Mathematical Modelling and Optimization of Synthes Process of Dihydroxyfumarate Acid Sodium Salt

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Abstract

In this paper the results of a study concerning the obtaining of dihydroxyfumarate acid sodium salt via oxidation of tartaric acid with hydrogen peroxide in the presence of Fe^{2+} ions as catalyst and hydroquinone are presented. A mathematical empirical model describing the dependence between the synthesis yield and process factors has been settled. On the basis of this equation the optimal conditions of the experiment have been determined. Given these conditions the final products yield is the best i.e. 36,7 %.

Keywords: *tartar acid, acid salt of sodium dihydroxyfumarate, antioxidant, mathematical model, experiment optimisation.*

Introduction

At present in order to stabilize the red-ox potential of the obtaining process of raw winery material, a number of conservation agents is used. To this end, processes that imply the use of endogen wine substances that do not pose any threat to human health are being developed. This category is represented by dihydroxyfumarate acid sodium salt that is used for practical purposes to stabilize the raw winery material.

There are two methods of obtaining dihydroxyfumarate acid sodium salt by oxidation of tartaric acid according to the Fenton reaction. The shortcoming of these methods consists in low yields of the final products, in particular – 8,8% and 17,1% [1,2]. These procedures are performed in the presence of hydroquinone and Fe^{2+} ions as catalyst and at temperatures ranging from –5°C to -3°C with the use of 30 % hydrogen peroxide.

In dihydroxyfumaric acid aqueous phases a tautomeric equilibrium between the enole and ketone form is established. In the result of a study [3] it has been determined that the solid state of this acid represents the ketone form, namely oxaliglycolic acid. In the aqueous phase, at acid pH there prevails the ketone form, and with an increase in pH value, the equilibrium shifts to the enole form (at pH 4 there exist 80% of oxaliglicolic acid and 20% dihydroxyfumaric acid).

COOH COOH COOH

H – C – OH H_2O_2, Fe^{2+} C – OH C = O

| ⟵ ⟶ | ⟶ | H – C – OH C –

OH CH – OH

COOH COOH COOH

Separation of dihydroxyfumaric acid from the reaction mixture is performed via adding sodium chloride.

This particular study has as purpose the obtaining of higher yields of dihydroxyfumarate acid sodium salt by settling the optimal conditions of the experimental process.

Materials and Methods

Reagents

During the experiment the following reagents have been used: (+) – tartaric acid *Reahim* (Ural, Russia), hydrogen peroxide*Reahim* (Ural, Russia), hydroquinone *Reahim* (Ural, Russia), the Mohr's salt *Reahim* (Ural, Russia), sodium chloride *Reahim* (Ural, Russia).

Apparatus

A reaction vessel provided by an agitation and a cooling system has been used.

Procedure

The method of dihydroxyfumarate acid sodium salt synthesis consists in the oxidation of tartaric acid with hydrogen peroxide at a temperature ranging from -5°C to - 3°C in the presence of Fe^{2+} as catalyst and hydroquinone. In order to separate dihydroxyfumaric acid from the aqueous phase, sodium chloride has been added with the intention to precipitate the sediment that was formed as a result of the reaction:

Fe^{2+} + NaCl

→ → $C_4H_6O_6$ + H_2O_2 $C_4H_4O_6$ +

$2H_2O$ $C_4H_3O_6Na$ + HCl

$C_6H_4(OH)_2$

In the reaction vessel, provided by an agitation and a cooling system, 150 g of tartaric acid were introduced followed by their dissolution in 100 ml of distilled water. The 4.2 g of Mohr's salt and 0.15 g of hydroquinone have been added, and the mixture was cooled down to –10°C. Then, 45 ml of H_2O_2 have been carefully inserted since the temperature didn't have to exceed the values comprised between –5°C and –3°C. As the entire amount of hydrogen peroxide was added, the mixture was agitated at established temperature for 30 minutes. Then 300 ml of cold prepared 300 g/l NaCl solution was added, permanently maintaining the reaction at a 0°C temperature. The reaction mixture was stored in a cool place for 24 hours, then the sediment was filtered, washed with small quantities of cold water and dried.

