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TARTARIC STABILIZATION OF GRAPE JUICE WITH IONIC EXCHANGE RESINS

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Abstract. The limpidity of grape juice is a quality requirement asked at placing in trade networks, because consumers prefer a drink with clear transparency. A specific phenomenon is the formation of tartaric crystals during long storage or maintenance at temperatures below 0 -1°C. The traditional tartaric stabilization procedures indicates disadvantages on power consumption and duration, requirements specific to the equipment, etc. For this aim were studied the effect of five types of anionic resin to grape juice, developed a method for grape juice tartaric stabilization based on mathematic model the central rotary matrix, using the most effective resin Purolite A-400.

Keywords: *potassium bitartrate, anionic resin, duration of process, limpidity of juice, mass of formed crystals, mathematical model.*

Introduction

The limpidity of grape juice is a quality requirement asked at placing in trade networks, because consumers prefer a drink with clear transparency, this fact gives more confidence in the safety of the product. A specific phenomenon for grape products is the formation of tartaric crystals during long storage or maintenance in premises with temperatures below 0-1°C. These crystals are the consequence of the chemical reaction of potassium and calcium ions with tartaric acid [1-3]. To prevent this phenomenon, several methods [11-12 and 18] are used in the manufacturing process as: cold treatment, electrodialysis and the introduction of metatartaric acid.

Tartaric stabilization of grape juice by cold treatment provides cooling of freshly pressed juice up to the temperature of 0 ± 1°C and maintaining 36-48 hours for tartar precipitation and clarification, the cooled juice is decanted and isothermal filtrated [4, 6, 7]. This traditional method requires a lot of time and energy, therefore, it has been proposed a faster process [20], lasting up to 2 hours, due to the introduction of obtained tartaric crystals in the juice which is cooled to the stabilization temperature of the 0 ± 1°C and using centrifugation for juice clarification.

Tartaric stabilization of grape juice by electrodialysis [9-10] consists in reducing the initial concentration of potassium ions from 1200 mg·dm^{-3} to 1800 mg·dm^{-3} to values from 800 mg·dm^{-3} to 900 mg·dm^{-3}, under the action of the potential difference with values from 120 V to 180 V between the working and intermediate installation block sections. Juice is transferred in the working sections and the intermediate ones contain rinsing water. The pressure of the juice and water respectively in the installation should be more than 0.3 MPa.

The third tartaric stabilization method [4, 8] requires that the juice cooled to 25-30 °C and double filtered should be transferred to the tanks where metatartaric acid is added in the amount from 0,5 $g \cdot dm^{-3}$ to 6 $g \cdot dm^{-3}$. In advance to prepare solution of the acid metatartaric with a concentration from 250 $g \cdot dm^{-3}$ to 300 $g \cdot dm^{-3}$ in the clarified juice, then it is added to the tank to be mixed with all the juice, intended for packaging. Mixing takes 5-6 min then juice is heated since 60-70 °C and packaged. Hot filling with metatartaric acid is not allowed. The analysis of the tartaric acid stabilization methods indicates that every one of them has disadvantages on power consumption and duration, requirements specific to the equipment, etc. Therefore, there was proposed to establish a method for tartaric stabilization of the grapes juice using resins of ionic exchange [13, 16 and 17] which can provide the necessary requirement of clarity in a manner that is simple, fast and economical.

Materials and methods

For tartaric stabilization of grape juice there were selected 5 types of anionic resins: Amberlite IRA-410 [14], Amberlite IRA-67 [15], AV-17 [18], AN-31 [18] and Purolite A-400 [21]. With these resins juice samples were treated and by high performance liquid chromatography (HPLC) method [19] was determined the variation of the organic acids composition. Depending on the lowest content of tartaric acid in the juice, it was decided which resin will be used in further research. A mathematical model was developed with the factorial design of the experiments [5], where the temperature had a constant value 30 ºC and 2 variable parameters were chosen*: resin quantity* (*C_R*) and *treatment duration (τ)*. By the response factor was established *the mass of crystals* formed in cold treatment that provided at cooling of grape products samples (acidifiers and juices) up to the temperature with values of 0-1°C and maintain at this temperature for 48 hours. The separation of the tartaric sediments from the liquid part of the samples was done cold by decanting procedure. The mass of the tartaric crystals was weighed at the analytical balance.

