by [5]:

$$\overline{Sh}_1 = 1.85 \left(Re\, Sc \frac{2\,d_c}{L} \right)^{0.33} \tag{23}$$

in laminar flow ($Re < 2500$), and

$$\overline{Sh}_t = 0.023\, Re^{0.8}\, Sc^{0.33} \tag{24}$$

in turbulent flow ($Re > 2500$).

For the cathode compartment of a parallel plate reactor, the dimensionless numbers are

$$Re = \frac{N_{\mathrm{rr}} + N_{\mathrm{br}} + N_{\mathrm{A}}}{H + d_c} \frac{2}{\mu_c n} \tag{25}$$

where the mass flow rate through the cathode compartment is $N_{\mathrm{rr}} + N_{\mathrm{br}} + N_{\mathrm{A}}$ (Fig. 2), and

$$Sc = \frac{\mu_c}{\rho_c D} \tag{26}$$

and

$$\overline{Sh} = \frac{\bar{k}\, 2d_c}{D} \tag{27}$$

The minimum cathode area needed for a fixed azoxytoluene production rate is:

$$A_{\mathrm{e,min}} = \frac{z_{\mathrm{A}} F \cdot N_{\mathrm{A}}}{\eta_i M_{\mathrm{A}} \cdot i_1} \tag{28}$$

For a fixed azoxytoluene production rate we calculate the total mass flow rate in the electrochemical reactor as a function of the parameters, a, $\Delta x_{\mathrm{A,c}}$, $\bar{x}_{\mathrm{N,2}}$ and η_s.

To calculate the Reynolds number of the solution in one cell of the electrochemical reactor, the number of cells, n, should be known. By means of numerical iteration the electrode area, following from the number of cells ($A_e = L\,H\,n$), and the area following from the calculation of $A_{\mathrm{e,min}}$ (according to Equation 28) are equalized. With this electrode area the correct limiting current density is found from Equation 22.

3.2.2. *The electrical energy costs.* From the electrical power relation $P_e = E_b\, i A_e$, the current efficiency and the electricity costs it can be derived that the energy costs per kg azoxytoluene are

$$C_{\mathrm{en}} = \frac{E_b\, i A_e f}{3.6 \times 10^6\, \eta_i N_{\mathrm{A}}} \tag{29}$$

The applied cell voltage (E_b) is given by Equation 6.

3.2.3. *The investment costs.* The investment costs of the electrochemical reactor are proportional to the electrode area:

$$C_r' = a_b\,(c_a + c_c + c_m)\,A_e \tag{30}$$

The investment costs of the current rectifier are calculated with the method of [6].

During the electrolysis heat is generated. The heat production rate is

$$Q = (E_b - E_r)\, i\, A_e \tag{31}$$

The costs of the heat exchangers, used for cooling both solutions, are calculated according to the method described by [7], with cost figures given by [8]. Water of 288 K is used as the cooling medium. The total investment costs (C'_{inv}) of the complete electrolysis unit are the sum of the investment costs of the separate parts, multiplied by a factor of 1.75 [9], that includes all costs for piping, instrumentation, etc., that are related to this unit.

Generally, to calculate investment costs per kg azoxytoluene (C_{inv}), the depreciation and capital costs are included. It can be derived [9], that:

$$C_{\text{inv}} = C'_{\text{inv}} \frac{(1+r)^{t_d}}{(1+r)^{t_d}-1} \; \frac{1}{t_d N_A t_p \eta_s} . \tag{32}$$

3.2.4. The total formation costs. (part 1 of Fig. 1). The investment and energy costs for recirculation pumps and specific vessels do not affect i_{opt}. The pressure loss due to the reactor is much lower than the pressure loss in the rest of the circuits because of its larger cross section. Consequently, both the investment and the energy costs of the recirculation pumps (C_p) depend on the mass flow, which can be calculated from the mass balance and on the pressure loss in the circuit, excluded the reactor [8, 7]. The costs of vessels (C_v) have been calculated according to [8]. C_p and C_v also include piping and instrumentation costs, related to those pumps and vessels. By optimization with respect to the lowest costs of azoxytoluene formation, and with the limitation $i < i_1$, the formation costs per kg azoxytoluene are found. Consequently,

$$C_{A,f} = C_{\text{inv}}(i_{\text{opt}}) + C_{\text{en}}(i_{\text{opt}}) + C_p + C_v \tag{33}$$

3.3. *The costs of the azoxytoluene isolation*

A useful method of separation of the azoxytoluene from the catholyte is crystallization of the azoxytoluene followed by filtration and washing of the crystals with ethanol.

