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Diffusion of Benzoic Acid in Flour Confectionery Products during Baking

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Abstract

Diffusion of benzoic acid (BA) in flour confectionery during baking of puff pastries with fruit jam has been experimentally studied in the present paper. BA was added to jam as an ingredient for 5 variants in the following shares of the weight of jam: 0.1%; 0.2%; 0.3%; 0.5% and 1.0%. It has been established that in the process of baking puff pastries, BA penetrates from jam into the dough due to diffusion after baking for 20 minutes at 200 °C. The concentration of BA in samples of jam and dough in a ready puff pastry was determined by the method of capillary electrophoresis using a KAPEL 105M device (Russia), with obtaining electrophoretograms. The process of BA diffusion in jam and dough was described based on the equation of one-dimensional nonstationary diffusion in partial derivatives, which had been solved by the numerically by the grid method according to the implicit scheme. At each time layer, a system of linear equations with three-diagonal matrix was solved. Diffusion coefficient BA in the dough was $5.6 \cdot 10^{-12}$ m^2/sec. Describing the experimental data with constant coefficient of BA diffusion in jam proved impossible. The dependence of BA diffusion coefficient in jam on BA concentration had been proposed in the form of an exponential function. Information had been provided about the convergence of material balance and graphic dependencies of changing the average BA concentrations on a temporary layer in jam in baking puff pastry. Experimental and calculation data were in acceptable qualitative and quantitative agreement.

Keywords: benzoic acid, diffusion, flour confectionery, jam, dough.

INTRODUCTION

Benzoic acid (BA) and its salts are widely used in food industry as preservative E210 for conservation of fruit purees, fruit juices, jams, canned vegetables, margarine, candies, liqueurs, flour confectionery, etc. BA is white, and can dissolve in fats, alcohols and water. In natural products, it is contained in bilberries, blueberries and cranberries. However, BA obtained by industrial oxidation of toluene is mostly added into food products. E210 has strong antiseptic action on yeast and mold, extending the shelf life of food products, which is one of the main reasons for using it.

Antimicrobial effect is only manifested by undissociated acid. Due to the high dissociation constant ($6.46 \cdot 10^{-5}$), BA is used for preservation of only highly acidic products. At pH>5 to 6, efficiency of this preservative is sharply reduced [1].

In manufacturing flour confectionery with fruit filling, various ingredients are used, those not containing BA, and those containing it. The baking process is not long, and the resulting product is a heterogeneous system that consists of various phases with distinct interfaces. The problem of BA migration in such systems is complex, which requires experimental studies.

RELATED WORK

Literature provides information about BA solubility in various solvents. In work [2] BA solubility was studied in pure solvents like ethanol, toluene, heptane, cyclohexane, pentane and chloroform in the temperature range between 278.15 and 323.15 K and in binary mixtures "ethanol-toluene" and "ethanol-heptane". It has been established that BA solubility is high in ethanol, quite high in chloroform, low in toluene, and significantly low in heptane, cyclohexane and pentane. In binary mixtures, BA solubility increases with increasing ethanol concentration. BA solubility increases with increasing the temperature.

BA solubility and thermodynamic constants of dissociation in water were studied in work [3]. It has been experimentally shown that there is no regular correlation between BA thermodynamic dissociation constant and the temperature in the interval between 16 °C and 41 °C.

In work [4] a laboratory setup is shown for measuring solubility of dissolved solids in liquids. BA solubility in water was assessed at 293-338 K, of 2-naphthol in water - at 293-373 K, and of salicylic acid in water - at 293-343 K. The obtained data are well in agreement with the theoretical solubility values shown in the literature. Empirical correlations are provided for predicting solubility in the entire range of the studied temperatures, and good agreement is shown between the experimental and the calculated data.

The process of BA adsorption by granular activated carbon (GAC) from waste waters has been studied [5]. Experimental curves of BA adsorption by GAC isotherms at various temperatures between 25 and 60 °C have been built. Experimental data were compared to the calculated data using models like Langmuir, Freundlich, Reddlich-Peterson, Toth and Radke and Prausnitz. It has been shown that model Radke and Prausnitz describes best the experimental data. A new model of temperature effect term (T. E. T) has been developed to account for the effect of temperature on the adsorption curve that more accurately describes the experimental data.

