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Studies Regarding the Variation of Carbon Dioxide in Certain Carbonated Beverages Stored in Polyethylene Terephthalate Bottles

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Abstract: 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 (polyethylene terephthalate). Along with this change new problems have appeared regarding preservations of the beverage’s qualities and the sensorial standard of quality. In this study is analysed the variation of carbon dioxide in certain carbonated beverages stored in polyethylene terephthalate bottles. The possibilities of obtaining mathematical statistical models have been analysed basis on the experimental data in order to predict the variation of the CO_2 inside the samples as a function of volume and time. Another concern of this study was the CO_2’s losses starting from the bottling process as well as a comparative average analysis of products proportioning with CO_2 and its loss for three types of concurrent carbonated beverages existing on the market. The obtained results allowed the analyses of the optimal term of validity in accordance with the bottle’s volume. In the mean time the obtained results contributed to the improvement of the carbonated beverage’s quality allowing the obtaining of a complete beverage.

Keywords: Carbonated soft drinks, carbon dioxide, PET bottles, mathematical modeling.

1. Introduction

Carbonated soft drinks are filled into either bottles or cans. Thick-walled, reusable, glass bottles were used for many yeas, but are being replaced by thin-walled, non-reusable glass and, increasingly, PET bottles. Pet bottles were originally used only for large 2-3 l sizes, but are now also used for smaller, individual sizes and thus also compete with cans. Cans are of the ring-pull type; resealable cans have been introduced have been introduced, but found little application.

Carbonation may be considered as the impregnation of a liquid with CO_2 gas. In older plants the pre-syruping method was employed, in which carbonated water and sugar syrup were metered separately into the bottle or other container. This method has been superseded in modern practice by premix filling in which sugar syrup, water and CO_2 gas are combined in the correct ratio, before transfer to the filler as a complete beverage.

CO_2 is a colourless gas of slightly pungent odour, which, in part, forms carbonic acid on dissolving in water. This acid is instable.

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. The gas is also inert, non-toxic and virtually tasteless, and is available in liquefied form at moderate cost [1].

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. Up to present, the studies have concluded that the CO_2 losses in the carbonated products are distributed as follows:

- 30% through to the cap;
- 60% through the PET walls.

Polyethylene terephthalate is a polymer obtained as the result of a polymerisation process of the terephtalic acid and monoethylene glycol. It is a linear polymer, having in its composition a large number of crystals and thermoplastics, witch allows its transformation during an extrusion, injection, blown injection and technical forming. It presents a good mechanical resistance, high natural flexibility, high waterproof when in contact with water steam and a high shock resistance [2].

Carbonated soft drinks in a sealed container are in an equilibrium condition where gas in the headspace provides the necessary equilibrium pressure to maintain the remainder of the gas in solution. The equilibrium pressure varies according to the amount of CO_2 in solution and the liquid temperature. The fundamental role of the carbonator is to obtain close contact between CO_2 gas and the liquid being carbonated.

In recent years filling equipment has achieved a high level of sophistication in terms of throughput and automation. Lightweight cans and PET bottles present problems not in encountered with robust glass bottles and a number of modifications to filling procedures have been required. Product refrigeration (to 3-4^{0}C) has been widely used to overcome design problems in filling machines and to permit maximum output while maintaining a high standard of fill [1].

2. Experimental

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 analysed 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 [3].

Very important for this study were the results from the first and from the last day of the experiment.

3. Results and discussion

The experiment's main objective is the mathematical modeling of the influence factors on the replay function of the system.

In physical systems, the following connection between the response function η and the class of meaningful factors $x_1, \dots, x_k$ is settled:

$$\eta = \eta(x_1, x_2, \dots, x_k) \tag{1}$$

Except the meaningful factors, a large number of random factors $z_1, \dots, z_m$ influence the system.