For mathematical model elaboration the central rotary matrix was selected, where by x_1, x_2 were encoded the variable parameters of the tartaric stabilization process: the *resin quantity* and *the treatment duration*. The minimum, centre and maximum values used were noted, see Table 1.

Table 1

The attribution matrix of influence factor values in the mathematical model

Input factor in the mathematical model	Coding	Min. (-)	Center	Max. (+)
Ionic exchange resin quantity, $g \cdot dm^{-3}$ juice	x_1	5	10	15
Duration of treatment of juice with resin, min.	x_2	5	10	15

Results and discussions

Treatment of grape juice samples with different types of anionic resins, during 20 min., had the effect of decreasing the concentrations of organic acids, established by the method of high performance liquid chromatography (see Table 3). Maximum efficiency had resin Purolite A-400, strong basic anionite, with polystyrene-divinylbenzene matrix and quaternary ammonium functional groups with a high operating capacity. This type of resin was selected for conducting the experiment of tartaric stabilization of grape juice.

Table 3

Effect of treatment of grape juice on the content of organic acids

Organic acids in grape juice	Content of organic acids after treatment with ionic exchange resins ($g \cdot dm^{-3}$)					
	untreated juice	Amberlite IRA 410	Amberlite IRA 67	Purolite A-400	AV 17	AN 31
Tartaric	7.52	7.31	7.29	6.91	7.11	7.26
Malic	6.34	6.20	6.23	4.89	5.15	5.79
Citric	1.42	1.37	1.30	1.25	1.29	1.34

The juice treatment process was developed with Purolite A-400 resin, similar to the resin separation of carboxylic acids [13], based on a rotary compound central plane (see Table 4).

For the calculation of regression coefficients *b* the matrix with factors $\bar{y} \cdot x_{ij}$ was made and the obtained results are presented in the Tables 5 and 6.

Table 4

Rotary compound central plan for juice treatment with ionic exchange resin

C_R		τ		x_0	x_1	x_2	$x_1{*}x_2$	$(x_1')^2$	$(x_2')^2$	y_1	y_2	$\bar{y}$
Z1 min	5	Z2 min	5	1	-1	-1	1	1	1	2.880	2.900	2.890
Z1 max	15	Z2 min	5	1	1	-1	-1	1	1	2.100	2.080	2.090
Z1 min	5	Z2 max	15	1	-1	1	-1	1	1	0.900	0.920	0.910
Z1 max	15	Z2 max	15	1	1	1	1	1	1	0.080	0.060	0.070
Z1 -α	3	Z2 0	10	1	-1.414	0	0	2	0	2.330	2.320	2.325
Z1 +α	17	Z2 0	10	1	1.414	0	0	2	0	0.225	0.235	0.230
Z1 0	10	Z2 -α	3	1	0	-1.414	0	0	2	2.880	2.920	2.900
Z1 0	10	Z2 +α	17	1	0	1.414	0	0	2	0.110	0.120	0.115
Z1 0	10	Z2 0	10	1	0	0	0	0	0	0.940	0.920	0.930
Z1 0	10	Z2 0	10	1	0	0	0	0	0	0.930	0.910	0.920
Z1 0	10	Z2 0	10	1	0	0	0	0	0	0.915	0.935	0.925
Z1 0	10	Z2 0	10	1	0	0	0	0	0	0.900	0.920	0.910
Z1 0	10	Z2 0	10	1	0	0	0	0	0	0.940	0.910	0.925

Table 5

Factor matrix $\bar{y} \cdot x_{ij}$ of the rotating composite central plan of experiences

Exp.	C_R	τ	y_1	y_2	$\bar{y}$	σ^2	$\bar{y} \cdot x_0$	$\bar{y} \cdot x_1$	$\bar{y} \cdot x_2$	$\bar{y} \cdot x_{1,2}$	$\bar{y} \cdot (x_1')^2$	$\bar{y} \cdot (x_2')^2$
1	5	5	2.880	2.900	2.890	0.000200	2.890	-2.890	-2.890	2.890	2.890	2.890
2	15	5	2.100	2.080	2.090	0.000200	2.090	2.090	-2.090	-2.090	2.090	2.090
3	5	15	0.900	0.920	0.910	0.000200	0.910	-0.910	0.910	-0.910	0.910	0.910
4	15	15	0.080	0.060	0.070	0.000200	0.070	0.070	0.070	0.070	0.070	0.070
5	3	10	2.330	2.320	2.325	0.000050	2.325	-3.288	0.000	0.000	4.650	0.000
6	17	10	0.225	0.235	0.230	0.000050	0.230	0.325	0.000	0.000	0.460	0.000
7	10	3	2.880	2.920	2.900	0.000800	2.900	0.000	-4.101	0.000	0.000	5.800
8	10	17	0.110	0.120	0.115	0.000050	0.115	0.000	0.163	0.000	0.000	0.230
9	10	10	0.940	0.920	0.930	0.000200	0.930	0.000	0.000	0.000	0.000	0.000