From a comparison of different types of crystallizers [7] it has been found that the scraped surface heat exchanger [10] is very useful in this case because it has the advantages of a high heat transfer coefficient and the non-occurrance of blocking of the heat exchanger by crystals.

Evaporating freon-12 has been chosen as the cooling medium because of its appropriate physical properties [7]. The cooling system consists of a reciprocating compressor and an air cooled condensor (Fig. 2).

Before entering the crystallizer, the catholyte is cooled with water of 288 K to decrease its temperature to the crystallization temperature. This reduces the size of the cooling system.

In a combined rotating drum filter–washing unit [7], the azoxytoluene crystals are separated from the mother liquor by filtration and are washed with ethanol to remove residual catholyte, in particular nitrotoluene, from the crystals. It has been found that a volume of washing ethanol equal to the volume of filtered solution is sufficient to obtain azoxytoluene crystals with a nitrotoluene content less than 0.5 wt %.

The basis of the cost calculation of the crystallizer, the heat exchange for cooling the washing ethanol and the cooling system is the solubility relation of azoxytoluene given by Equation 2.

The concentrations of azoxytoluene in the solution at the inlet and outlet of the crystallizer are calculated in Equations 11 and 14. The average nitrotoluene concentration in the crystallizer is $\bar{x}_{N,c} = (x_{N,1} + x_{N,2})/2$. The concentrations $x_{N,1}$ and $x_{N,2}$ are calculated in Equations 10 and 15. The loss of azoxytoluene caused by filtering and washing is neglected.

Using Equation 2 the decrease in temperature of the solution to produce N_A azoxytoluene, is calculated as a function of the optimization parameters a, $\Delta x_{A,c}$, $\bar{x}_{N,r}$ and η_s. The quantity of heat, that has to be removed from the solution, to obtain a production of N_A is:

$$Q_c = c_{p,c}(N_N + N_{br})\,\Delta T_c + N_A\,\Delta H_{A,c} + Q_{1,c} \tag{34}$$

The external heat loss and the heat produced by scraping are assumed to be $Q_{1,c} = 0.1\,Q_c$. The crystallization enthalpy of azoxytoluene ($\Delta H_{A,c}$) and the specific heat of the solution ($c_{p,c}$) are not given in the literature. The crystallization enthalpy of azotoluene from ethanol (namely 126 kJ kg^{-1}; [11]) has been used. The specific heat of the solution has been estimated from the specific heat of its components at 273 K (namely 2.5 kJ kg^{-1} K^{-1}).

With the same cooling system, the washing ethanol is cooled from room temperature (293 K) to the temperature of the solution at the outlet of the crystallizer.

The quantity of heat that has to be removed from the washing ethanol is

$$Q_E = c_{p,E} (N_N + N_{br}) \Delta T_E + Q_{1,E} \quad (35)$$

It is assumed that the external heat loss $Q_{1,E} = 0.05\, Q_E$.

With the method described in [7] the cooling system is fully designed as a function of $Q_E + Q_c$ and the used evaporation temperature of freon-12 in both heat exchangers. The evaporation temperature of freon-12 has a great influence on the size of both heat exchangers and the cooling system. Optimization of the investment and energy costs of the heat exchangers and the cooling system, with respect to the evaporation temperature of freon-12 shows that the optimum temperature is 1 K lower than the solution temperature at the outlet of the crystallizer. Prices from [8] are used in the calculations. The total costs for isolating the azoxytoluene are the sum of the optimized costs of the crystallization and washing, and the costs of precooling and filtration.

