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Aspects Concerning the Mathematical Statistical Modeling of CO_2 Variation in Soft Drinks Stored in Polyethylene Terephthalate Bottles

The quality of the soft drinks found on the market is determined by a series of physical, chemical, biological and mechanical factors, which cause important organoleptic changes. The present study is necessary because of the problems that the soft drinks producers have as a consequence of CO_2 losses through the walls of polyethylene terephthalate bottles (PET). The experimental investigations were centered upon measuring the CO_2 over a period of time for several soft drinks stored in polyethylene terephthalate bottles. In this paper, starting from the experimental determinations performed, a series of mathematical statistical models are elaborated. They emphasize aspects concerning the CO_2 variation of the samples as a function of their volume and time. The conclusions achieved can be used both for the improvement of the quality of soft drinks and for the forecasting of their optimum time of utilization.

1. Introduction

Like any other market, the drinks industry has had to respond to changing fashions and consumer tastes. Intense competition means no brand can be complacent. Revisions and enhancements will always be necessary to keep ahead of the field.

The necessity of storing carbonated beverages in more practical and lighter bottles has come to the replacement of the more traditional glass with the new PET. At the beginning PET was well accepted on the market offering a combination of attractive eye-catching bottle designs and maximum consumer convenience. But, in the mean time the material was not able to offer the necessary protection for long enough to provide a viable ambient packaging alternative for oxygen sensitive products such juices [1,8,9].

In practice, CO_2 is the only gas suitable for producing the "sparkle" in soft drinks. The solubility is such as to allow retention in solution at ambient temperature and get also allow the release of an attractive swirl of bubbles from the body of the drink when slightly agitated [2].

Using the PET bottles requires a higher carbonation compared to the classical bottles in order to compensate the CO_2 losses through the PET walls during the storage and at every cap open [3]. Up to present, the studies have concluded that 30% of CO_2 losses in the carbonated products take place through to the cap and the rest through the PET walls.

Starting from this necessities and premises, on the basis of the experimental determinations the achievement of a variables correlation is necessary. It will allow the process characterization with the view to establish the mathematical statistical model.

In the situation of knowing the variation of process parameters without knowing the analytical model, an empirical model is possible to develop by using the statistical correlation relations. The general form of such relation is [4,7]:

$$y = f(x_1, \dots, x_n), \tag{1}$$

where:

$x_1, \dots, x_n$ – the independent variables of studied process;

y – the dependent variable.

The determination of coefficients values is made by different methods in accordance with the type of the model (linear or nonlinear in variables and coefficients). By replacing in equation (1) the numerical sets of values $\left(\hat{y}_j, x_{ij}, \dots, x_{nj}\right)$ experimentally obtained, a system of m equation is generated. m is the total number of the experiments.

The unknowns of the system are his coefficients. For choosing those values witch better satisfy all the equations, an optimization criterion is necessary to adopt. It will be minimizing.

The most used criterion for the processing of experimental data is the least squares method. This method assumes that the best-fit curve of a given type is the curve that has the minimal sum of the deviations squared (least square error) from a given set of data. The mathematical equation is:

$$S = \sum_{j=1}^{m} (\hat{y}_j - y_j)^2 = \min. \tag{2}$$

Where:

$\hat{y}_j$ – experimental measured values for the dependent variable;

y_j – calculated values on the basis of proposed model for the same values of independent variables $x_{ij}, \dots, x_{nj}$;

m – total number of the experiments.

The minimization of objective function (2) is realized by using an adequate optimization method. If the regression equation is linear (polynomial model) or it can be convert in a linear one, the S criterion will be partial derivate in function of each coefficient. The solving of the system obtained by annulling the derivates leads to the search solution.

2. Analysis

The experiments covered almost a year time, but the results upon which this study relies cover only the time between 0 and 204 days. The laboratory research analyzed the measure of carbon dioxide in time, comparing the carbonated beverage samples, bottled in 0,5; 1; 1,5; 2 and 2,5 litre PET bottles. The samples were different trademark carbonated beverages existent on the market. The CO_2 level has been verified approximately every 3 weeks.

The purpose of this study is to identify the sample in which the CO_2 is better preserved and dosed. Another purpose is to analyse the causes of its preservations.

A special device was used to verify the CO_2 pressure inside the sealed bottles. This device is formed from a body, a mobile part, a rubber ring, a piercing needle, a manometer and a sealing mechanism.