In view of gaining a superior effect of process performance the synthesis yield of dihydroxyfumarate acid sodium salt has been used as optimization criteria calculated as follows:

$$Y = (m_p / m_t) \cdot 100\% \qquad (1)$$

where Y – final product's synthesis yield, %; m_p – mass of final product obtained experimentally, g; m_t - mass of final product calculated theoretically, g.

Results and Discussion

Process Modelling

The studies concerning the mathematical modelling of dihydroxyfumarate acid sodium salt synthesis process were aimed at establishing a correlation between the synthesis yield and the variables influencing the process, i.e. the quantities of hydrogen peroxide, sodium chlorate, Mohr's salt and hydroquinone.

Thus, real values of process variables were chosen arbitrarily, their limits and encoding being given in (**Table 1**).

In order to determine the empirical model of the process the planning of the experiment has been carried out. The rotable experimental design used, of the 2^4 type, is given in (**Table 2**).

The mathematical model of the process, in a general form, represents a second order polynomial as follows:

(1)

Coefficients of regression equation have been calculated by means of equation (3) [4]:

$$b = (X^T \cdot X)^{-1} \cdot X^T \cdot Y \qquad (3)$$

where **b** – column matrix of regression coefficients;

X – expansive matrix of code variables;

Y – column matrix of synthesis yield.

In a final manner, the process of dihydroxyfumarate acid sodium salt obtaining is described by the regression equation (4).

$$\hat{Y} = 14.414 + 4.049 \cdot x_1 + 2.886 \cdot x_2 - 3.901 \cdot x_4 - 1.808 \cdot x_1^2 + 2.944 \cdot x_1 x_2 \qquad (4)$$

Regression coefficients of the equation (4) represent meaningful coefficients retained via testing significance of all coefficients. The test involved comparison of absolute values of the variables with their confidence intervals - Δb:

$$|b_p| > |\Delta b_p| \qquad (5)$$

If the condition (5) is true the b_p coefficient is considered significant, else the corresponding factor is not meaningful and isn't involved in the mathematical modelling.

The confidence intervals have been settled by calculating dispersions of the regression coefficients and multiplying these values with tabulated value of Student's test ($t_{0.05(6)}$=2.45). The correspondence between the mathematical model and experimental data has been verified by applying Fisher's test. In this sense, the calculated value of the Fisher's test (F_C) was compared to the tabulated value (F_T). The calculated value of the Fisher's test was F_C = 3.62. Since for a confidence level p = 0.05 and f_1 = 25, f_2 = 6 degrees of freedom result $F_T(f_1,f_2)$ = 3.88 and $F_C < F_T(f_1,f_2)$, the mathematical model is truthfully, i.e. the accordance between the model and experimental data is statistically confirmed [4, 5].

In **Figures 1**, **2** and **3** the dependencies between the variables and synthesis yield are depicted. Contours lines show that increasing of x_1 factor will give higher values of the process yield, due to of the significant positive linear coefficient corresponding to this factor. The enhancing of x_2 factor also will improve the yield but in the reduced mode. The influence of $x_4$factor on the process yield is of the other way when compared to x_1 and x_2, i.e. the increase of the x_4 variable will diminish the process performance.

The not significant influence on the process performance is attributed to the x_3 factor since in accordance with the Student's test it was eliminated from the regression equation.

Process Optimization

Since the regression equation represents an objective function the next step of the investigation was meant to optimize the restricted objective function:

$$max\ \{\hat{Y}\ (x_1, x_2, x_4)\}$$

$$-\square\ \square\ x_i\ \square\ \square,\quad i = 1,2,4\ \ and\ \ \hat{Y}\ \square\ 100\ \% \qquad (6)$$

First of all, in order to determine the stationary point (S-center) the attempt of finding solution for the following equations system has been accomplished.

Since the determinant of the (7) equations system turns to zero the response surface has no center. In this case, the origin of a new coordinate system is located in the reference point that is the best experimental point with the coordinates $x_s = [1, 1, -1]^T$(see **table 2**).

