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THE FUZZY EXPERIMENTAL MULTIOBJECTIVE OPTIMIZATION OF THE ELECTROCHEMICAL REDUCTION PROCESS OF MALEIC ACID TO SUCCINIC ACID

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The fuzzy experimental multiobjective optimization (FEMO) of the electrochemical reduction of maleic acid(I) to succinic acid is presented.

As partial criteria the yield of succinic acid (II) were taken and the amount of wastes obtained.

The objective function was presented in the form the ideal points. The values of weights of the partial criteria form the ideal points. The values of weights and ideal points were presented in a fuzzy form. As polyoptimal such a solution was assumed for which the yield of succinic acid (II) was 87% and the amount of wastes was 0.14 kg H_2SO_4/kg product.

Introduction

Succinic acid (II) is an important intermediate product in pharmaceutical, pesticides and cosmetic industries. In commercial production it is produced by reduction of maleic anhydride or maleic acid (I) with hydrogen in the presence of catalysts [1]. In literature there are some publications concerning investigations on electrochemical reduction of I or other electrochemical methods of II synthesis [2-5]. It was proved that this compound could be obtained in electrochemical elimination of Br from bromoacetic acid and next, dimerization of the intermediate product [6].

The aim of the present paper is to determine the optimum conditions for conducting the electrochemical reduction of I to II in a pilot-plant scale. The optimal process conditions may be determined in two ways: when the model of the process is known or without using the model of the process.

The first optimization method is recommended mainly when a good model reflecting strictly the process considered is available. In our case the mathematical model of the process should include a system of equations describing, among other things, the chemical kinetics of the process, mass transfer and hydrodynamics. In these equations such constants would appear (e.g. kinetic constants, diffusion coefficients) which could be determined on the basis of a number of experiments. Having this in mind it was decided to carry out the optimization without using the model of the process, i.e. to employ an experimental optimization.

The aim of the experiment was to find such values of independent variables x_i , $i = 1,...,5$, for which the degree of I to II inversion, that is y_1 , attains the highest possible value and the amount of wastes produced in the process, that is y_2, is possibly the lowest. As it is not possible to satisfy the condition that $y_1 = \max y_1$ and $y_2 = \min y_2$, in a given range of changes for x_i, $i = 1,...,5$, the solution we are searching for, will not be an optimal but a compromise one. A problem posed in this way should be solved by multiobjective experimental optimization (MEO). Due to the form of objective function the application of MEO requires the knowledge of utopia points and weights determining the significance of both criteria. The selection of weights and utopia points has been discussed in paper [7]. This problem needs the application of a fuzzy set theory. Therefore in the present work a fuzzy multiobjective experimental optimization is employed (FEMO). A more detailed description of this optimization method was given in papers [8-12].

Table 1. Experimental conditions and results

Sample	Concentration		Current intensity, x_3, [A]	Temperature, x_4, [K]	Electric charge, x_5, [F/mol]	Yield, y_1, [%]	Amount of wastes per 1 kg of product, y_2, [kg]
	I, x_1, [mol/dm^3]	H_2SO_4, x_2, [%]					
1	0.50	3.55	0.91	297.2	1.87	42	1.43
2	1.50	3.55	0.91	297.2	1.87	58	0.35
3	1.00	7.89	0.91	297.2	1.87	62	1.08
4	1.00	5.00	1.65	297.2	1.87	82	0.52
5	1.00	5.00	1.10	301.2	1.87	81	0.52
6	1.00	5.00	1.10	298.0	2.64	89	0.48
7	1.00	2.50	1.35	299.1	2.18	85	0.25
8	1.00	2.80	1.27	301.0	2.30	59	0.40
9	1.00	2.50	0.57	299.8	2.47	85	0.25
10	1.00	2.50	0.91	302.0	2.00	81	0.26
11	1.70	2.45	1.09	302.4	2.40	87	0.14

Experimental

Equipment

Experiments were carried out in a typical electrolyser of H type with a sintered glass diaphragm G-4.

Volume of cathode compartment - 0.05 dm^3
Volume of anode compartment - 0.03 dm^3
Cathode: acid-proof sheet 1H18N9T - 0.04 dm^2
Anode: platinum grid - 1.0 dm^2
Anolyte: 10% H_2SO_4

The composition of catholyte and process conditions are given in *Table 1*. Feeder cable, type 5353M (UNITRA-UNIMA), thermostat U-2 (MLW), magnetic stirrer, type 318 (UNIPAN) were applied.

The degree of inversion of I into II was determined by analysis of ^{1}H NMR for an investigated sample and a standard sample with a given amount of II (internal standard H_2O, Tesla 80 Mhz, comparison with integration of methylene groups II). The error of the method is less than 5 %.