The device's body is fixed on the superior part of the bottle, vertically, allowing the rubber ring and the needle to rest upon the bottle's cap. Pressing the sealing mechanism, the needle penetrates the cap up to the space above the liquid. On this way, the manometer indicates the CO_2 pressure from this space. Using a correlation table, the CO_2 beverage content can be measured (g CO_2/litre) as a function of the manometer reading and the temperature of the sample [5].

3. Results and discussion

In order to correlate the values of CO_2 content in analyzed samples depending on their volume and the time of preservation, a two degree polynomial relation with two independent variables was proposed. It has the following form:

$$y = c_0 + c_1 \cdot x_1 + c_2 \cdot x_2 + c_{11} \cdot x_1^2 + c_{12} \cdot x_1 \cdot x_2 + c_{22} \cdot x_2^2 \quad (3)$$

In accordance with those presented in the introductive part of this article, the values of c_0, c_1, c_2, c_{11}, c_{12} şi c_{22} coefficients correspond with the minimum of objective function:

$$S = \sum_{j=1}^{m} (\hat{y}_j - (c_0 + c_1 \cdot x_{1j} + c_2 \cdot x_{2j} + c_{11} \cdot x_{1j}^2 + c_{12} \cdot x_{1j} \cdot x_{2j} + c_{22} \cdot x_{2j}^2))^2 \quad (4)$$

By annulling the partial derivates of S function in function of each coefficients c a linear equation system resulted.

The coefficient system matrix (A) and the vector of free terms (B) are:

$$A = \begin{bmatrix} \sum_{j=1}^{m} 1 & \sum_{j=1}^{m} x_{1j} & \sum_{j=1}^{m} x_{2j} & \sum_{j=1}^{m} x_{1j}^2 & \sum_{j=1}^{m} x_{1j}x_{2j} & \sum_{j=1}^{m} x_{2j}^2 \\ \sum_{j=1}^{m} x_{1j} & \sum_{j=1}^{m} x_{1j}^2 & \sum_{j=1}^{m} x_{1j}x_{2j} & \sum_{j=1}^{m} x_{1j}^3 & \sum_{j=1}^{m} x_{1j}^2 x_{2j} & \sum_{j=1}^{m} x_{1j}x_{2j}^2 \\ \sum_{j=1}^{m} x_{2j} & \sum_{j=1}^{m} x_{1j}x_{2j} & \sum_{j=1}^{m} x_{2j}^2 & \sum_{j=1}^{m} x_{1j}^2 x_{2j} & \sum_{j=1}^{m} x_{1j}x_{2j}^2 & \sum_{j=1}^{m} x_{2j}^3 \\ \sum_{j=1}^{m} x_{1j}^2 & \sum_{j=1}^{m} x_{1j}^3 & \sum_{j=1}^{m} x_{1j}^2 x_{2j} & \sum_{j=1}^{m} x_{1j}^4 & \sum_{j=1}^{m} x_{1j}^3 x_{2j} & \sum_{j=1}^{m} x_{1j}^2 x_{2j}^2 \\ \sum_{j=1}^{m} x_{1j}x_{2j} & \sum_{j=1}^{m} x_{1j}^2 x_{2j} & \sum_{j=1}^{m} x_{1j}x_{2j}^2 & \sum_{j=1}^{m} x_{1j}^3 x_{2j} & \sum_{j=1}^{m} x_{1j}^2 x_{2j}^2 & \sum_{j=1}^{m} x_{1j}x_{2j}^3 \\ \sum_{j=1}^{m} x_{2j}^2 & \sum_{j=1}^{m} x_{1j}x_{2j}^2 & \sum_{j=1}^{m} x_{2j}^3 & \sum_{j=1}^{m} x_{1j}^2 x_{2j}^2 & \sum_{j=1}^{m} x_{1j}x_{2j}^3 & \sum_{j=1}^{m} x_{2j}^4 \end{bmatrix} \quad B = \begin{bmatrix} \sum_{j=1}^{m} \hat{y}_j \\ \sum_{j=1}^{m} x_{1j}\hat{y}_j \\ \sum_{j=1}^{m} x_{2j}\hat{y}_j \\ \sum_{j=1}^{m} x_{1j}^2\hat{y}_j \\ \sum_{j=1}^{m} x_{1j}x_{2j}\hat{y}_j \\ \sum_{j=1}^{m} x_{2j}^2\hat{y}_j \end{bmatrix}$$

By using the program MATLAB, there were processed and analysed the experimental data, obtaining a series of statistic models pointing out the variation of the samples content in CO2 depending on their volumes and time. The experimental data and the surfaces generated by the statistical mathematical models are presented in figures 1, 2 and 3.