Continuation *Table 5*

10	10	10	0.930	0.910	0.920	0.000200	0.920	0.000	0.000	0.000	0.000	0.000
11	10	10	0.915	0.935	0.925	0.000200	0.925	0.000	0.000	0.000	0.000	0.000
12	10	10	0.900	0.920	0.910	0.000200	0.910	0.000	0.000	0.000	0.000	0.000
13	10	10	0.940	0.910	0.925	0.000450	0.925	0.000	0.000	0.000	0.000	0.000
						$\Sigma\ \bar{y} \cdot x_{ij}$	16.140	-4.602	-7.938	-0.040	11.070	11.990

In order to obtain the results of the output parameter *the mass of the tartaric crystals* formed, 13 experiments were performed each in 2 repetitions, where the input parameters *the resin quantity* and *the treatment duration* had maximum, minimum and center values. The average response $\bar{y}$ was the average of the two parallel experiments y_1 and y_2, which represent the weighed masses of tartaric crystals formed in juice during maintenance for 48 hours at low temperature values 0…+1°C.

Table 6

Regression coefficients of the second order equation of the rotary compound central plane

b_0	b_1	b_2	$b_{1,2}$	b_{11}	b_{22}
0.9220	-0.5753	-0.9922	-0.0100	-0.0227	0.1096

The coefficients $b_{1,2}$ and b_{11} have insignificant values and were subsequently omitted the regression equation of the treatment process with ion exchange resin of grape juice, the following form was obtained:

$$y = 0.9220 - 0.5753 \cdot x_1 - 0.9922 \cdot x_2 + 0.1096 \cdot x_{22} \qquad (1)$$

After decoding and transformation into real factors, the regression Eq (1) obtained the polynomial function form of a second degree, containing 2 variable factors:

$$M = f\,(R; \tau) = 4.6500 - 0.0930 \cdot R - 0.2824 \cdot \tau + 0{,}044 \cdot \tau^2 \qquad (2)$$

where: **M –** mass of tartaric crystals formed in grape juice cooled at 0-1°C, g;
R – amount of resin used for treatment, $g \cdot dm^{-3}$; **τ** – duration of treatment, min.

Dispersions on the periphery, in the plan center and degrees of freedom *m* were calculated, the obtained results are presented in Table 7:

Table 7

Dispersions on the peripheries and centre of the rotary compound central plan

$S_1^2 = \Sigma(y_j - \bar{y}_j)^2$	$S_1^2 = \Sigma(y_{0j} - \bar{y}_{0j})^2$	$S_3 = S_1^2 - S_2^2$	n	m_1	n_0	m_2	m_3
0.001750	0.000230	0.001520	13	12	5	4	8

The Fisher criterion was calculated according to the formula:

$$F_{calculated} = \frac{0.001520/8}{0.000230/4} = 3.30$$

In order to ascertain the veracity of the hypothesis that the developed mathematic model it is true, it has been determined the number of degrees of freedom of the m_3 (for the dispersion of the non-volatile S_3), also m_2 (for the dispersion of the reductibility S_2^2).

Depending on the degrees of freedom and chosen error level q = 0.05 Fisher criterion value $F_{tab}(q; m_3; m_2)$ was found therefore were obtained following values:

$$q=0.05;\ m_3=8;\ m_2=4;\ F_{tab}(0.05;8;4) = 3.63$$

Since the condition *3.30 < 3.63* was established, respectively $F_{calculated} < F_{tab}(0.05;8;4)$ follows that the regression Eq is true, respectively and the mathematical model developed on the basis of the rotary compound central plan is also true.

Based on the regression Eq (2) values of the mass of tartaric crystals were calculated depending on the values of the quantity of the ionic exchange resin and the treatment duration. As a consequence, it was determined what values of the mentioned variation factors in grape juice are not formed tartaric crystals, that the response function has values equal to „0". Using the MS Excel 2007 software, the mathematical model was developed in the form of a 3D surface, see figure 1.