Chemicals used

Maleic acid (I) purum POCH - Gliwice
Sulphuric acid purum 98% POCH - Gliwice

Results and Calculations

On the basis of preliminary investigations the following ranges of variables x_i, $i = 1,...,5$ were selected.

Concentration of maleic acid (I) $0.2 \leq x_1 \leq 2.0$ [mol/dm^3]
Concentration of H_2SO_4 $0 \leq x_2 \leq 10$ [%]
Current intensity $0.2 \leq x_3 \leq 2.0$ [A]
Temperature $293 \leq x_4 \leq 303$ [K]
Electric charge $1 \leq x_5 \leq 3$ [F/mol]

The optimization criteria were the functions y_1, y_2, where y_1 is degree of inversion I to II , y_2 is the amount of wastes produced during the process. The value of y_2 was determined as an amount of H_2SO_4 (in kg) which should be used in an electrochemical process to obtain 1 kg of II.

The values of x_i^* , $i = 1,...,5$ were standardized according to *Eq. 1*

$$x_1 = p_i + x_i^* \Delta_i \qquad (1)$$

where :

$$p_i = \frac{\max x_i + \min x_i}{2}$$

$$\Delta_i = \frac{\max x_i + \min x_i}{2} \qquad i = 1,...,5$$

x_i = the standardized value of independent variables max x_i, $i = 1,...,5$. The experimental optimization was performed using a simplex method [13].

In the first step coordinates of six vertexes of the basic simplex were determined. These coordinates and the values of functions y_1 and y_2 of the vertexes are presented in *Table 1* (samples 1 through 6). In every point of the experiment the value of objective function was calculated

$$F = \tilde{w}_1 \otimes [y_1 - \tilde{y}_1^u] \oplus \tilde{w}_2 \otimes [y_2 - \tilde{y}_2^u] \qquad (2)$$

Table 2. Values of fuzzy weights and utopia points

	a	b	α	β
$\tilde{w}_1$	0.75	0.75	0.05	0.05
$\tilde{w}_2$	0.25	0.25	0.05	0.1
$\tilde{y}_1^0$	1	1	0.2	0
$\tilde{y}_2^0$	2	2	0	11

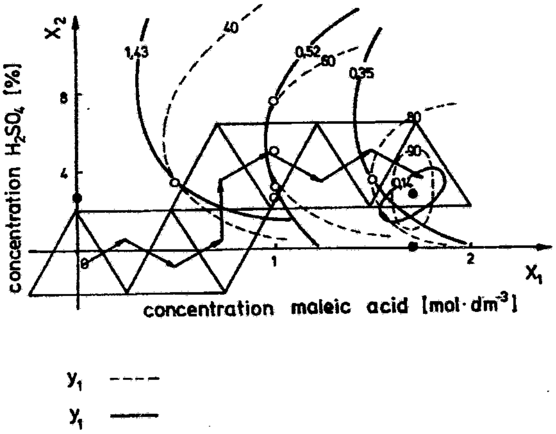

Fig.1. Geometrical interpretation of a following simplex method in X_1OX_2 plane x_1 - concentration of maleic acid, x_2 - concentration of H_2SO_4

where:

$\tilde{w}_1$ = the fuzzy weight of objective y_1

$\tilde{w}_2$ = the fuzzy weight of objective y_2

$\tilde{y}_1^0$, $\tilde{y}_2^0$ = fuzzy and utopia points of optimization criteria, respectively

y_1, y_2 = the values of optimization criteria.

The values of fuzzy weights and utopia points are illustrated in *Table 2*.

The form of the objective function is a result of the multiobjective optimization method called the utopia point method [14].

In the next step, from six vertexes of the simplex a vertex in which the value of function F was a maximum one, was rejected. The coordinates of a new simplex vertex were calculated according to the following equation:

$$x_i=\frac{2}{n}\left(x_1+x_2+\dots x_{j-1}+x_{j+1}+\dots+x_{n+1}\right)-x_j=\frac{2}{n}\sum_{i=1}^{n+1}x_i-\left(\frac{2}{n}+1\right)x_j \qquad (3)$$

$$i=1,\dots,5$$

where n is the number of independent variables, j is the number of the simplex vertex for which the value of function (2) is a maximum one.

The vertex determined by *Eq. (3)* is symmetrical to the vertex rejected in relation to hypersurface containing the other vertexes. After the procedure was repeated 4 times, it was observed that values of function (2) in subsequently determined simplex vertexes differ slightly from one another. This was the reason why the procedure was stopped in the 11th vertex. A geometrical interpretation of the simplex following method is presented in *Fig. 1-4*.