The costs of the filtration-washing unit are fixed on Dfl* 40000 [8], and assumed to be independent of the crystal production, owing to the small production rates.

The total costs for azoxytoluene isolation are a function of the optimization parameters a, $\Delta x_{A,c}$, $\bar{x}_{N,r}$ and η_s. In the last section of this paper the optimum parameters will be calculated.

3.4. *The costs of the removal of water*

Water can be removed from the catholyte in various ways. Absorption of water on a selective absorbent has the problem of the regeneration of the absorbent. To separate the water by crystallization requires very low temperatures [11]. For these reasons distillation has been chosen.

Distillation experiments have shown that the volatilities of nitrotoluene and azoxytoluene are much lower than those of ethanol and water. This implies that this multicomponent distillation can be regarded as a binary distillation of ethanol and water.

Because the molar enthalpies of liquid and vapour mixtures of ethanol and water do not change with the composition [7], the number of equilibrium stages needed for separation are numerically calculated analogous to the McCabe–Thiele method [7] from the equilibrium data given in [12]. The mass flows and compositions of the distillation and of the bottom-product are calculated with Equations 17–20.

A randomly packed distillation column, with a packing of Ceramic Intalox Saddles, is appropriate for small separation processes [13, 14]. The packing size, packed-bed height per theoretical stage and the packed-bed diameter are calculated with the method described in [13]. The investment costs of the column without packing are calculated from the column size [9]. The packing costs are given in [7]. The total costs for the column with piping, isolation, instrumentation, etc. is calculated from a correlation diagram [9].

The energy demand of the distillation is calculated in the McCabe–Thiele procedure [7]. It is assumed that the reboiler is heated by steam of 30 bar (663 K). The azoxytoluene process is considered to be a part of a big plant with its own steam generation. In this case the steam price is known [8].

The investment costs of the following heat exchangers are calculated: reboiler, feed-heater, condenser, distillate cooler and bottom-product cooler (see Fig. 1). These heat exchangers are calculated by the method described in [7]. Their prices are given in [8].

The investment costs of the vessel for separation of the bottom-product in a nitrotoluene and a water phase are assumed to be fixed at Dfl 10 000 for a 1 m^3 vessel [8].

Finally, the total dewatering costs are calculated by summation of all costs, mentioned above. The total costs are a function of the optimization parameters a, $\Delta x_{A,c}$, $\bar{x}_{N,r}$ and η_s.

3.5. *The costs of the removal of by-products and additional process parts*

No extensive research has been done on determining the nature of the by-products, probably aromatic amines, and the methods of removing

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* Dfl is the Dutch Guilder; at its December 1981 value.

them from the catholyte. Therefore, the following cost calculation is a fairly rough estimation.

It is assumed that the by-products, which are in the nitrotoluene phase after the separator, can be easily washed out with acidified water. The price of the washing column is estimated Dfl 20 000 [8] and assumed to be independent of the optimization parameters.

The polluted water, coming from the washing column and the phase separation vessel, is treated by a specialized firm. The cost of this treatment is Dfl 0.50 per kg of delivered waste water and is independent of the pollutant concentration. The amount of produced waste water is the sum of $N_W + N_E + N_B$ (Equations 7, 9 and 18) and the amount of water from the washing column. The latter is assumed to be one-tenth of the nitrotoluene flow, N_{br} (Equation 12).

The costs of the additional parts of the process, i.e. the nitrotoluene and ethanol storage vessels of 1 m^3 each, and four small pumps, are estimated Dfl 40 000 totally.

4. An example of the economic evaluation

The calculations, outlined in the previous sections, are used to evaluate the process costs of an azoxytoluene production rate of 5 kg h^{-1}. Production rates of this magnitude are often used in the dyestuff industry. The constants used in the calculations are given in Table I.