The form and the structure of the physical systems' real model and especially of technological systems are not generally known. The real model contains both the influence of the significant factors and the influence of insignificant factors, which can be correctly expressed through the influence (regression) coefficients $ß_1$, $ß_2$, …, $ß_d$. The response function for the real model becomes:

$$\eta = \varphi(x_1, x_2, \dots, x_k, z_1, z_2, \dots, z_m, \beta_1, \dots, \beta_d) \tag{2}$$

As a consequence of the system modeling, the real values β_1, β_2, ……., β_d of the regression coefficients, for a given model, are replaced with their statistic estimations b_1, b_2, …, b_d determined as a consequence of the experimental data processing. The influence of aleatory factors is included in the experimental error, following its minimization.

Thus, from the real model we pass to the empiric model, where the real response function is replaced through the its statistic estimation, as a function of the existence factors and of the statistical estimations of the real regression coefficients [5]:

$$y = y(x_1, x_2, \dots, x_k, b_1, b_2, \dots, b_d) \tag{3}$$

In order to pass from the general shape of the empiric model, at the real shape, the connection between the response function and the regression coefficients is expressed through basis functions. The shape of these functions may be polynomial, exponential, logarithmical.

In this work an empirical model is elaborated. It is characterized by a polynomial function of 2nd order:

$$y = b_0 + \sum_{j=1}^{k} b_j x_j + \sum_{j=1}^{k} b_{j,j} x_j^2 + \sum_{i,j=1}^{k} b_{i,j} x_i x_j \tag{4}$$

By using the program Statistica 6.0, there were processed and analysed the experimental data, obtaining a series of statistic models pointing out the variation of the samples content in CO_2 depending on their volumes and time. The obtained equations are as follows:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{12} x_1 x_2 + b_{22} x_2^2 \tag{5}$$

where:

y – the content of CO_2;
$b_0, b_1, b_2, b_{11}, b_{22}$ – coefficients of polynomial regression;
x_1 – volume of PET;
x_2 – time of samples keeping.

The experimental data and the surfaces generated by the statistical mathematical models are presented in figures 1, 2 and 3.

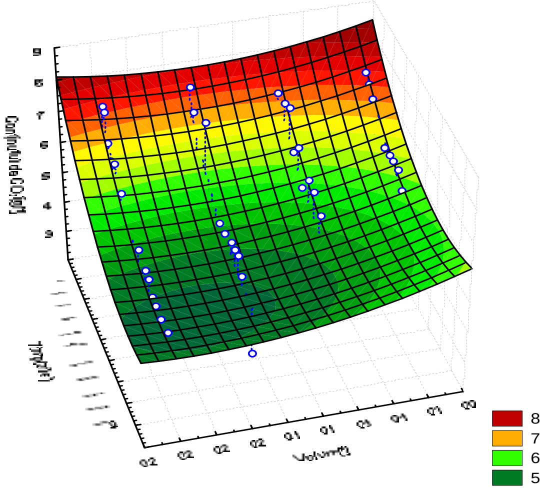

Figure 1. The variation of CO_2 content in sample I depending on the volume of sample and time

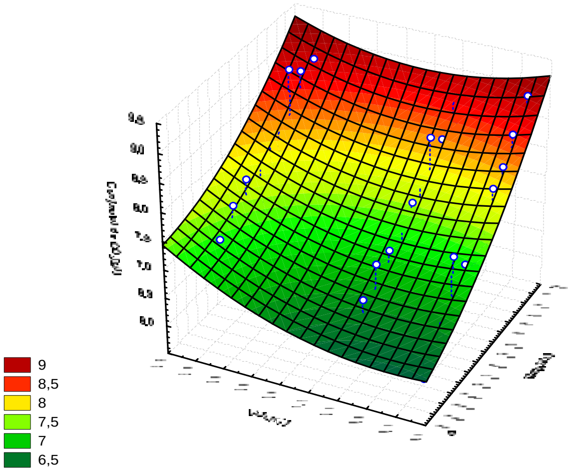

Figure 2. The variation of CO_2 content in sample II depending on the volume of sample and time.

