

## Mathematical Modelling and Optimization of Tartaric Acid Separation Process from Aqueous Phase by Reactive Extraction

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### Abstract

*This paper presents the results of the study concerning the tartaric acid reactive extraction process from aqueous phase using Amberlite LA-2-butyl acetate mixture. A regression equation has been proposed to express the correlation between process performance and the independent variables influencing the process, i.e. extraction time, amine concentration and vibrational intensity. Based on this equation optimal conditions of the experiment have been determined. The spatial representation of extraction yield versus independent variables were drawn.*

**Keywords:** Reactive extraction, tartaric acid, wine-making wastes, mathematical modelling, experimental optimization.

### Introduction

Tartaric acid represents an economical significant oxyacid due to of using in various industrial branch like food, bread-making, pharmaceutical, textile, photochemical and electrotechnical industry. This oxyacid is obtained from wine-making wastes (wine yeast, tartar, squeezing and grain comes from the raw wine distillation).

In industry, tartaric acid is obtained via a series of the technological operations that require the consuming of large amounts of materials and energy. The conventional technology of the tartaric acid separation and purification involved the running of the following main stages: dissolving of tartaric compounds from wine-making wastes, precipitation of this compound in the calcium salts form, delivering of tartaric acid via sulphuric acid adding, concentration and crystallisation of finite product [1, 2].

Nowadays, the liquid-liquid reactive extraction process using amines compound represents an intense field of study. The main advantages of using these extraction agents are: i) the mechanism of reaction is similar with that one of the ion exchange separation, this fact allows estimation of the reaction course; ii) the reactive extraction process gives the high performances; iii) the large range of chemical compound can be separated using this procedure. Applications of the extraction process using amines compound are numerous. These extraction agents are used in order to separate metals, mineral acids and some organic compound like carboxylic acids, oxyacids, antibiotics and so on.

The separation of tartaric acid from aqueous phase via applying reactive extraction process represents an extremely advantageous alternative. This technique offers reduced consuming of materials and energy and, implicit, a lowering cost of the process realisation [3, 4].

## Materials and Methods

### Reagents

Amberlite LA-2 *Sigma-Aldrich* (Steinheim, Germany), butyl acetate *Merck* (Darmstadt, Germany), (+) – tartaric acid *Reahim* (Ural, Russia), sodium metavanadate *Reahim* (Ural, Russia), glacial acetic acid *Reactivul* (Bucharest, Romania) were used.

### Apparatus

An extraction device and the MLW T23D centrifugal separator have been used in order to extract tartaric acid from aqueous phase. The colorimetry assays were made by means of Spectromom 410 VIS spectrophotometer.

### Procedure

The experimental study deals with the tartaric acid separation from aqueous phase using reactive extraction process with Amberlite LA-2-butyl acetate mixture (organic phase). Amberlite LA-2 represents an amine extraction agent with high molecular weight.

Aqueous phase was composed of tartaric acid solution with concentration – 5 g/L. Organic phase was prepared by dissolving diverse quantities of Amberlite LA-2 in butyl acetate.

In order to achieve superior yields the extraction device with vibrational stirring has been used. This system offered the possibility to enhance the interfacial surface between both phases.

The experimental equipment was consisted of a glass column with 37 mm diameter and 240 mm height. The both phases were intensely mixed by means of the vibrational stirrer made-up of metallic perforated disk with 45 mm diameter and 17 per cent of free section. The vibrations were generated with a frequency of 50 Hz and an amplitude ranged from 0 to 4 mm.

The resulting emulsion was removed at the bottom of the extraction column and was separated in the centrifugal separator operated at the 2000 rotations per minute. The reactive extraction process was performed at the 1:1 volume proportion using 25 ml volumes.

The process evolution has been assessed via colorimetry measuring with potassium metavanadate at the 525 nm wavelength.

The reactive extraction yield (process performance) has been calculated using the equation (1):

$$Y = \left( 1 - \frac{C_{ar}}{C_a} \right) \cdot 100 \% \quad (1)$$

where  $Y$  – reactive extraction yield, % ;  
 $C_{ar}$  – tartaric acid concentration in organic phase, g/L;  
 $C_a$  – initially tartaric acid concentration in aqueous phase, g/L.

## Results and Discussion

### Process Modelling

The studies regarding the modelling of the tartaric acid reactive extraction process were aimed to settle a correlation between the extraction performances and the variables influencing the process, i.e. extraction time, amine concentration and vibration intensity.