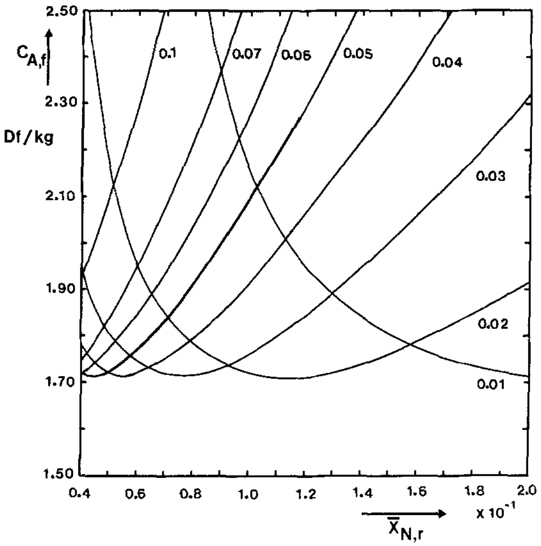

Fig. 4. The azoxytoluene formation costs ($C_{A,f}$) in Dfl kg^{-1} produced azoxytoluene versus $\bar{x}_{N,r}$, with parameter a. Conditions; $\eta_s = 0.80$, $\Delta x_{A,c} = 0.16$.

4.1. *The azoxytoluene formation*

The formation costs ($C_{A,f}$), as a function of the optimization parameters a, $\bar{x}_{N,r}$, $\Delta x_{A,c}$ and η_s, are shown in Figs. 4–6. The figures only show the cost curves for $x_{N,r} \geqslant 0.04$ (see section 2.3).

Table 1. Important constants used in the calculations

Symbol	*Value*
N_A	5 kg h^{-1}
a_s	0.82
b_s	0.04
M_A	226 kg kmol^{-1}
M_N	137 kg kmol^{-1}
H	0.5 m
L	0.5 m
d_c	2 mm
z_N	3
z_A	6
f	0.125 Dfl kWh^{-1}
c_a	500 Dfl m^{-2}
c_c	2500 Dfl m^{-2}
c_m	1000 Dfl m^{-2}
a_b	1.75
r	0.1 fraction year^{-1}
t_d	5 year
t_p	7000 h year^{-1}

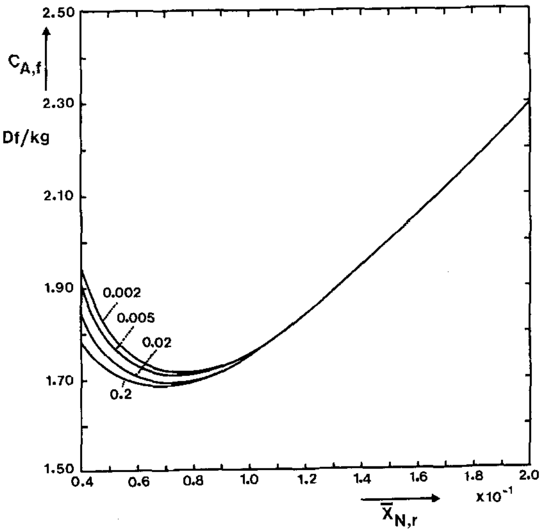

Fig. 5. The azoxytoluene formation costs ($C_{A,f}$) in Dfl kg^{-1} versus $\bar{x}_{N,r}$ with parameter $\Delta x_{A,c}$. Conditions; $\eta_s = 0.81, a = 0.03$.

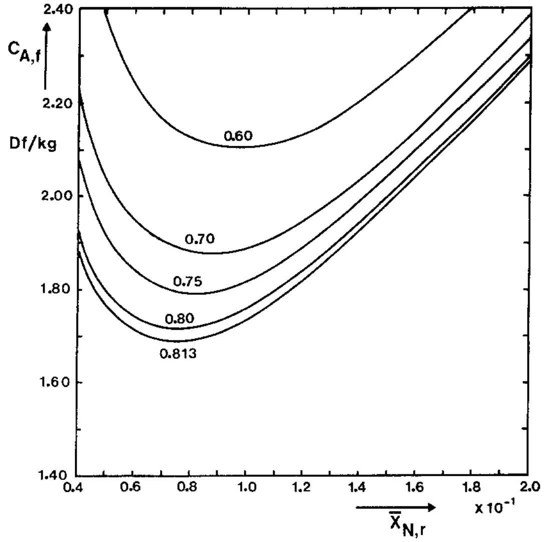

Fig. 6. The azoxytoluene formation costs ($C_{A,f}$) in Dfl kg^{-1} versus $\bar{x}_{N,r}$ with parameter η_s. Conditions; $\Delta x_{A,c} = 0.16, a = 0.03$.