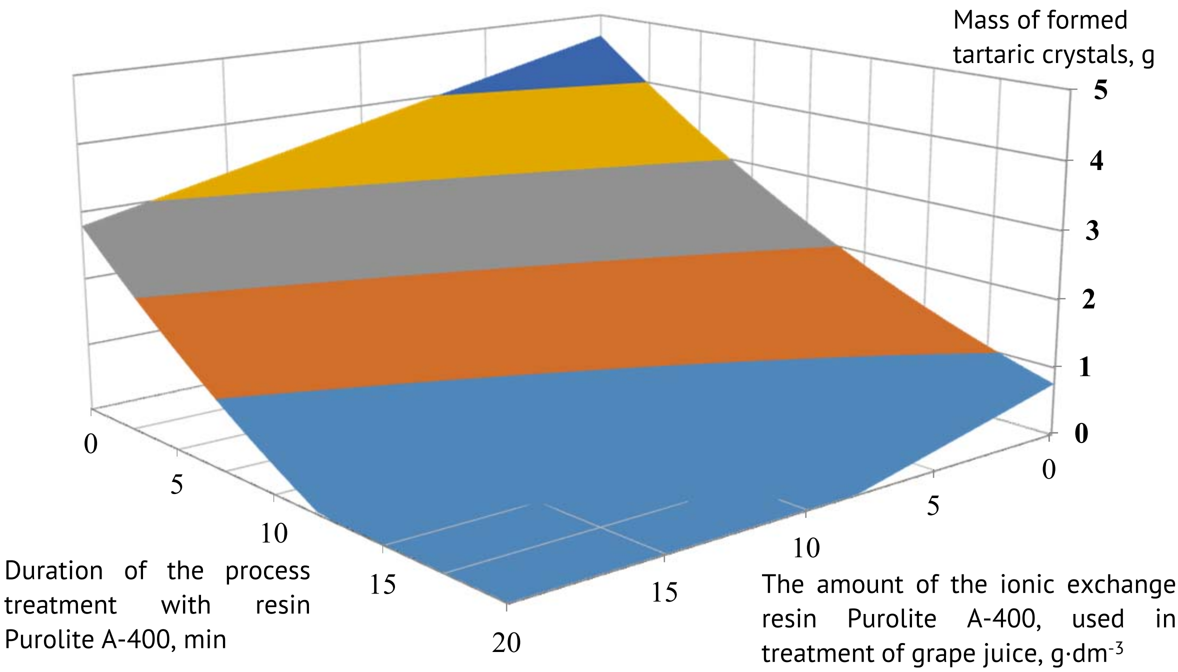

Figure 1. Graphical representation of the mathematical model of diminishing the formation of tartaric crystals in grape juice treated with ionic exchange resin.

In accordance to the values of the Eq of the applied mathematical model and the graphic representation obtained, it has been determined the optimum parameters to ensure the tartaric stability of grape juice which includes: resin Purolite A-400 has reducing effect to the crystalline tartaric sediments formation at amount since 10 g at 1 dm^3 of juice and treatment duration from 12 min. Tartaric crystalline sediments were not formed in grape juice when Purolite A-400 ionic exchange resin was applied in amounts of 16-18g·dm^{-3} and the treatment time was between 15-16 min.

The process of acidity stabilization in grape juice with ionic exchange resin can be scientifically explained based on the results obtained in the quantitative analysis by the HPLC method. They show 20 % decrease of the amount of tartaric acid in Isabella variety acidifier from values of 7.7-8.0g·dm^{-3} to values of 6.0-6.1g·dm^{-3}. Tartaric acid was adsorbed on the surface of the ionic exchange resin spheres and the amount of malic acid with the value of 10.9g·dm^{-3} (its was decrease) had buffer effect. That's why favorable conditions were not created for sedimentation of potassium acid tartrate, sodium-potassium neutral tartrate and calcium tartrate.

Conclusions

A process of grape juice tartaric stabilization with ionic exchange resins was proposed as alternative to traditional methods (cold treatment, electrodialysis and introduction of metatartaric acid). From five types of anionic resins there was selected Purolite A-400, which most effectively diminished the content of tartaric acid in juice samples, as it was demonstrated by the method of high performance liquid chromatography. The development of tartaric stabilization process was based on mathematic model, ensuring the limpidity of grape juice by adding Purolite A-400 resin in the count of 18g·dm^{-3} during 15-16 min.

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