Isotherms of BA adsorption by activated carbon at various pH values and high temperatures (300 °C and 800 °C) are also shown in work [6]. It has been shown that Freundlich and Langmuir equations were successfully applied to the adsorption isotherm data of BA.

In work [7] BA diffusion coefficient in water was measured at 25 °C, depending on the concentration. It has been found that the diffusion coefficient decreases from $1.25 \cdot 10^{-9}$ m^2/s down to $1.07 \cdot 10^{-9}$ m^2/s when the concentration increases from 0.27 mol/m^3 to 5.44 mol/m^3. This effect has also been found in this work.

Thus, works [2-7] experimentally proved BA ability to dissolve in various solvents and to be adsorbed in the pores of the adsorbent (to penetrate into a solid absorbent).

The present work presents the experimental data on BA composition in jam and dough of a ready stuffed flour confectionery product puff pastry "Curly" as a result of BA diffusion from jam into the dough.

METHODS

BA concentration in samples of jam and dough (in a ready puff pastry) was determined by capillary electrophoresis using the KAPEL 105M device (Russia), which was a fully computer-controlled device with a switchable wavelength photometric detector, a system for automatic sample replacement and a water cooling system for the capillary. The method is based on diluting samples of distilled water, separation of components of complex mixtures in a quartz capillary under the action of electric field and the quantification of acids. The components were detected at the wavelength of 254 nm. Microvolume of the analyzed solution was injected into the capillary prefilled with the background electrolyte: 20 mmol/dm^3 of sodium tetraborate and 40 mmol/dm^3 of sodium dodecyl sulfate. Using Elphoran software, electrophoretograms were recorded for each aliquot of the sample, and components were identified in the sample by matching the components' migration times in the sample and in the reference mixture.

RESULTS AND DISCUSSION

The BA diffusion from jam into dough experiment was made in 5 variants of BA content as an ingredient in jam (Table 1) and the absence of BA in the dough. According to the recipe, 233.94 g of jam were taken per 1,000 g of ready product, that is, ~47 g of jam per variant. The recipe of confectionery product puff pastry "Curved" with filling is shown in Table 2. The process of preparing puff pastries is shown in Figure 1.

According to the recipe, the amount of margarine required per 1,000 kg is 280.73 kg, i.e. ~56.15 g of margarine for each variant; the amount of water required for kneading is 459 ml.

After baking flour confectionery (puff pastries), electrophoretograms were taken and compared to the material balance (Table 3).

Table 1 – Initial data

Variant number	BA content in jam to the weight of jam	Amount of BA added to jam	Dough weight, g
1	0.1%	47	200
2	0.2%	94	200
3	0.3%	141	200
4	0.5%	235	200
5	1.0%	470	200

Table 2 – Composition of stuffed confectionery product puff pastry "Curly"

Ingredients	dry matter, %	natural, g	in dry substances, g
Wheat flour	85.50	467.87	400.03
Margarine	84.00	280.73	235.81
Fruit filling "Jam Apricot"	68.00	233.94	159.08
Sugar	99.85	140.38	140.17
Rice flour	91.00	37.43	34.06
Salt	96.50	7.47	7.21
Losses	2.7	167.82	26.36
Total	-	1,167.82	976.36
Output	95	1,000	950

Table 3 – Material balance

% of BA introduced into jam from the weight of jam	BA in the dough of ready puff pastry, *D*, mg/kg	BA in jam of ready puff pastry, *F*, mg/kg	BA amount in a ready puff pastry, *G*, mg/kg	Amount of BA added to jam, mg	Deviation, %
0.1	121.6	128.8	36.85	47	23.7
0.2	276.3	469	89.74	94	4.54
0.3	419	1223	160.14	141	13.57
0.5	670.1	1392	229.60	235	2.30
1	1140	3216	430.45	470	8.41

a) b) c)

d) e)

f) g) h)

