Egyptian Journal of Chemistry

Mathematical Model of Mother Liquor Deposition in Industrial Sugar

D.V. Arapov*[a], A.V. Skrypnikov[a], V.V. Denisenko[a], I.A. Vysotskaya[a], M.A. Zaitseva[a]

[a]Voronezh State University of Engineering Technologies, 19, Revoljucii Avenue, Voronezh, 394036, Russian Federation

Abstract

In this article, an object of a research is the mechanism of incorporation of mother liquor components in the growing crystals of sucrose and establishment of the dependence allowing to estimate quantitatively inclusion of components of the mother liquor in industrial crystals of granulated sugar. Water and a complex of not sugars are considered as components of sugar solution. To date, experimental estimates of the inclusions of various non-sugars in sugar crystals have been accumulated, and a qualitative and quantitative analysis of impurities in crystals have been made, which showed that the number of inclusions depends on the purity of the crystallized solution, the rate of crystallization, the hydrodynamic situation in the apparatus, temperature and concentration fields, the viscosity of the solution, and other factors. These factors are mainly due to the technological regime of the crystallization process, and understanding the degree of their influence on the inclusion of impurities allows authors to minimize the capture of non-sugars by growing crystals. It is shown that the inclusion of non-sugars occurs mainly during the formation of crystals and their subsequent growth at a high supersaturation coefficient. However, the available data is not sufficient to identify and formalize all the laws of this rather complex phenomenon. At this stage, it is more appropriate to use the mathematical methods of probabilistic interpretation. The purpose of the study was a creation of a mathematical model that could be used to estimate the amount of components of the masterbatch solution (non-sugar and water) passing from solution to crystal, depending on the supersaturation of the solution, its temperature, viscosity, purity, and dry matter content. Based on the probability theory, a mathematical model of the deposition of the mother liquor in industrial crystals of granulated sugar has been developed. The mother liquor includes water in which sucrose and a complex of non-sugars are dissolved. Some of the non-sugars and water can be trapped by the growing crystal. The model allows you to calculate the amount of non-sugars and water that have passed into the sucrose crystal during its growth. The average relative error of the model is 8-10%.

Keywords: mathematical model; multicomponent solution; sugar crystal; non-sugar; mother liquor

1. Introduction

The study of the inclusion of non-sugars in sugar crystals is important, first, from the point of view of achieving modern quality indicators: the mass fraction of reducing substances is ☐0.03-0.04 %, the mass fraction of ash is ☐ 0.027-0.036 %, the chromaticity in solution is ☐ 45.0-60.0 ICUMSA units. Secondly, the amount of impurities in sugar crystals should be minimized when using the latest in the technology of mother liquor as a crystal base when boiling masscuite in modern crystallization schemes [1-3]. The efficiency of the beet sugar plant directly depends on the quality of the product obtained [4].

Qualitative estimates and explanations of the inclusion of non-sugars in sugar crystals are given in [1-2, 5-8]. In particular, the effect of the specificity of the inclusion of individual non-sugars inside sugar crystals has been established. For example, colloidal impurities of beet sugar products have a negative charge, and sucrose is weakly positively charged, so colloidal particles can serve as centers of crystallization and can be introduced into the crystal lattice due to electrostatic forces. Some caramels with

_____

_____

a negative charge are easily absorbed by adhesion on the surface of the crystal and color it. The colored substances of molasses have a high adsorption capacity in relation to sucrose. Some non-sugars that are isomorphically bound to the crystal lattice, such as iron and potassium are absorbed by the crystal faces and are fairly uniformly distributed within the crystal.

In view of the great practical significance of the problem under consideration for the technology of sugar crystallization, we are going to analyze in more detail such a most common defect of real crystals as the inclusion of an intercrystalline solution and indicate the reasons for its occurrence.