In this purpose, real values of process variables and their variation limits were chosen in accordance with the preliminary tests and coding (**Table 1**).

**Table 1.** Real and coded values of the process variables ( $\alpha = 1,215$ ).

| Process variables            | Code           | Real values of coded levels |      |       |       |            | Step |
|------------------------------|----------------|-----------------------------|------|-------|-------|------------|------|
|                              |                | - $\alpha$                  | -1   | 0     | +1    | + $\alpha$ |      |
| Amine concentration, (g/l)   | x <sub>1</sub> | 15,7                        | 20,0 | 40,0  | 60,0  | 64,3       | 20,0 |
| Extraction time, (s)         | x <sub>2</sub> | 14                          | 20   | 50    | 80    | 86         | 30   |
| Vibrational intensity, (m/s) | x <sub>3</sub> | 39,2                        | 50,0 | 100,0 | 150,0 | 160,7      | 50,0 |

In order to determine the empirical equation of the extraction process the planning of the experiment has been performed. The used orthogonal experimental matrix, of the 2<sup>3</sup> type, is given in (**Table 2**).

**Table 2.** Orthogonal Experimental Matrix of the 2<sup>3</sup> type.

| No. of Experiment | x <sub>1</sub> | x <sub>2</sub> | x <sub>3</sub> | Y, %  |
|-------------------|----------------|----------------|----------------|-------|
| 1                 | 1              | 1              | 1              | 99,12 |
| 2                 | -1             | 1              | 1              | 85,41 |
| 3                 | 1              | -1             | 1              | 98,12 |
| 4                 | -1             | -1             | 1              | 85,83 |
| 5                 | 1              | 1              | -1             | 99,79 |
| 6                 | -1             | 1              | -1             | 85,41 |
| 7                 | 1              | -1             | -1             | 98,75 |
| 8                 | -1             | -1             | -1             | 82,08 |
| 9                 | $\alpha$       | 0              | 0              | 99,16 |
| 10                | - $\alpha$     | 0              | 0              | 75,00 |
| 11                | 0              | $\alpha$       | 0              | 99,16 |
| 12                | 0              | - $\alpha$     | 0              | 76,66 |
| 13                | 0              | 0              | $\alpha$       | 98,12 |
| 14                | 0              | 0              | - $\alpha$     | 98,00 |
| 15                | 0              | 0              | 0              | 97,50 |
| 16                | 0              | 0              | 0              | 98,14 |

The mathematical model of the process, in a general form, represents a second order polynomial of the following form [5]:

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

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

$b_0, b_i, b_{ij}, b_{ii}$  – coefficients of regression equation ;

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

The coefficients of the regression equation were calculated by following relationship [5]:

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

where  $\mathbf{b}$  – column matrix of the regression coefficients;

$\mathbf{X}$  – expansive matrix of code variables;

$\mathbf{Y}$  - column matrix of the extraction performance.

The equation describing correlation between the performance and variables influencing the tartaric acid reactive extraction process is of the following form:

$$\hat{Y} = 90.383 + 7.889 \cdot x_1 + 2.948 \cdot x_2 - 3.358 \cdot x_1^2 - 2.795 \cdot x_2^2 + 4.086 \cdot x_3^2 \quad (4)$$

Regression coefficients in equation (4) represent meaningful coefficients retained testing the significance of all coefficients. The test involved comparing of absolute values of the variables with their confidence intervals -  $\Delta b$ :

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

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

The confidence intervals were determined by calculating dispersions of the regression coefficients and multiplying these values with tabulated value of Student's test ( $t_{0.05(1)}=12.71$ ). The accordance between the model and experimental data was verified by applying Fischer's test. In this sense, the calculated value of the Fisher's test ( $F_C$ ) was compared with tabulated value ( $F_T$ ). The calculated value of the Fisher's test was  $F_C = 115$ . Since for a confidence level  $p = 0.05$  and  $f_1 = 9$ ,  $f_2 = 1$  degrees of freedom result  $F_T(f_1, f_2) = 240$  and  $F_C < F_T(f_1, f_2)$ , the mathematical model is truly, i.e. the accordance between the model and experimental data is statistically accepted [5, 6].

The both calculated and experimental values of the extraction yield are shown in (Figure 1). These values were settled for sixteen runs that had been performed.