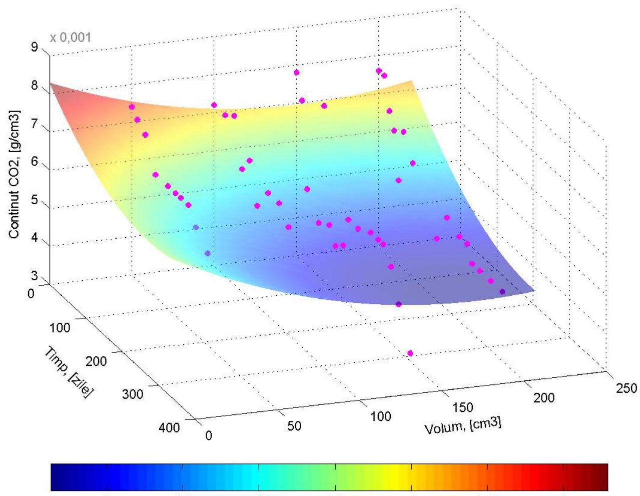

Figure 1. The variation of CO_2 content in sample I depending on the volume of sample and time

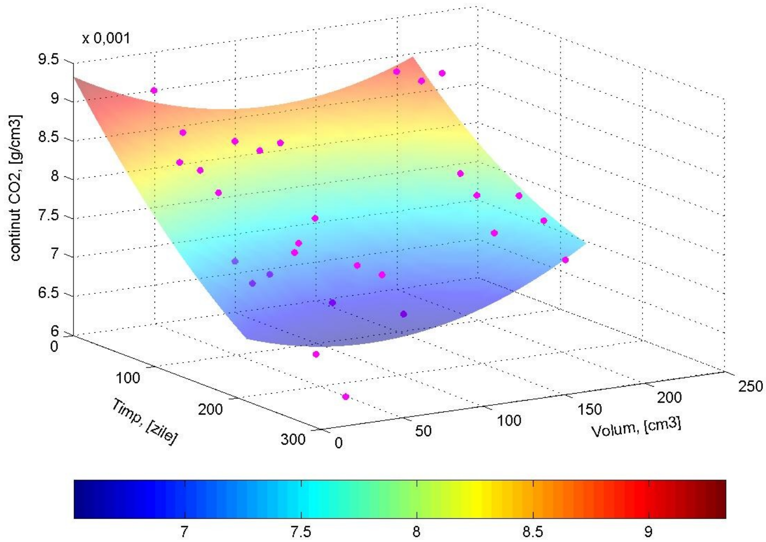

Figure 2. The variation of CO_2 content in sample II depending on the volume of sample and time

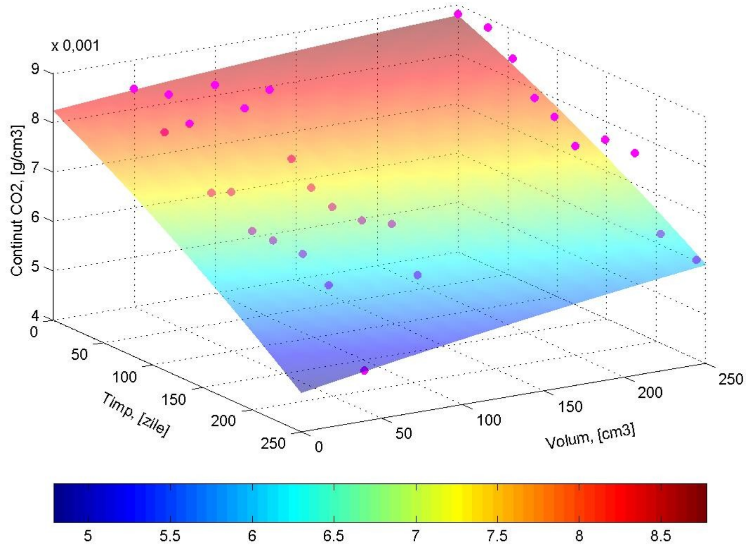

Figure 3. The variation of CO_2 content in sample III depending on the volume of sample and time

The equations of statistical mathematical models obtained as a consequence of multiple polynomial regressions are presented in table 1.