Figure 1 – The process of flour confectionery preparation (stuffed puff pastry "Curly"): a) weighing jam; b) adding BA; c) weighing dough samples; d) dough samples; e) the process of making curly puff pastries; g) puff pastries prepared for baking; h) ready puff pastries

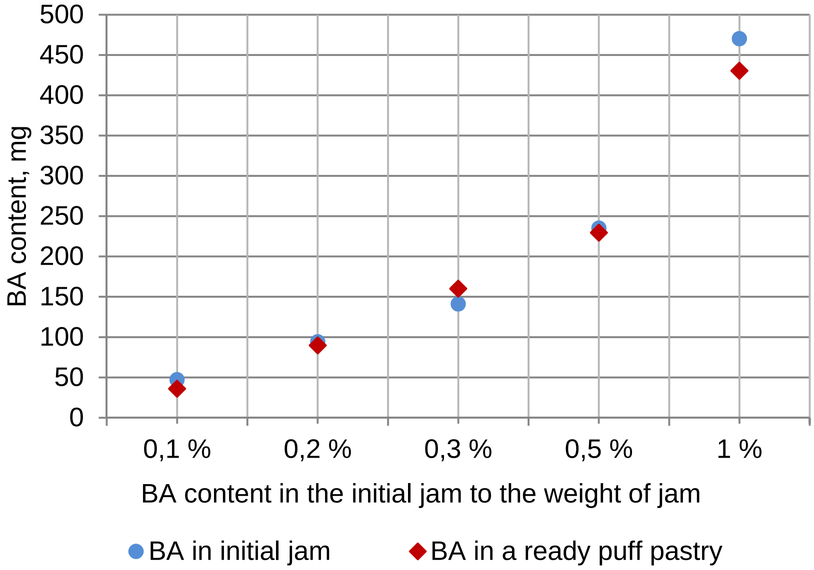

Figure 2 – Repeatability of the material balance

BA amount in a finished puff pastry, G, mg, is defined as follows.

$$G = D \cdot \frac{245}{1000} + F \cdot \frac{47}{1000},$$

where it is assumed in the first approximation that the weight of jam remains constant in the baking process, and in each variant is equal to 47 g, and the weight of wet dough is taken in an amount of 200 g, including margarine pit into it, in the amount of 56.15 g is reduced due to evaporation of moisture during baking and is equal to 245 g for each variant. It has been taken into account that in the baking process, humidity inside the product remains high, the loss of water during the baking process (oven loss) is about 12-15%. Repeatability of the material balance is shown in Figure 2.

Description of the process of BA diffusion in jam has been made in the first approximation, based on the equation of unsteady one-dimensional diffusion, where BA concentration varied in time and along a single spatial coordinate. The change in the layer thickness (jam, dough) in the process of baking was not considered in the mathematical model.

The equation of one-dimensional nonstationary diffusion is

$$\frac{\partial C}{\partial \tau} = D(\mathrm{C})\frac{\partial^2 C}{\partial x^2}, \quad (1)$$

where C is the BA concentration in jam that changes in time and space, m^3 BA/m^3 of jam; τ is the baking time, s; x is the coordinate in the direction perpendicular to the plane of the tray with puff pastries, m; $D(C)$ is the coefficient of BA diffusion in jam, m^2/s.

Equation (1) in finite difference has the form

$$\frac{C_{i,j+1}-C_{i,j}}{\Delta\tau} = D(\mathrm{C})\frac{(C_{i-1,j+1}-C_{i,j+1})-(C_{i,j+1}-C_{i+1,j+1})}{(\Delta x)^2}, \quad (2)$$

where i denotes layers by the coordinate, and j – by the time.

After transformations, we get

$$C_{i,j+1} - C_{i,j} = \frac{D(\mathrm{C})\Delta\tau}{(\Delta x)^2}\left(C_{i-1,j+1} - 2C_{i,j+1} + C_{i+1,j+1}\right). \quad (3)$$

Let us denote

$$\mathrm{Fo} = \frac{D(\mathrm{C})\Delta\tau}{(\Delta x)^2}, \quad (4)$$

where Fo is an analog of the Fourier criterion.