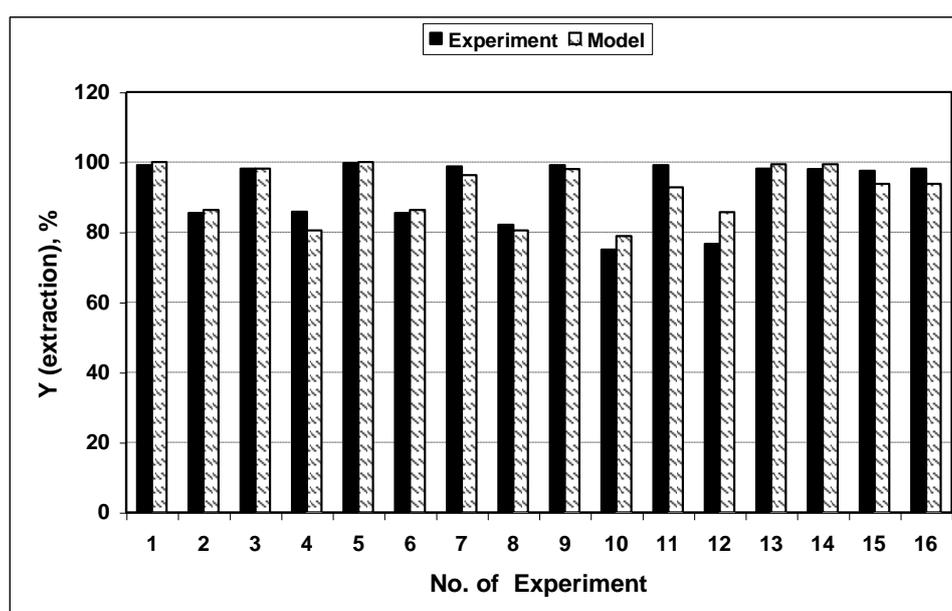


Figure 1. The yield of tartaric acid extraction process, experimental data versus model data.

In (Figures 2, 3 and 4) the dependence between the extraction performance and process factors are illustrated. Contours diagrams show that increasing of  $x_1$  factor will give superior values of the extraction yield, due to of significant positive linear coefficient corresponding to this factor. The enhancing of  $x_2$  factor also will improve the extraction yield but in the lessened manner. The least influencing on the process performance is attributed to  $x_3$  factor.

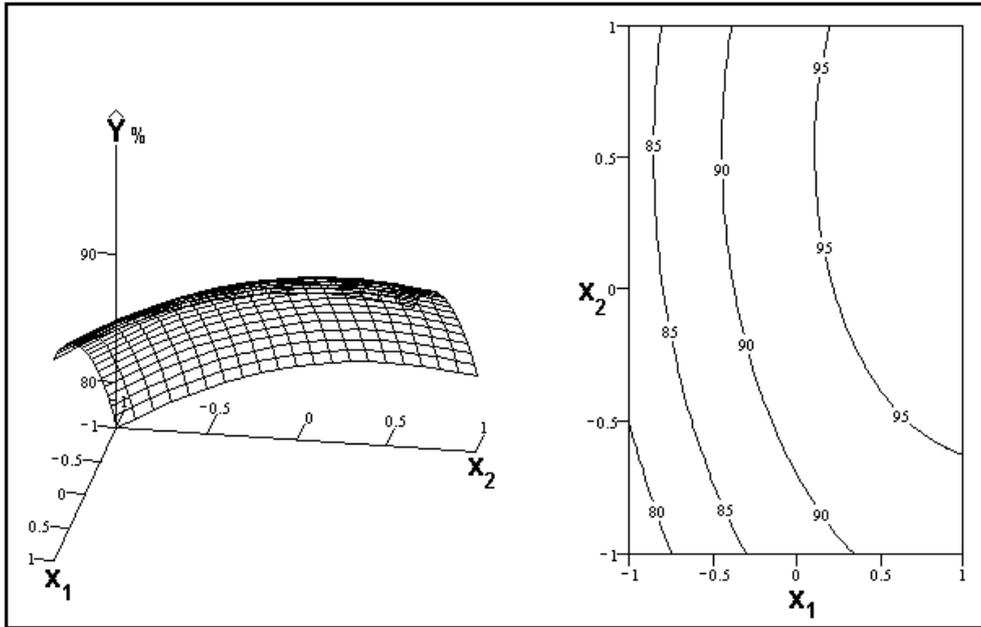


Figure 2. Response surface and contour response surface depending on  $x_1$  and  $x_2$ ,  $x_3=0$ .