Using the microscopy we can observe interlayer of the intercrystalline solution in the middle part of the crystal. The reason for this is that at the periphery of the face, at the corners and edges of the crystal, the solution is more supersaturated than in the middle of the face, where it can be unsaturated. This is due to the fact that in the corners and edges the resumption of supersaturation occurs faster than in the middle of the face. Thus the inhomogeneity in the solution surrounding the growing crystal is created by the process of crystal growth itself. At the periphery, the germ of a new layer appears which quickly grows tangentially along the face, overlapping the unsaturated solution in the middle of the face. The solution in the middle of the face differs from the rest of the solution not only by a lower concentration of sucrose, but also by a higher temperature, which also reduces the degree of supersaturation since the crystallization of sucrose is accompanied by the release of energy in the form of heat. Without intermediate layers of intercrystalline solution, the layers are adjacent to each other only on the peripheral parts of the face, at the vertices and edges. After drying the crystal, the solution in the interlayers partially crystallizes, leaving voids in the crystal in the form of pores, cracks and capillaries. The crystal becomes inhomogeneous and cloudy.

In most cases, it is possible to obtain homogeneous crystals without inclusions of intercrystalline solution only from weakly supersaturated solutions. Since the solubility of sucrose decreases with decreasing temperature, it is possible to obtain homogeneous crystals with a gradual slow decrease in temperature throughout the entire crystallization process.

To obtain the accelerated growth of homogeneous crystals from strongly supersaturated solutions it is necessary to look for a way to eliminate the main cause of the inhomogeneity of the crystals that is the overlap of the layers of the unsaturated solution by growing layers. By intensive stirring of the solution, preferably vibrational one with the alternating action of the driving force it is necessary to neutralize the difference in concentrations at different points near the growing face of the crystal, which has a very strong effect in highly supersaturated solutions. Therefore for accelerated crystal growth, it is necessary to prevent the formation of a "courtyard of crystallization" in which the concentration is lowered [8].

It follows from the above that at each certain speed of motion of the crystals relative to the solution there is a certain upper limit of the supersaturation of the solution, above which turbid spots appear on the crystal indicating that the intercrystalline solution is overlapped by growing layers.

Thus, the internal imperfections of crystals are associated with the inclusion of intercrystalline solution and various foreign substances suspended in the solution in the form of turbidity or in the form of dissolved impurities. These impurities are arranged in layers, and as the crystal moves, the overlap of impurities by layers growing on the face either stops completely or weakens significantly.

In the industrial crystallization of sucrose, practically no crystal has an ideal surface structure [9-11], and each crystal has imperfections. When falling between lattice sites or going out to the surface and completing the lattice, sucrose molecules can leave vacant places. Molecules or ions of non-sugars can replace some lattice elements or penetrate between them, thereby violating the stoichiometric ratio. Another type of defect, called a dislocation, which is a geometric imperfection, ensures the presence of ready-made steps on the crystal face, which can trap impurities on the surface.

The interaction of a growing crystal with impurities leads to a change in the growth rate [10], the capture of impurities and the formation of defects or internal stresses, dislocations, microcracks, build-ups [9-11] which divide the crystal into separate microcrystalline blocks bonded to each other some way. The presence of the block structure of real crystals is proved by experimental data on the study of the intensity of X-rays reflected from the crystal as

_____

well as the results of testing the resistance of crystals to rupture which is always less than the theoretical one, analysis of etching patterns on the surface and laue patterns (diffraction image of a stationary single crystal obtained using X-rays) mechanically deformable crystals [7, 9, 10].

Growths, cracks and other lattice imperfections make it easier for active molecules and non-sugar ions to be adsorbed on the surface of the sucrose crystal. According to [7] the condition for the incorporation of non-sugars into growing sugar crystals is a high positive hydration of these impurities, for example, substances in a colloidal state. Impurities can be held on the crystal faces by the force of the surface tension of the solution, their adsorption can slow down or even stop further crystallization of these faces [7-11]. In research works [7, 12] it is noted that substances of colloidal dispersion are distributed uniformly in the mass of the crystal, and ash is distributed most often in the surface layers. At a high crystallization rate or a decrease in temperature the amount of co-crystallizing impurities increases. Surface adsorption of substances in a colloidal state is most often carried out [9] in places called active centers. As time passes, active sites with adsorbed impurities overlap the surfaces of other growing crystal faces, and non-sugar ends up inside the sugar crystal. These inclusions further contribute to the formation of crystals in the form of a crystalline body, consisting of micro blocks.

2. The purpose and the object of the study

It follows from the above that the distribution of impurities in crystals can have the following picture.

