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 H₂SO₄/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 \( x_i \), \( i = 1, \ldots, 5 \), 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 \( x_i \), \( i = 1, \ldots, 5 \), 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

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I, x_1, [\text{mol/dm}^3]$</th>
<th>$H_2SO_4, x_2, [%]$</th>
<th>Current intensity, $x_3, [\text{A}]$</th>
<th>Temperature, $x_4, [\text{K}]$</th>
<th>Electric charge, $x_5, [\text{F/mol}]$</th>
<th>Yield, $y_1, [%]$</th>
<th>Amount of wastes per 1 kg of product, $y_2, [\text{kg}]$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
<td>3.55</td>
<td>0.91</td>
<td>297.2</td>
<td>1.87</td>
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<td>1.43</td>
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<td>3.55</td>
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<td>297.2</td>
<td>1.87</td>
<td>58</td>
<td>0.35</td>
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<td>7.89</td>
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<tr>
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<td>5.00</td>
<td>1.65</td>
<td>297.2</td>
<td>1.87</td>
<td>82</td>
<td>0.52</td>
</tr>
<tr>
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<td>1.00</td>
<td>5.00</td>
<td>1.10</td>
<td>301.2</td>
<td>1.87</td>
<td>81</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>1.00</td>
<td>5.00</td>
<td>1.10</td>
<td>298.0</td>
<td>2.64</td>
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</tr>
<tr>
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<td>2.50</td>
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</tr>
<tr>
<td>8</td>
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<td>2.80</td>
<td>1.27</td>
<td>301.0</td>
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<td>0.40</td>
</tr>
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<td>2.50</td>
<td>0.57</td>
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<td>2.47</td>
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<td>0.91</td>
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<td>1.09</td>
<td>302.4</td>
<td>2.40</td>
<td>87</td>
<td>0.14</td>
</tr>
</tbody>
</table>

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$_2$SO$_4$

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$_2$O, 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 $x_i, i = 1,\ldots, 5$ were selected:

- Concentration of maleic acid (I) $0.2 \leq x_1 \leq 2.0$ [mol/dm$^3$]
- Concentration of H$_2$SO$_4$ $0 \leq x_2 \leq 10$ [%]

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$_2$SO$_4$ (in kg) which should be used in an electrochemical process to obtain 1 kg of II.

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

$$x_i = p_i + x_i^* \Delta_i$$

where:

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

$$\Delta_i = \frac{\text{max} x_i + \text{min} x_i}{2} \quad i = 1,\ldots, 5$$

$x_i$ = the standardized value of independent variables $x_i, i = 1,\ldots, 5$. 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

$$F = \bar{w}_1 \otimes (y_1 - \bar{y}_1) \otimes \bar{w}_2 \otimes (y_2 - \bar{y}_2)$$

(2)
Table 2. Values of fuzzy weights and utopia points

<table>
<thead>
<tr>
<th></th>
<th>a</th>
<th>b</th>
<th>α</th>
<th>β</th>
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</thead>
<tbody>
<tr>
<td>$\tilde{w}_1$</td>
<td>0.75</td>
<td>0.75</td>
<td>0.05</td>
<td>0.05</td>
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<tr>
<td>$\tilde{w}_2$</td>
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<td>0.25</td>
<td>0.05</td>
<td>0.1</td>
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<tr>
<td>$\bar{y}^1$</td>
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<td>1</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>$\bar{y}^2$</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>11</td>
</tr>
</tbody>
</table>

Fig. 1. Geometrical interpretation of a following simplex method in $X_1OX_2$ plane $x_1$ - concentration of maleic acid, $x_2$ - concentration of H2SO4

where:
- $\tilde{w}_1$ = the fuzzy weight of objective $y_1$
- $\tilde{w}_2$ = the fuzzy weight of objective $y_2$
- $\bar{y}^1$, $\bar{y}^2$ = 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:

$$x_i = \frac{2}{n} \left( x_1 + x_2 + \cdots + x_{i-1} + x_{i+1} + \cdots + x_{n+1} \right) - x_j =$$

$$\frac{2}{n} \sum_{i=1}^{n+1} x_i - \left( \frac{2}{n+1} \right) x_j$$

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.

Using the fuzzy experimental multiobjective optimization methods such values of independent variables $x_i$, $i = 1, \ldots, 5$ 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(l): 1.70 mol/dm³
- $x_2$ - concentration of H2SO4: 2.45 %
- $x_3$ - current density = (current intensity)/(geometric surface): 27.25 A/dm²
- $x_4$ - 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. 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 H2SO4, $x_3$ - current density
On the basis of the investigation a unit for production of II from I in a continuous operation has been designed.

Acknowledgement

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REFERENCES

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