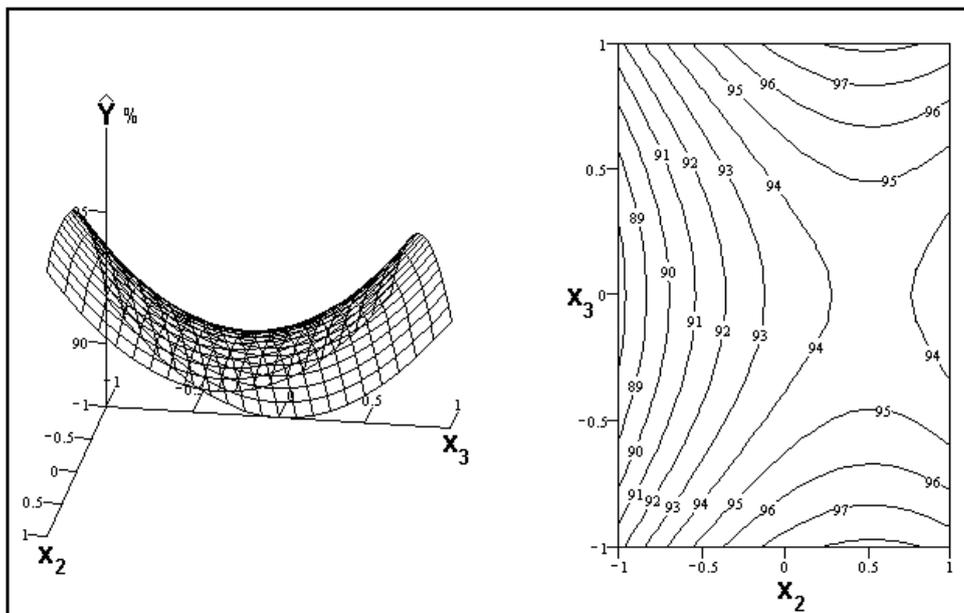


Figure 3. Response surface and contour response surface depending on  $x_2$  and  $x_3$ ,  $x_1=0$ .

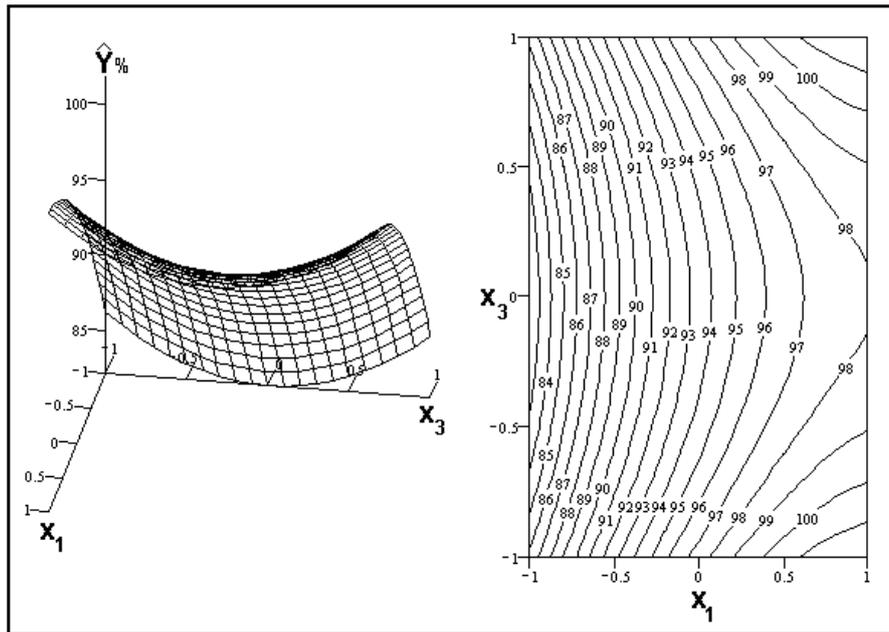


Figure 4. Response surface and contour response surface depending on  $x_1$  and  $x_3$ ,  $x_2=0$ .

## Process Optimization

After determining the regression equation that represents virtually an objective function the next step of the investigation was to optimize the restricted objective function:

$$\begin{aligned} & \max \{ \hat{Y}(x_1, x_2, x_3) \} \\ & -\alpha \leq x_i \leq \alpha, \quad i = 1 \dots 3 \text{ and } \hat{Y} \leq 100 \% \end{aligned} \quad (6)$$

In this sense, first of all, the stationary point (S - center) has been determined by solving the subsequent system of equations [7]:

$$\frac{\partial \hat{Y}}{\partial x_1} = 0, \quad \frac{\partial \hat{Y}}{\partial x_2} = 0, \quad \frac{\partial \hat{Y}}{\partial x_3} = 0 \quad (7)$$

The solving of the equations system (7) gives the coordinates of stationary point, i.e.  $\mathbf{x}_s = [1.175 \quad 0.527 \quad 0]^T$ .