Table 1. The equations of the statistical mathematical models obtained in the case of the 3 studied samples

Sample	The equations of the statistic mathematical models
I	$y = 8.0849-0.0168\cdot x_1-0.0097\cdot x_2+2.6081e-5\cdot x_1^2+9.2800e-6\cdot x_1\cdot x_2+2.0471e-5\cdot x_2^2$
II	$y = 9.3274-0.0162\cdot x_1-0.0120\cdot x_2+1.9742e-5\cdot x_1^2+2.2032e-5\cdot x_1\cdot x_2+4.8927e-5\cdot x_2^2$
III	$y = 8,2339-0.0112\cdot x_1+0.0031\cdot x_2-1.0235e-5\cdot x_1^2+1.0632e-5\cdot x_1\cdot x_2-3.6130e-6\cdot x_2^2$

After calculating the model's coefficients, a comparison between the model predictions and the data supplied by the real process is needed. As indicators of the model adequacy there have been used: the variance, the standard deviation, the indicator of the precision of the model and the correlation coefficient of the CO_2 content as a function of on volume and time [6].

Table 2. The concordance indicators of determined statistical models

Concordance indicators	Sample I	Sample II	Sample III
Variance, σ^2	0.42	0.13	0.14
Standard deviation, σ	0.65	0.37	0.37
Indicator of the precision of the model, R^2	0.61	0.78	0.85
Correlation coefficient, R	0.78	0.88	0.92

4. Conclusion

The bottle PET of 0,5 litre requires a supplementary dosage because of its small volume. This is the reason for which it is recommended to guarantee the 0,5 litre packed product only for 6 months, compared to the other volumes where the validity term can be increased to 1 year.

The thickness of the PET bottle walls must be kept uniform on the entire surface. In this way, there aren't areas of more intense CO_2 losses. Also, the increase of mass bottle constitutes a barrier for the CO_2 losses.

By using the obtained equations of statistical mathematical models we can correlate the variation of CO_2 as a function of time and bottle volume. Thus, the manufacturing companies of carbonated soft drinks can precisely control the product quality.

From the mathematical statistical equations resulted the ideea that the influence of PET bottles volum on CO_2 content in soft drinks is greater than the time of preservation.

In the same time, the elaboration of statistical mathematical models in the means of expressing the CO_2 variation in PET bottles, allows the forecast of maintenance period of carbonated soft drinks.

References

[1] Degroote L. *Active barriere extending the shelf life of PET*. Innovations Tehnologiques en Plasturgie: Procedes de Transformation Integres, Douai, 20 Janvier, 2005.

[2] Varnam A.H., Sutherland J.P. *Food Products Series. Technology, chemistry and microbiology*. vol.2, Aspen Publication, 1999.

[3] Marinescu I., Segal B., Georgescu A., Ciobanu A., Olaru M., Hobincu A., *Tehnologii moderne în industria conservelor vegetale*. Tehnical Publishing house, Bucureşti, 1976.

[4] Nichici A., Cicală E. *Prelucrarea datelor experimentale*. Politehnica Publishing house, Timişoara, 1996.

[5] Segal B., Segal R., Novăceanu M., Centurianu – Popescu C. *Îndrumar de control chimic şi tehnic pentru industria băuturilor nealcoolice*. Nr. 26, Teaching aid centre, Bucureşti, 1977.

[6] Todinca T., Geantă M. *Modelarea şi simularea proceselor chimice*. Politehnica Publishing house, Timişoara, 1999.

[7] Vardeman, S.B. *Statistics for engineering problem solving*. Politehnica Publishing house, Timişoara, 1994.

[8] Pîrvulescu L., Perju D., Filimon M. *The Quality Improvement of the Apple Juice trough Technological Process Optimization.* Chemical Bulletin of "Politehnica" University of Timişoara, n°47(61), 1-2, 2002, p. 44-46.

[9] Pîrvulescu L., Perju D. *Quality Research of Fruit Juice Using a Measuring System of the Global Antioxidant Capacity.* Chemical Bulletin of "Politehnica" University of Timişoara, n°47(61), 1-2, 2002, p. 47-50.

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