The growth of a sucrose crystal face consists in the deposition of molecules from solution on it. The presence of a layer in front of the face with an increased concentration of impurities hinders the growth of the face. After a while a blocking monomolecular layer may form, covering the facet and so its growth is hampered because impurity particles prevent the basic substance from penetrating to the crystal. However, two cases are possible here: 1) the impurity is not adsorbed by the crystal surface and it is simply washed off by convection currents; 2) the impurity consists of a surfactant; it is adsorbed on the crystal faces and slows down their growth. In this case, the impurity is incorporated into the crystal in layers parallel to the faces.

It is understood that different faces of the growing

crystal adsorb impurities on their surface in different ways. Those faces on which more impurities are captured slow down their growth more, and this explains the appearance of new faces in the case of the addition of surfactants.

Mechanical impurities are usually pushed aside by the growing edge. However, if the particle tightly touches the face, then the crystal cannot grow in this place, because sucrose molecules cannot get between the crystal and the foreign particle. In this case, the crystal grows around the particle, which turns out to be included in it. Mechanical impurities play an important role in the formation of all kinds of distortions in crystals. To restore normal growth of sucrose crystals, the layer of foreign particles (non-sugars) must be removed either by diffusion or by convection.

Thus, the inclusion of impurities in the sucrose crystal is carried out continuously as it grows, and the production sugar crystal itself, which is not an exception from the class of real crystals, can be represented in the form of a crystalline body consisting of separate microcrystalline blocks separated by micro cracks and attached to each other at different angles. These microcrystalline blocks consist of elemental 1 nm crystal cells from which sucrose crystals are constructed [11].

3. Materials and methods

For most crystalline bodies [9−11] the linear size of these blocks ranges from 10 to 100 nm. The linear dimensions of the sucrose molecule [13] along the axes a, b, c are $a = 1,089$ nm, $b = 0,869$ nm, $c = 0,777$ nm. If we take the average sizes of non-sugar molecules equal to the sizes of a sucrose molecule, and the size of the microblock is about ~ 10 nm, then on the surface of the block, under favorable conditions, no more than 10 molecules of non-sugars of accepted sizes can be deposited.

Let us assume that the deposition of a new molecule of non-sugars on one or another facet of the surface occurs regardless of the presence of one or several particles already adsorbed in this migration area. With a relatively small number (no more than 10-13) of adsorbed non-sugar particles, this assumption is physically quite justified, since the linear size of the migration region is within the order of ~ 10-15 nm, and the forces of adsorption interaction affect the distances about several tenths of a nm [10, 11].

_____

To derive the equation for the distribution of impurity molecules over the surface of a sucrose crystal by analogy with [9] let us determine the probability of formation of a molecular deactivating complex in the migration area m. Let us denote by F the total surface of 1 g-mol of granulated sugar crystals, and by f the averaged surface of the microblock of one crystal at a given temperature. Suppose that non-sugar molecules are adsorbed on the common surface, then the average number of non-sugar molecules in one microregion f will be equal to:

$$\mu = M \frac{f}{F}.$$

(1)

The probability of P formation of m – molecular deactivating complex of non-sugars in the cell with the surface of f equals to:

$$P = \left(\frac{f}{F}\right)^m \left(\frac{F-f}{F}\right)^{M-m},$$

(2)

where $\left(\frac{f}{F}\right)^m$ is the probability of deposition of m non-sugar molecules in the cell f;

$\left(\frac{F-f}{F}\right)^{M-m}$ is the probability of adsorption of other $M-m$ molecules on the surface $F-f$.

Let us assume that on the surface of a sugar crystal, molecules of non-sugars of a quite specific type, for example, colloidal degree of dispersion, are deposited. Then, assuming the equivalence of these molecules, we multiply the right-hand side of (2) by the number of m combinations of from the total M amount:

$$P = \frac{M!}{m!(M-m)!}\left(\frac{f}{F}\right)\left(\frac{F-f}{F}\right)^{M-n}.$$

(3)

Combining (1) and (3) we obtain the full probability of the formation of m-molecular deactivating complex poisoning the active surface of a sucrose f microcrystal:

$$P = \frac{\mu^m}{m!} \frac{M!}{M^m(M-m)!}\left(1-\frac{\mu}{M}\right)^{M-m}.$$

(4)