(7)

To determine the optimal point the objective function was brought to the standard form. In considered case the standard form of the regression function is expressed via the following formula [4, 5]:

$$\hat{Y} -$$

$$Y_s = \square_1\square\square_1^2 + \square_2\square\ \square_2^2 + \square_4\square\square_4^2 \qquad (8)$$

where Y_s – value of the objective function in the reference point (Y_s = 26.386);

$\square_1$, $\square_2$, $\square_4$ - values of factors in the new coordinate system;

$\square_1$, $\square_2$, $\square_4$ – standard regression coefficients;

The standard regression coefficients have been calculated by determining the eigenvalues of (9) quadratic matrix [**5**]:

$$\det (\mathbf{B} - □ □ \mathbf{E}) = 0 \qquad (9)$$

where **B** denotes quadratic matrix of regression coefficients; **E -** identity matrix.

The obtained values of the standard regression coefficients are: $□_1$ = -2.631, $□_2$ = -0.823, $□_4$ = 0, thus, the standard equation that describing investigated process is:

$$\hat{Y} -26.386 = -2.631□□_1^2 + 0.823□□_2^2 \qquad (10)$$

In order to settle the optimal point of experiment the response surface has been explored in the region of the reference point by moving upon axis direction of positive coefficient, i.e. $□_2$. The displacement from the reference point upon the axis $□_2$ direction will improve the objective function. To maximize the performance of the extraction process the objective function has taken the values $\hat{Y} > Y_s$ and the moving upon axis $□_2$ has been accomplished. In this case $□_1$=0 and the standard equation becomes:

$$x_2 = \pm\sqrt{\frac{\hat{Y} - Y_s}{\lambda_2}}\ ; \qquad (11)$$

Modifying the value of function $\hat{Y}$ the keeping of imposed restriction upon the process variables has been checked. The optimal value of synthesis yield (adopted feasible maximum) calculated by the model is 40,64 % for next values of the code variables: x_1=2.0; x_2=2.0 and x_3=-2.0. So, the founded optimum is located on the boundary of valid region. The real optimal values of the process variables and the corresponding experimental yield are shown in (**Table 3**).

The synthesis yield obtained in the adopted optimal conditions represents the best experimental output. All calculations were carried out by means of MathCAD PRO software.

Conclusions

An empirical mathematical model has been developed in order to give the dependence between the performance and variables of the synthesis process of dihydroxyfumarate acid sodium salt.
The regression coefficients and contour lines show that increasing the H2O2 amount will give higher values of the process yield. Also, the higher quantities of sodium chlorate will

improve the synthesis yield but in a lesser manner than hydrogen peroxide. In the case of the hydroquinone, the increase of the hydroquinone amount will diminish the synthesis yield. The least influence on the process performance is attributed to Mohr's salt factor.
In order to determine the optimal conditions of experiment the regression equation settled via experiment design was brought to the standard form. The found optimum is situated on the boundary of the valid region.
The optimal conditions of the synthesis process are: hydrogen peroxide – 1.3 mol; sodium chloride – 292.5 g; hydroquinone – 0.07 and Mohr's salt – 4.2 g (adopted constant level). The experimental yield obtained under adopted optimal conditions represents the best experimental yield of the synthesis process of dihydroxyfumarate acid sodium salt that is 36.7 %.

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$$\hat{Y} = b_0 + \sum_{i=1}^{k} b_i \cdot x_i + \sum_{\substack{i=1 \\ j=1 \\ i \neq j}}^{k} b_{ij} \cdot x_i \cdot x_j + \sum_{i=1}^{k} b_{ii} \cdot x_i^2 \qquad (2)$$

where: $\hat{Y}$ - denotes the system response function (calculated synthesis yield);

b_o, b_i, b_{ij}, b_{ii} – coefficients of regression equation ;

x_i, x_j – independent variables (coded values) i,j=1 ... k.