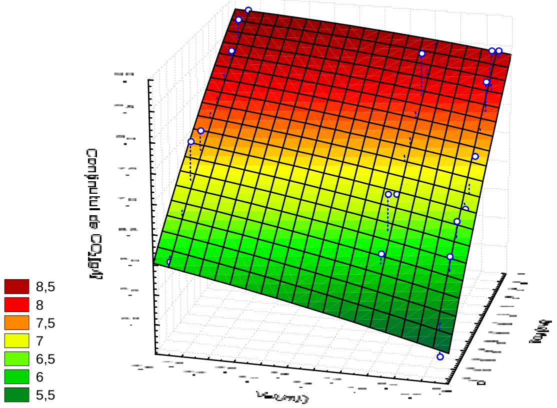

Figure 3. The variation of CO_2 content in sample III depending on the volume of sample and time.

The equations of statistical mathematical models obtained as a consequence of multiple polynomial regression 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	$y= 8{,}2866-1{,}7798\cdot x_1-0{,}0131\cdot x_2+0{,}5957\cdot x_1^2-0{,}0012\cdot x_1\cdot x_2+$ $+2{,}426E\text{-}5\cdot x_2^2$
II	$y = 9{,}3274-1{,}201\cdot x_1-0{,}0162\cdot x_2+0{,}4893\cdot x_1^2+0{,}0022\cdot x_1\cdot x_2+$ $+1{,}9742E\text{-}5\cdot x_2^2$
III	$y= 8{,}2339+0{,}3062\cdot x_1-0{,}0112\cdot x_2-0{,}0361\cdot x_1^2+0{,}0011\cdot x_1\cdot x_2-$ $-1{,}0235E\text{-}5\cdot x_2^2$

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 [4]:

- the indicator of the precision of the model, R^2:

$$R^2 = \frac{\sum_{i=1}^{n}(y_{icalc} - \bar{y})^2}{\sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2} \qquad (6)$$

n – number of data sets;

y – dependent variable, content in CO_2 of carbon-gaseous juices;

y_{icalc} – value resulted for y on the basis of the regression equations;

$\hat{y}_i$ – experimental value;

$\bar{y}$ - average value.

- the correlation coefficient of the CO_2 content as a function of on volume and time. Their corresponding values were calculated with the formula:

$$R = \sqrt{1 - \frac{\sum_{i=1}^{n}(\hat{y}_i - y_{icalc})^2}{\sum_{i=1}^{n}(\hat{y}_i - \bar{y})^2}} \qquad (7)$$

The values of the concordance indicators obtained as a consequence of the application of calculus formulas above are presented in table 2.

Table 2. The concordance indicators of determined statistical models

Concordance indicators	Sample I	Sample II	Sample III
Indicators of model precisions, R^2	0.60	0.78	0.84
Correlation coefficient, R	0.77	0.88	0.92

The comparative analysis of samples in the bottling moment and after a period close to the maximum limit of the validity term (204 days), there were obtained the results presented in figures 4 and 5:

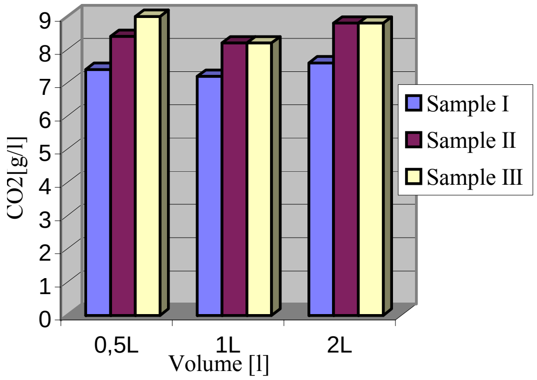

Figure 4. CO_2 content in samples, in the moment of bottling, for three different volumes