From Fig. 4 it follows that the lowest costs are almost independent of a.

Figure 5 shows that the influence of $\Delta x_{A,c}$ on $C_{A,f}$ is very small. The influence of the chemical yield (η_s) on $C_{A,f}$ is high. The lowest formation costs will, of course, occur at the maximum chemical yield of 0.813, determined by the restriction given in Equation 11.

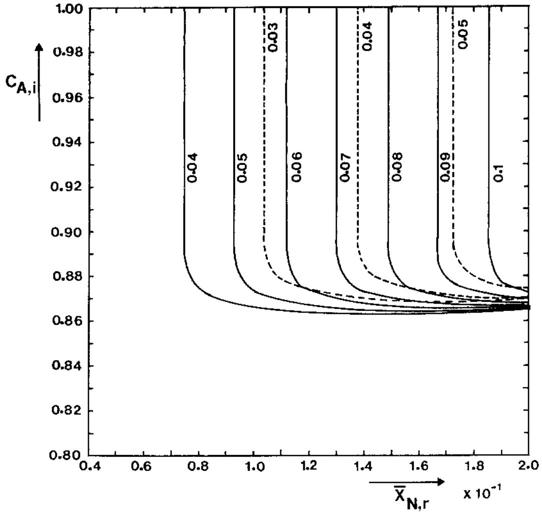

Fig. 7. The azoxytoluene isolation costs ($C_{A,i}$) in Dfl kg^{-1} produced azoxytoluene versus $\bar{x}_{N,r}$ with parameter $\Delta x_{A,c}$. Conditions; dotted line, $\eta_s = 0.81, a = 0.1$; solid line, $\eta_s = 0.80, a = 0.01$.

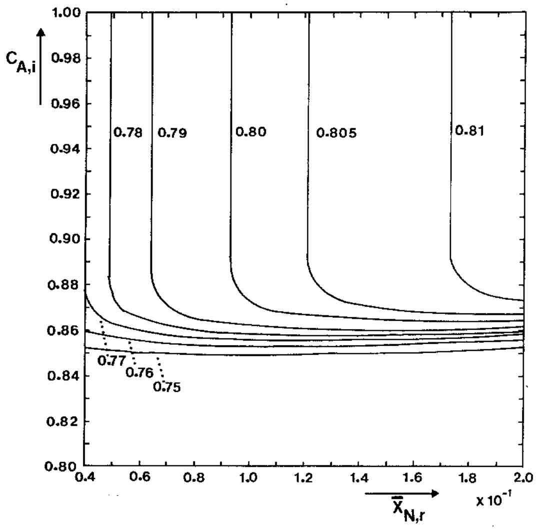

Fig. 8. The azoxytoluene isolation costs ($C_{A,i}$) in Dfl kg^{-1} versus $\bar{x}_{N,r}$ with parameter η_s. Conditions; $\Delta x_{A,c} = 0.05, a = 0.1$.

4.2. *The azoxytoluene isolation*

Calculations show that the influence of a on the isolation costs ($C_{A,i}$) is low. The isolation costs, as a function of $\bar{x}_{N,r}$, η_s and $\Delta x_{A,c}$ are represented in Figs. 7–8.