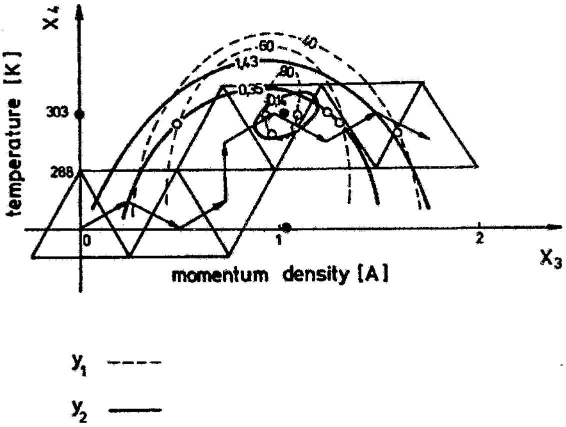

Fig.2. Geometrical interpretation of a following simplex method in X_3OX_4 plane

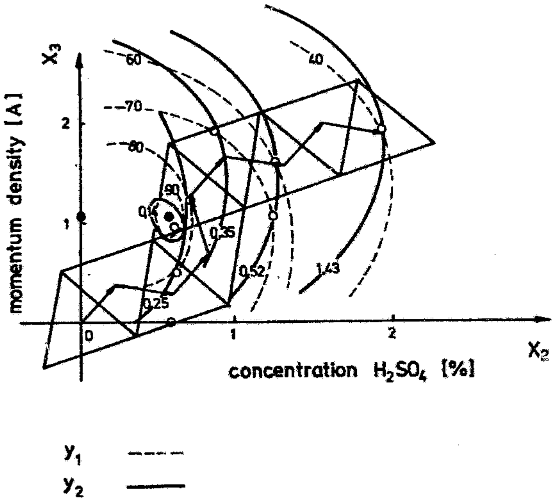

Fig.3. Geometrical interpretation of a following simplex method in X_4OX_5 plane
x_2-concentration of H_2SO_4, x_3 - current density

Using the fuzzy experimental multiobjective optimization methods such values of independent variables x_i, $i = 1,\dots,5$ were found, for which the yield of y_1 reduction and the amount of wastes y_2 attain a compromise solution achieve the values:

x_1 - concentration of maleic acid(I): 1.70 mol/dm^3

x_2 - concentration of H_2SO_4: 2.45 %

x_3 - current density = (current intensity)/(geometric surface): 27.25 A/dm^2

x_4 - temperature 302.4 K

x_5 - electric charge 2.4 F/mol

The yield of I reduction to II in those conditions is 87% and the amount of wastes is 0.14 kg per 1 kg of product.

On the basis of the above investigations a pilot-plant installation for a continuous production of II was designed [15].

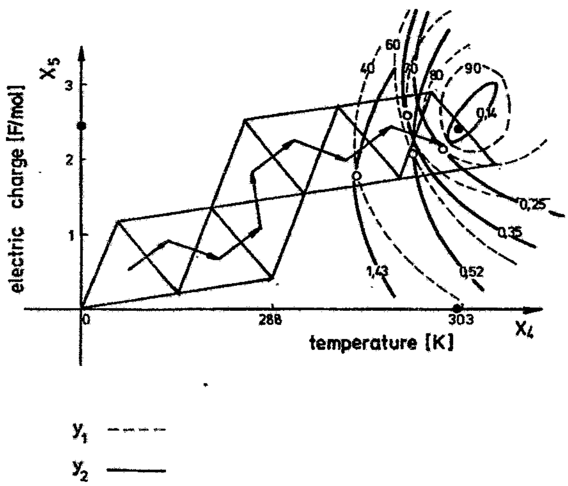

Fig.4. Geometrical interpretation of a following simplex method in X_4OX_5 plane
x_4 - temperature , x_5 - electric charge

Conclusions

In the paper the applicability of the fuzzy experimental multiobjective optimization method to the electrochemical reduction of maleic acid (I) to succinic acid (II) has been presented. The method enables omitting of the stage of building a mathematical model of the process and ensures flexibility in the optimization by employing the fuzzy numbers theory. The application of multioptimality allows various aspects of the process investigated to be treated in a more detailed way.

The following optimal values of the independent variables were obtained:

x_1 - concentration of maleic acid (I) 1.7 mol/dm^3
x_2 - concentration of H_2SO_4 2.45 %
x_3 - current density 27.25 A/dm^2
x_4 - temperature 302.4 K
x_5 - electric charge 2.4 F/mol

For the above variables the yield of succinic acid was 87% and the quantity of wastes was 0.14 kg/1 kg of product.

On the basis of the investigation a unit for production of II from I in a continuous operation has been designed.

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