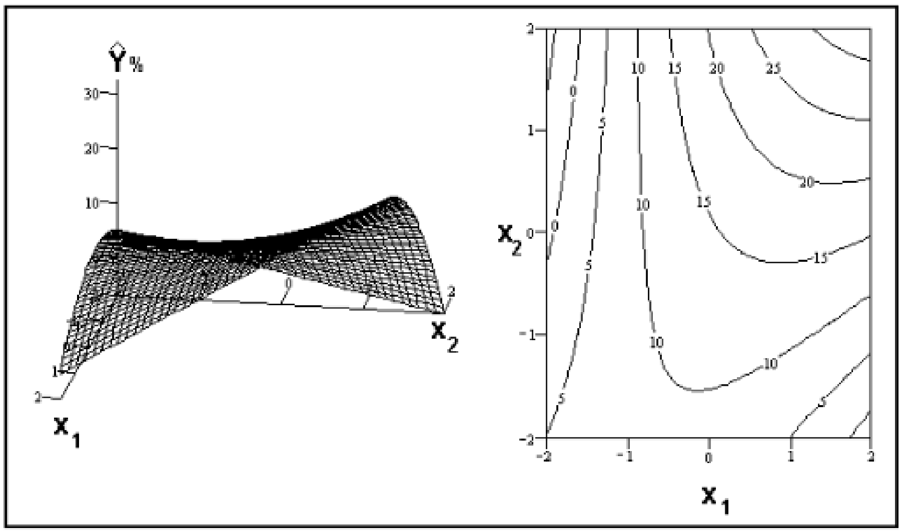
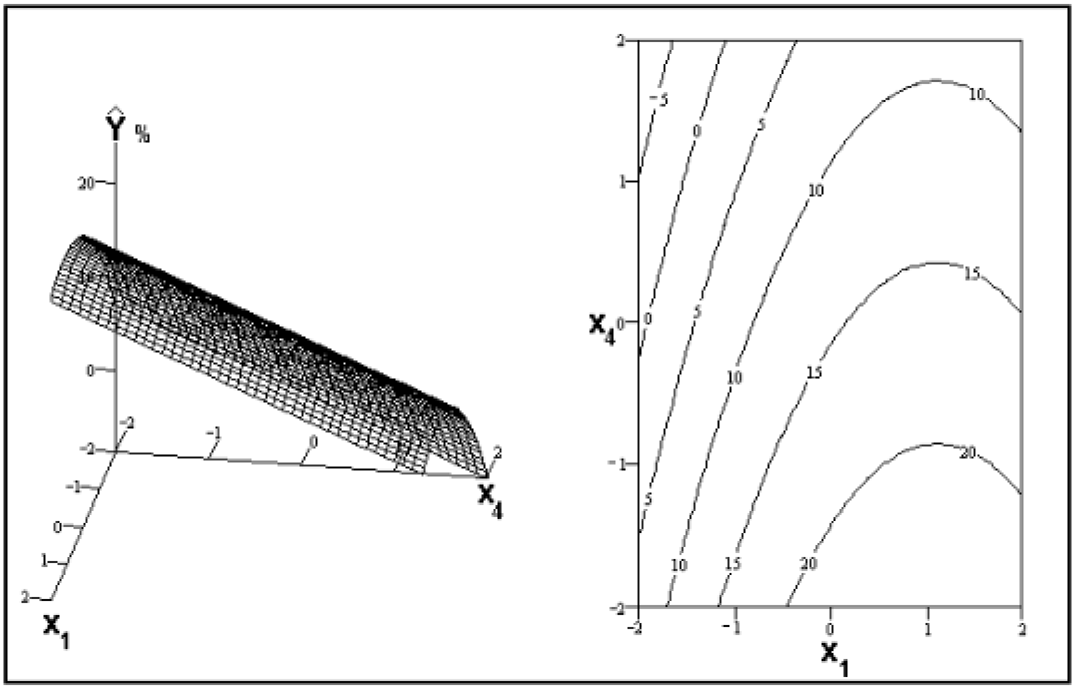


Figure 1. Response surface and contour response surface depending on x_1 and x_2 , x_4=0.

Figure 2. Response surface and contour response surface depending on x_2 and x_4 , x_1=0.