4.3. *The removal of water*

It has been found that the influence of a on the

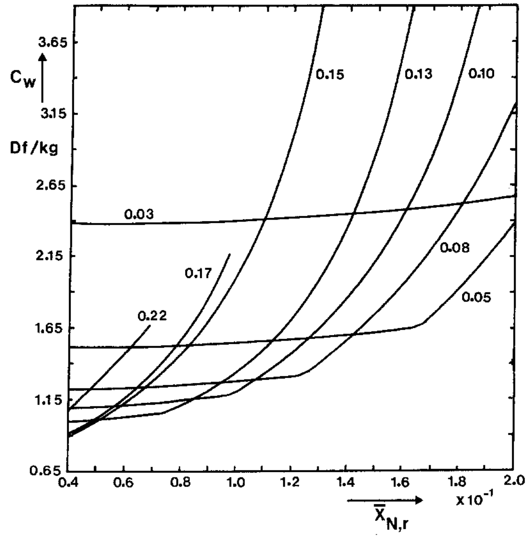

Fig. 9. The water removal costs (C_W) in Dfl kg^{-1} produced azoxytoluene versus $\bar{x}_{N,r}$ with parameter $\Delta x_{A,c}$. Conditions; $a = 0.05$, $\eta_s = 0.813$.

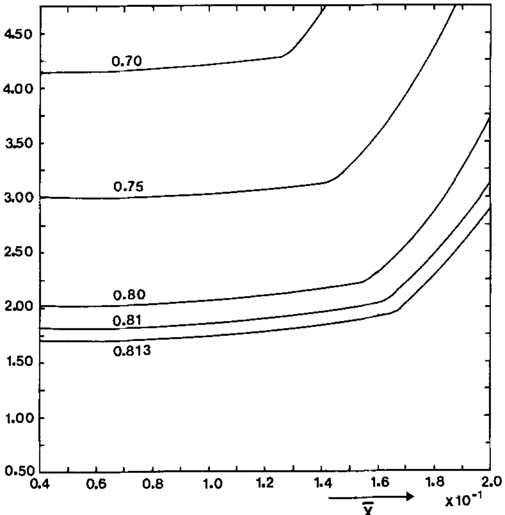

Fig. 10. The water removal costs (C_W) in Dfl kg^{-1} versus $\bar{x}_{N,r}$ with parameter η_s. Conditions; $\Delta x_{A,c} = 0.05$, $a = 0.05$.

water removal costs (C_W) is low. C_W as a function of $\bar{x}_{N,r}$, η_s and $\Delta x_{A,c}$ is represented in Figs. 9–10.

If $\Delta x_{A,c}$ and $\bar{x}_{N,r}$ are low, C_W is high because a large flow of solution has to be distilled. If $\Delta x_{A,c}$ and $\bar{x}_{N,r}$ are high, C_W is also high because a small flow of solution needs a very good separation. At very high values of $\Delta x_{A,c}$ and $\bar{x}_{N,r}$ the flow of solution is too small to remove enough water. At low values of η_s, much water has to be distilled.

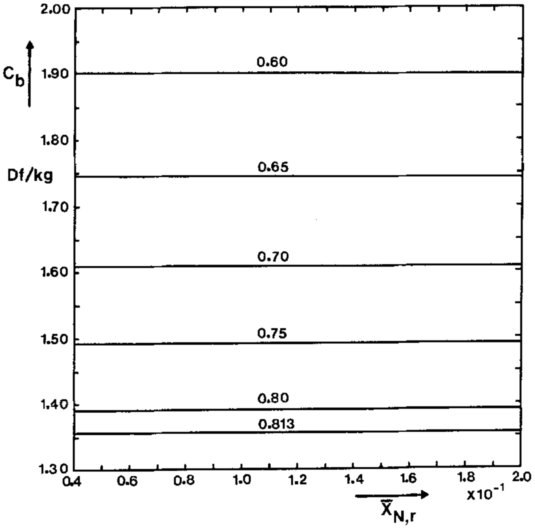

Fig. 11. The by-product removal costs (C_b) in Dfl kg^{-1} versus $\bar{x}_{N,r}$ with parameter η_s. Conditions; $\Delta x_{A,c} = 0.16$, $a = 0.03$.

4.4. *The removal of by-products*

The costs of the by-product removal $(C)_b$ are almost independent of $\bar{x}_{N,r}$, $\Delta x_{A,c}$ and a. Figure 11 represents C_b as a function of the chemical yield.