In order to determine the nature of the stationary point the objective function was brought to the standard form. The standard form of the regression function, in case of three factors, is expressed via next general formula [5, 7]:

$$\hat{Y} - Y_s = \lambda_1 \cdot \chi_1^2 + \lambda_2 \cdot \chi_2^2 + \lambda_3 \cdot \chi_3^2 \quad (8)$$

where  $Y_s$  – value of the objective function in the stationary point ( $Y_s = 98.794$ );

$\chi_1, \chi_2, \chi_3$  - values of factors in the new coordinate system;

$\lambda_1, \lambda_2, \lambda_3$  – the standard regression coefficients.

The standard regression coefficients were settled by determining the eigenvalues of next quadratic matrix, solving the characteristic equation [7]:

$$\det (\mathbf{B} - \lambda \cdot \mathbf{E}) = 0 \quad (9)$$

where  $\mathbf{B}$  denotes quadratic matrix of regression coefficients;  $\mathbf{E}$  - identity matrix.

The obtained values of the standard regression coefficients are:  $\lambda_1 = -3.358$ ,  $\lambda_2 = -2.795$ ,  $\lambda_3 = 4.086$ , thus, the standard equation describes investigated extraction process has the following form:

$$\hat{Y} - 98.794 = -3.358 \cdot \chi_1^2 - 2.795 \cdot \chi_2^2 + 4.086 \cdot \chi_3^2 \quad (10)$$

The nature of the stationary point has been settled via signs examinations of standard coefficients. Since the standard coefficients have different signs, i.e.  $\lambda_1$  and  $\lambda_2$  are lesser than zero and  $\lambda_3$  is greater than zero, the S-center represents a “*minimax*” [5, 7].

In order to settle the optimal point of experiment the response surface has been explored in the region of the “*minimax*” by moving upon axis direction of positive coefficient ( $\chi_3$ ). The displacement from S-center upon the  $\chi_3$  axis direction will improve the objective function. To maximize the performance of the extraction process objective function has taken the values  $\hat{Y} > Y_s$  and the moving upon  $\chi_3$  has been done. In this case  $\chi_1=0$ ,  $\chi_2=0$  and the standard equation comes to the subsequent form:

$$\chi_3 = \pm \sqrt{\frac{\hat{Y} - Y_s}{\lambda_3}} \quad (11)$$

Modifying the value of the  $\hat{Y}$  function the keeping of imposed restriction upon the process variables has been verified. The optimal value of extraction yield (adopted feasible maximum) calculated by the model was 100 % for next values of the coded variables:  $x_1=1,175$ ;  $x_2=0,527$ ;  $x_3=0,543$ . The real optimal values of the process factors and the corresponding experimental yield are shown in (Table 3).

**Table 3.** The optimal condition of the reactive extraction experiment.

| Amine concentration, (g/l) | Extraction time, (s) | Vibrational intensity, (m/s) | Extraction yield, [%] |
|----------------------------|----------------------|------------------------------|-----------------------|
| 63,5                       | 66                   | 127,1                        | 99,93                 |

The process performance obtained in the adopted optimal conditions represents the best experimental extraction yield of tartaric acid from aqueous phase. All calculations were performed by means of MathCAD PRO software.

## Conclusions

An empirical mathematical model has been developed in order to describe the dependence between the performance and variables of tartaric acid extraction process from aqueous phase by using Amberlite LA-2 –butyl acetate mixture as extraction agent.

Regression coefficients corresponding to linear terms as well as the sketched contours diagrams of surface response indicate that process performance of tartaric acid extraction is influenced considerably by amine concentration.

In order to determine the optimal conditions of the extraction process, the regression equation settled via experiment planning was brought to the standard form. The optimum point was localized in the region of stationary point of the surface response ("minimax" region).

The extraction yield obtained under adopted optimal conditions, i.e. amine concentrations –63.5 g/L; extraction time – 66 s; vibrational intensity –127.1 m/s represents the best experimental extraction yield of tartaric acid from aqueous phase that is 99.93 %.

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