_____

Since the number $M > m$ $\left(M > 10^{23}, m \le 13\right)$ we can apply the passage to the limit to (4) as a whole and its individual factors:

$$P_m = \lim_{m\to\infty} P.$$

Then we obtain:

a) $\lim_{M\to\infty} \frac{\mu^m}{m!} = \frac{\mu^m}{m!};$

b)

$$\lim_{M\to\infty} \frac{M!}{M^m(M-m)!} = \lim_{M\to\infty} \frac{M(M-1)...(M-m+1)}{M^m} =$$

$$= \lim_{M\to\infty} 1 \cdot \left(1-\frac{1}{M}\right)...\left(1-\frac{m+1}{M}\right) = 1;$$

c)

$$\lim_{M\to\infty}\left(1-\frac{\mu}{M}\right)^{M-m} \approx \lim_{M\to\infty}\left[\left(1-\frac{\mu}{M}\right)^{-\frac{M}{\mu}}\right]^{-\mu} = e^{-\mu}.$$

Finally we obtain:

$$P_m \approx \frac{\mu^m}{m!}e^{-\mu},$$

(5)

that is, under the assumptions made, the distribution of colloidal molecules over the surface of sucrose crystals can be described by Poisson's law.

Verification of the obtained law was carried out during the machine simulation process on the basis of known experimental data [5] of the dependence of the speed of sugar crystallization on temperature, purity of solution and content of solids. The speed of activation of non-sugars was expressed as follows

$$v_{_H} = a_1 \left(\frac{\eta}{T}\right)^{a_3} \cdot v P_m = a_1\left(\frac{\eta}{T}\right)^{a_3} \cdot v \frac{(a_2 v)^m}{m! e^{a_2 v}},$$

(6)

where v is active molten concentration of non-sugars in the intercrystalline solution: $v = n e^{a_4 N}$; η is the viscosity of the intercrystalline solution; T is absolute temperature; N is mass ratio of non-sugar / water.

Coefficients $a_1 \div a_4$, index of power m (integer number) were determined in the course of a numerical experiment on a computer, while the number m was determined from the range 1–13:

$$K_{HCX} = 0,1558 \cdot 10^{-11} \cdot N \cdot \exp(N) \cdot \left(0,3761 \cdot N \cdot \exp(N)\right)^{13} \times$$
$$\times \exp\left(-0,3761 \cdot N \cdot \exp(N)\right) \cdot \left(\eta / T\right)^{0,0275}.$$

(7)

It has been established [5] that the growth of a crystal due to the inclusion of water depends on its content in the solution, the purity of the solution, the absolute temperature, the dynamic viscosity and can be described by the formula:

$$K_B = \frac{0,1757875 \cdot 10^{-15}}{Q} \cdot \left(1 - CV + 0,27007 \cdot (1 - CV) \cdot (1 - Q)\right)^{5,31} \cdot \left(\frac{T}{\eta}\right)^{1,85}$$

, (8)

where Q is purity of the mother liquor, of mass fraction; $(1 - CV)$– concentration of water in intercrystalline mother liquor, mass fraction.

Using formulas (7) and (8), one can calculate the amount of impurities (non-sugars and water) that have been incorporated into the crystalline phase from a multicomponent sugar solution. When using these formulas the calculation error is about 8-10% rel.