4.5. *The total process costs at the optimal conditions*

Figures 7–8 show that the boundaries for $\Delta x_{A,c}$, η_s and $\bar{x}_{N,r}$ are determined by the azoxytoluene isolation process. These boundaries are almost independent of a. The optimum parameters $\Delta x_{A,c}$, η_s and $\bar{x}_{N,r}$ are determined by summation of $C_{A,i}$, $C_{A,f}$, C_W and C_b (Fig. 12). It has been found that the optimum parameters are $\eta_s = 0.81$, $\Delta x_{A,c} = 0.05$ and $\bar{x}_{N,r} = 0.18$. In practice it is more appropriate to use a broad minimum, because it can be controlled more easily. Therefore, a more convenient optimum is $\eta_s = 0.80$, $\Delta x_{A,c} = 0.06$ and $\bar{x}_{N,r} = 0.13$. Knowing these parameters, from Fig. 4 it follows that $a = 0.02$.

The total process costs at the optimal values of η_s, a, $\bar{x}_{N,r}$ and $\Delta x_{A,c}$ are Dfl 6.39 per kg produced azoxytoluene (specification in Table 2). The calculated price has only limited significance because the cost figures used in the calculations are estimations. The cost is much influenced by

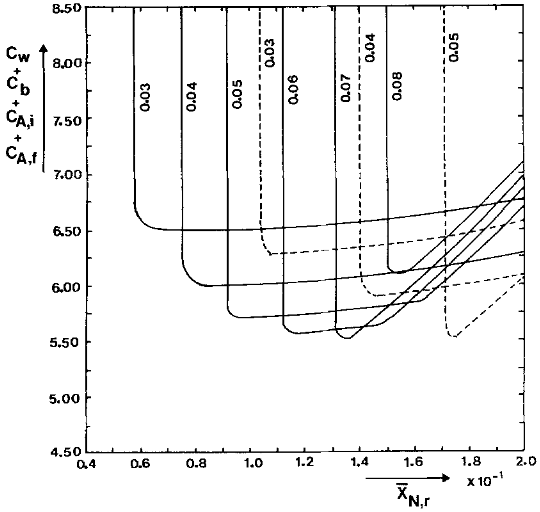

Fig. 12. The total production costs ($C_W + C_b + C_{A,i} + C_{A,f}$) in Dfl kg^{-1} produced azoxytoluene versus $\bar{x}_{N,r}$ with parameter $\Delta x_{A,c}$. Conditions; solid lines, $\eta_s = 0.80$, $a = 0.1$; dotted lines; $\eta_s = 0.81$, $a = 0.1$.

Table 2. The process costs specification at the optimum parameters; $\eta_s = 0.80$, $a = 0.02$, $\bar{x}_{N,r} = 0.13$, $\Delta x_{A,c} = 0.06$

Process part	*Costs per kg azoxytoluene* (Dfl)
Azoxytoluene formation	1.70
Azoxytoluene isolation	0.86
Water removal	1.85
By-product removal	1.38
Additional	0.60
Total process costs	6.39

external factors like integration of this process in a larger factory, the possibilities of treatment or regeneration of the waste water within the factor and local energy prices.

5. Final remarks

The calculations have shown that the economically optimum electrolysis conditions (current density, electrolyte composition) are strongly influenced by the additional processes, needed for isolation of the product and regeneration of the solution.

Consequently, the additional processes also have to be taken into account when designing the electrolysis process. The outlined cost calculation gives a general method to determine the influence of the process parameters on the total costs for the process scheme of Fig. 1.

The calculation has been done with ethanol–water mixtures as the catholyte solvent. From a brief literature study, it has been concluded that using methanol, instead of ethanol as the organic solvent, has a positive influence on the distillation performance. Moreover, it has been found experimentally, that this change of solvent has no negative effect on the isolation of azoxytoluene. Investigations on the reduction of nitrotoluene in methanol–water mixtures will give a decisive answer on the usefulness of methanol. The outlined calculation method can also be applied to calculate the process costs at the use of methanol, using the same process scheme.

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