Taking into account (4), after transformation we get

$$C_{i,j+1} - \mathrm{Fo}\cdot C_{i-1,j+1} + 2\mathrm{Fo}\cdot C_{i,j+1} - \mathrm{Fo}\cdot C_{i+1,j+1} = C_{i,j}. \quad (5)$$

Finally, we get

$$-\mathrm{Fo}\cdot C_{i-1,j+1} + (1+2\mathrm{Fo})C_{i,j+1} - \mathrm{Fo}\cdot C_{i+1,j+1} = C_{i,j}. \quad (6)$$

Equations (5) and (6) are valid for a purely diffusive process. They are solved by the grid method using an implicit scheme.

The initial conditions for considering diffusion in jam are: $\tau = 0 \quad C_{i,1} = C_0$,

where C_0 is equal to the initial BA concentration in jam.

The boundary conditions (at the interface with the dough) are $x = 0 \ (i = 0) \quad C_{0,j} = C_d^*$,

where C_d^* is the equilibrium BA concentration in jam at the interface.

It is assumed that mass transfer does not occur in the center of jam

$$\frac{\Delta C}{\Delta x} = 0, \text{ i.e., } C_{n-1,j} = C_{n,j}$$

where n is the layer adjoining to the center.

The initial conditions for considering diffusion in the dough are: $\tau = 0 \quad C_{i,1} = 0$,

where "zero" corresponds to the initial BA concentration in the dough.

The boundary conditions (at the interface between the dough and jam) are the following

$$x = 0 \ (i = 0) \quad C_{0,j} = C_m^*,$$

where C_m^* is the equilibrium BA concentration in the dough at the interface.

In considering the mass transfer in the dough, it is assumed that at the interface between the bottom of the tray on the one hand and dough on the another one, as well as between the dough and the air, mass transfer also not occurs, i.e. during baking BA remains in the puff pastry.

$$\frac{\Delta C}{\Delta x} = 0 \quad \text{i.e.,} \quad C_{k-1,j} = C_{k,j},$$

where k is the layer adjacent to the bottom of the tray and bordering the dough.

The profile of concentrations in the "jam-dough" system is shown in Figure 3: C_0 is the initial BA concentration in jam; C is the current BA concentration at the interface from the side of jam; C_d^* is the equilibrium BA concentration on the interface from the side of jam; C_m is the current BA concentration at the interface from the side of dough; C_m^* is the equilibrium BA concentration on the interface from the side of dough. The thickness of the interface is taken equal to zero.

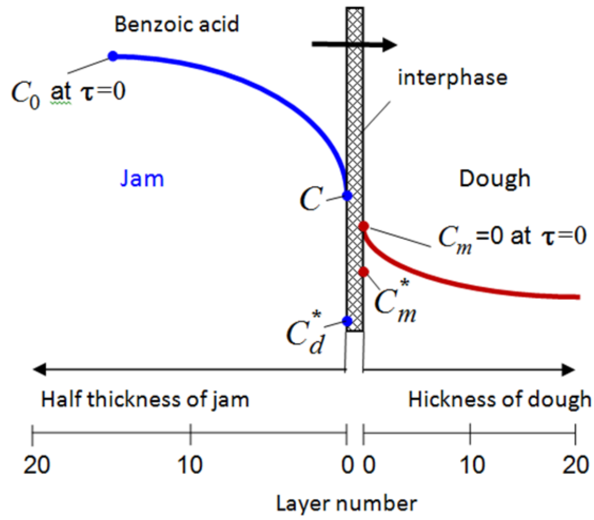

Figure 3 – Profile of BA concentrations in the "jam-dough" system

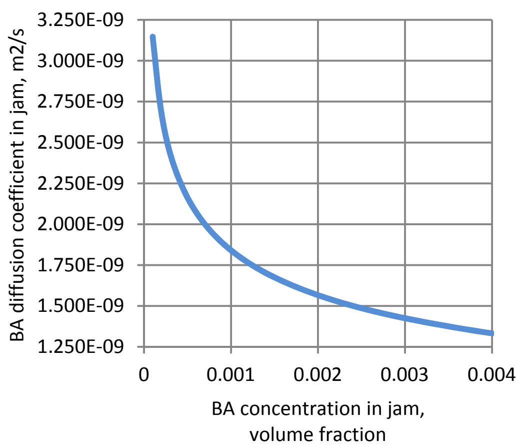

Figure 4 – Dependence of BA diffusion coefficient in jam on BA concentration in jam