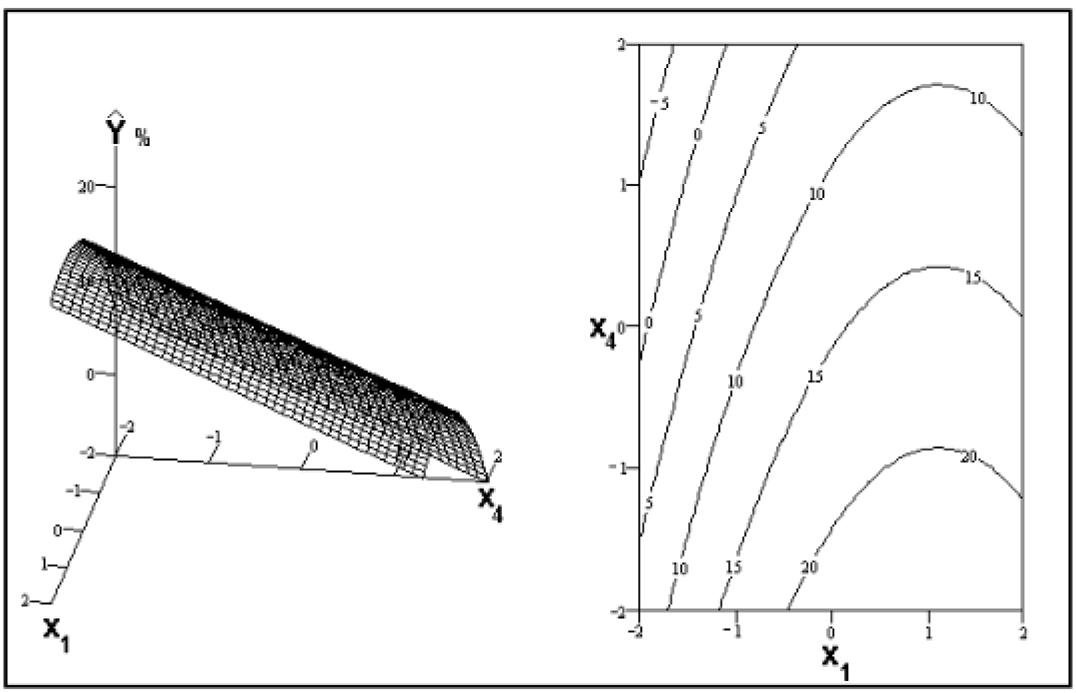


Figure 3. Response surface and contour response surface depending on x_1 and x_4 , x_2=0.

$$\frac{\partial \hat{Y}}{\partial x_1} = 0, \qquad \frac{\partial \hat{Y}}{\partial x_2} = 0, \qquad \frac{\partial \hat{Y}}{\partial x_4} = 0 \qquad (7)$$

Table 1. Real and coded values of the process variables (α = 2,04)

Process variables	Code	Real values of coded levels					Step
		- α	-1	0	+1	+α	
v H_2O_2, [mol]	x_1	0.2	0.4	0.7	1.0	1.4	0.3
m NaCl, [g]	x_2	45.0	90.0	157.5	225.0	315.0	167.5
m $(NH_4)_2SO_4$, [g]	x_3	2.10	4.20	7.35	10.50	14.70	3.15
m $C_6H_4(OH)_2$, [g]	x_4	0.075	0.150	0.262	0.375	0.525	0.112

Table 2. Experimental Design of the 2^4 type

No. of Experiment	x_1	x_2	x_3	x_4	Y, %
1	1	1	1	1	26.20
2	-1	-1	1	1	0.80
3	1	-1	-1	1	15.20
4	-1	1	-1	1	9.70
5	1	-1	1	-1	17.26
6	-1	1	1	-1	10.60
7	1	1	-1	-1	32.24
8	-1	-1	-1	-1	12.42
9	1	-1	1	1	0.50
10	-1	1	1	1	1.00
11	1	1	-1	1	22.20
12	-1	-1	-1	1	7.00
13	1	1	1	-1	28.00
14	-1	-1	1	-1	9.20
15	1	-1	-1	-1	27.20
16	-1	1	-1	-1	10.20
17	0	0	0	0	15.70
18	α	0	0	0	0.00
19	- α	0	0	0	6.00
20	0	α	0	0	15.00
21	0	- α	0	0	5.80
22	0	0	α	0	14.00
23	0	0	- α	0	9.30
24	0	0	0	α	0.00
25	0	0	0	- α	13.40

Table 3. The optimal conditions of the synthesis experiment of dihydroxyfumarate acid sodium salt

v H_2O_2, [mol]	**m NaCl, [g]**	m $(NH_4)_2SO_4$, [g]	**m $(C_6H_4(OH)_2$, [g]**	**Y, [%]**
1.3	292.5	4.20*)	0.07	36.7

*) – Adopted constant level.