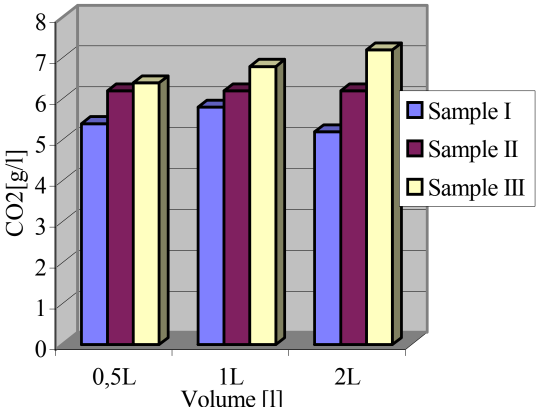

Figure 5. CO_2 content in samples, after 204 days after bottling, for three different volumes

From the figure 4, there is noticed that, at the bottling of the juice corresponding to sample I, the manufacturing company preferred an equal dosage of CO_2. The companies manufacturing the sample II and especially III have chosen a supplementary dosage of the 0.5 litre PET bottle and easily raised in case of the 2-litre bottle comparing to the other volumes.

After an interval of approximately 200 days, the values of CO_2 in PET bottles are presented in figure 5. To be pointed out that samples I have lost the most of the content of CO_2, especially in the bottles of 0.5 and 2 litres. The

CO_2 conservation in samples II is approximately equal, showing a correct initial dosage. For the sample III the CO_2 concentration is also found at high value, it even increases with the PET volume.

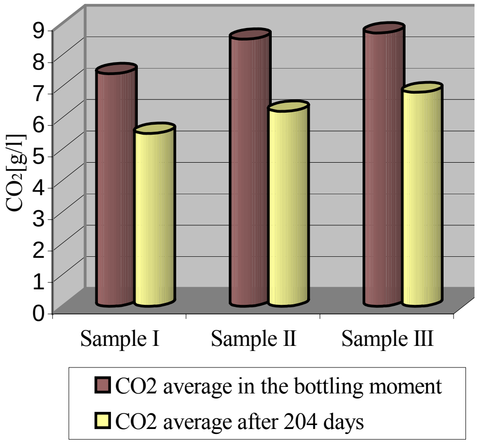

Figure 6. Comparative study of average CO_2 variation in time for the three samples

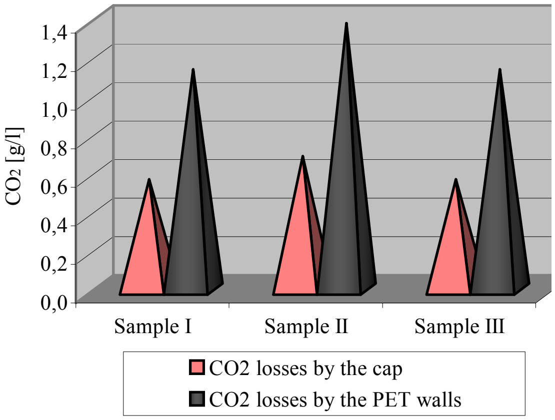

Figure 7. Comparative study of average CO_2 losses in time for the three samples

The sample I manufacturing company, usually insert in the manufacturing process a relatively low content of CO_2 in the carbonated soft drinks comparing to the other companies. This is the main factor (near PET quality, losses through the stopper etc.) for which a small quantity of CO_2 is found after 204 days in the bottles. The average of carbon dioxide is higher, especially for sample III, according to the graphical representation from the figure 6.

Seeing that the losses of carbon dioxide are distributed approximately as follows: one third due to the stopper tightness and the remaining part due to PET walls, in figure 7, was represented comparatively the medium CO_2's losses trough the stopper and trough the PET for the three studied samples.

The medium losses for the first and the third samples in time are approximately identical, but the CO_2 level after 204 days is different. One can notice this in figure 7, by comparing the first sample with the third sample. In case of sample II, the losses through the PET walls are significantly higher, but compensated through a supplementary proportioning of CO_2.

4. Conclusions

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.

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.

5. References

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