On each time layer, a system of linear equations with three-diagonal matrix [8] was solved, the sequence of equations and the solution algorithm were provided in [9, 10]. In solving this problem, the following has been adopted: the number of layers of jam and dough is 20; dough thickness is 2 mm; jam thickness is 6 mm (3 mm from the centre of jam to the interface). For expressing concentrations of components, it has been taken into account that BA density is 1,270 kg/m^3; jam density is 1,300 kg/m^3; and dough density is 350 kg/m^3.

For BA diffusion coefficient in jam D, m^2/s, we have obtained equation

$$D = 3.68 \cdot 10^{-10} \cdot C^{-0.233}, \qquad (7)$$

where C is the average value of BA concentration on a time layer, volume fraction.

Dependence of the BA diffusion coefficient in jam D, m^2/s, on BA concentration in jam C, volume fraction (m^3 BA/m^3 of jam) is shown in Figure 4. With increasing BA concentration in the original jam, the diffusion coefficient decreases.

Figure 5 shows the experimental values and calculated curves of BA concentration in jam from the time of baking at various BA concentrations in the initial jam. BA diffusion coefficient in jam D, m^2/s, was calculated for each time layer according to equation (7). Figure 5 shows good qualitative and quantitative correlation among BA concentrations in jam in a ready puff pastry, except for variant 3, where jam was added in the amount of 0.3% by weight of jam. This may be explained by an error in the homogenization of the sample of jam when BA concentration was determined in jam in a ready puff pastry.

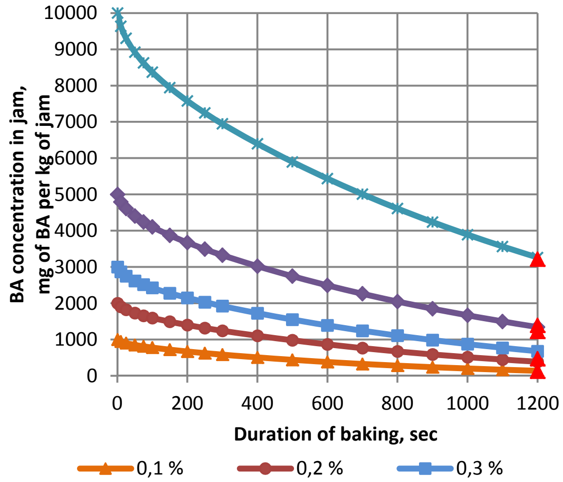

Figure 5 – Dependence of BA concentration in jam on the time of baking at various BA concentrations in the initial jam

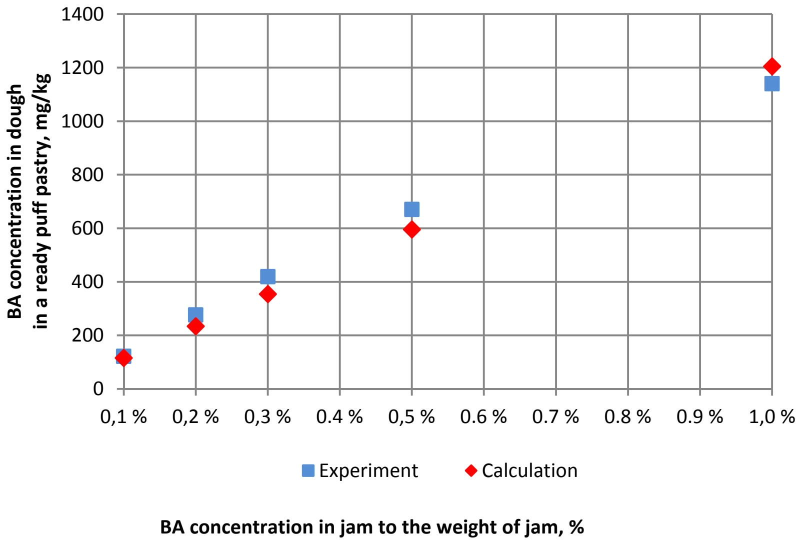

Figure 6 – Comparison of the calculated and experimental data of BA concentrations in the dough in a ready puff pastry

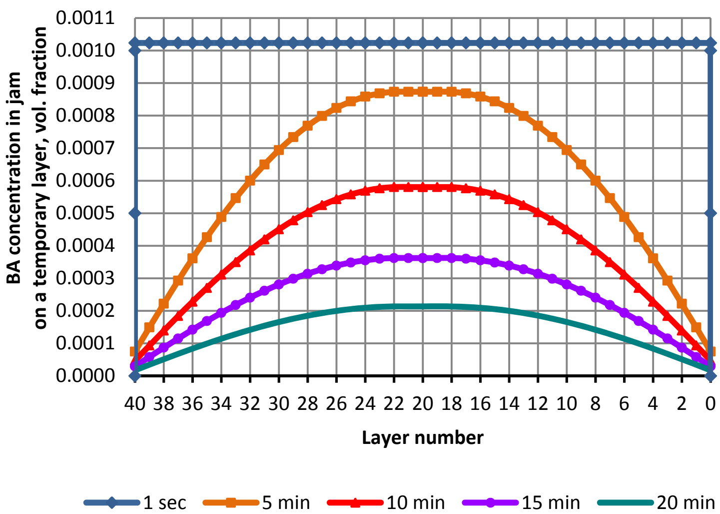

Figure 7 – Changes in BA concentration in jam in the baking process for variant 1

Figure 6 shows comparison of the calculated and experimental BA data in the dough of ready puff pastry. The calculation was made according to an implicit scheme with calculating the BA diffusion coefficient in jam at each time slot according to equation (7) and the constant BK diffusion coefficient in the dough equal to $5.6 \cdot 10^{-12}$ m^2/s.

Figure 7 shows changes in BA concentration in jam in the baking process for option 1 when BA is added to jam in the amount of 0.1% by weight of jam. Layer number "20" corresponds to the middle of jam thickness.

The calculation is made according to the number of layers with symmetry equal to 20. The calculations are made at equilibrium BA concentrations in jam at the interface between jam and dough, which is equal to $1 \cdot 10^{-8}$ vol. fraction. The equilibrium BA concentration in the dough at the interface between dough and jam at each time layer was calculated according to Henry's law

$$C_m^* = 0.54 \cdot C, \qquad (8)$$

where C was the current BA concentration in jam at the interface between dough and jam at each time layer; 0.54 was Henry's constant determined by model identification.

CONCLUSION

It is established that BA, due to diffusion, penetrates from jam into dough during baking of a filled flour confectionery puff pastry "Curved" at 200 °C for 20 min. BA diffusion coefficient in jam depends on BA concentration in jam. With the increase in concentration, the diffusion coefficient decreases. A dependence of BA diffusion coefficient in jam on BA concentration has been proposed in the form of an exponential function. BA diffusion coefficient in dough is assumed constant and equal to $5.6 \cdot 10^{-12}$ m^2/s. The BA diffusion process in jam and dough was described based on the equations of one-dimensional nonstationary diffusion, where BA concentration varied in time and in one spatial coordinate in the direction perpendicular to the plane of the baking pan. The solution was completed using the grid method according to the implicit scheme. The equilibrium BA concentration in the dough at the interface between dough and jam at each time layer was calculated according to Henry's law. Henry's constant was determined by model identification, and was equal to 0.54. Experimental and calculation data were in acceptable qualitative and quantitative agreement. Based on the identification model, a numerical experiment can be performed with various thicknesses of dough and jam, and various BA concentrations.

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