Fig. 1−3 shows the graphs of the dependence of the rate of incorporation of non-sugars into granulated sugar crystals, depending on the purity of the intercrystalline solution, the content of dry substances and temperature. A significant inclusion of non-sugars in the sugar crystal is observed when the solution purity is less than 70%. With an increase in the evaporation temperature, the rate of deposition of non-sugars in the crystal decreases, and with an increase in the concentration of dry substances, it sharply increases.
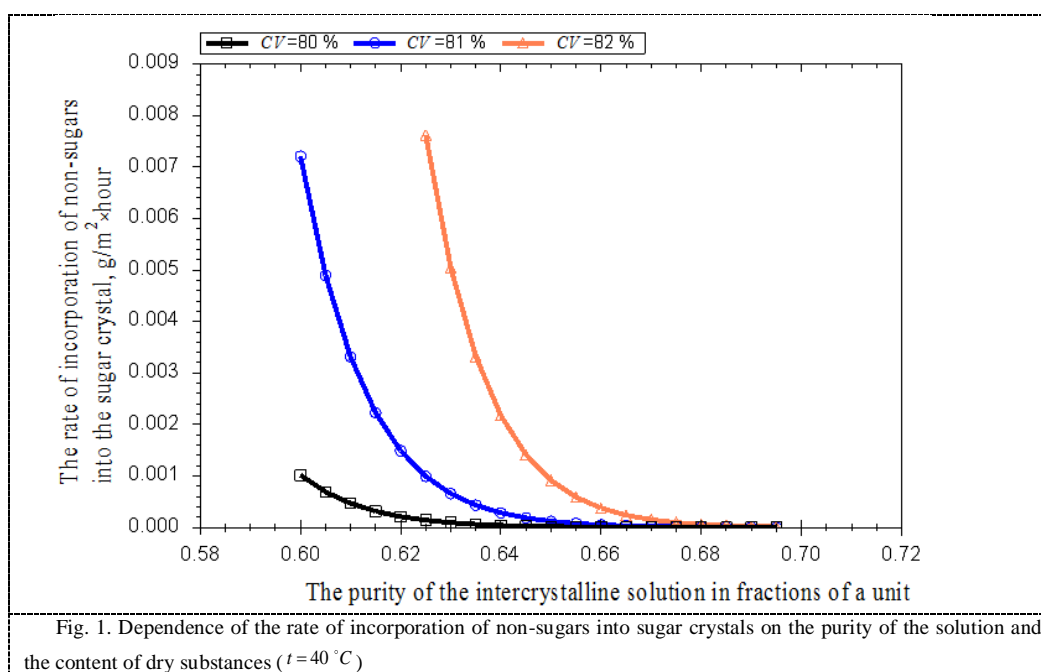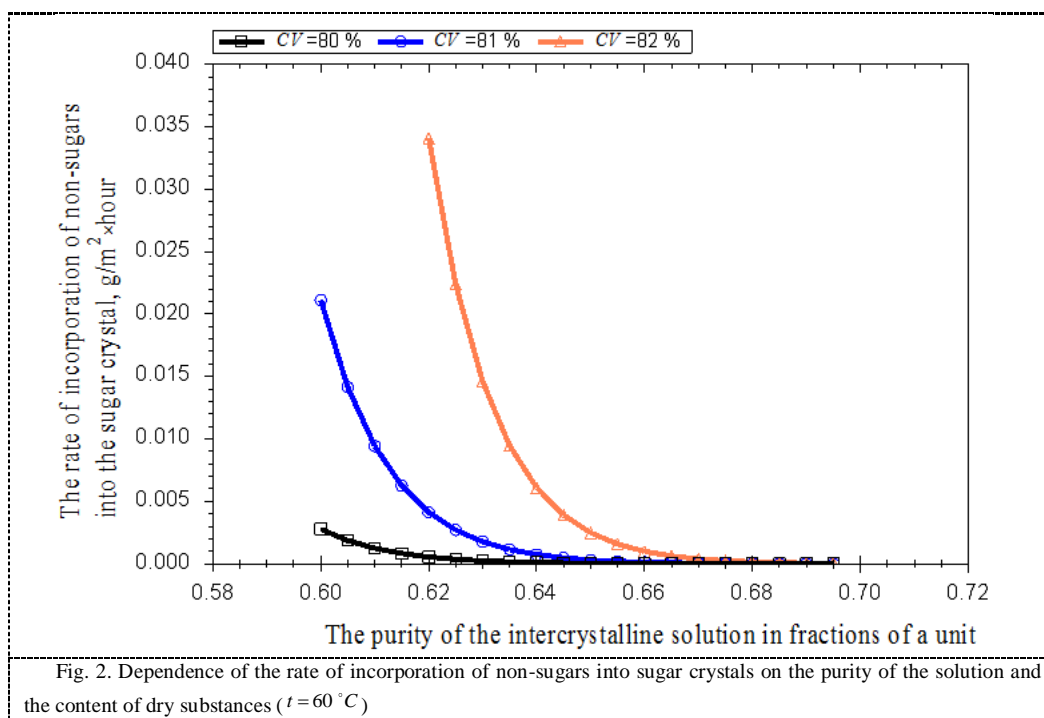

Fig. 1. Dependence of the rate of incorporation of non-sugars into sugar crystals on the purity of the solution and the content of dry substances ($t = 40\,^\circ C$)

Fig. 2. Dependence of the rate of incorporation of non-sugars into sugar crystals on the purity of the solution and the content of dry substances ($t = 60\ ^{\circ}C$)
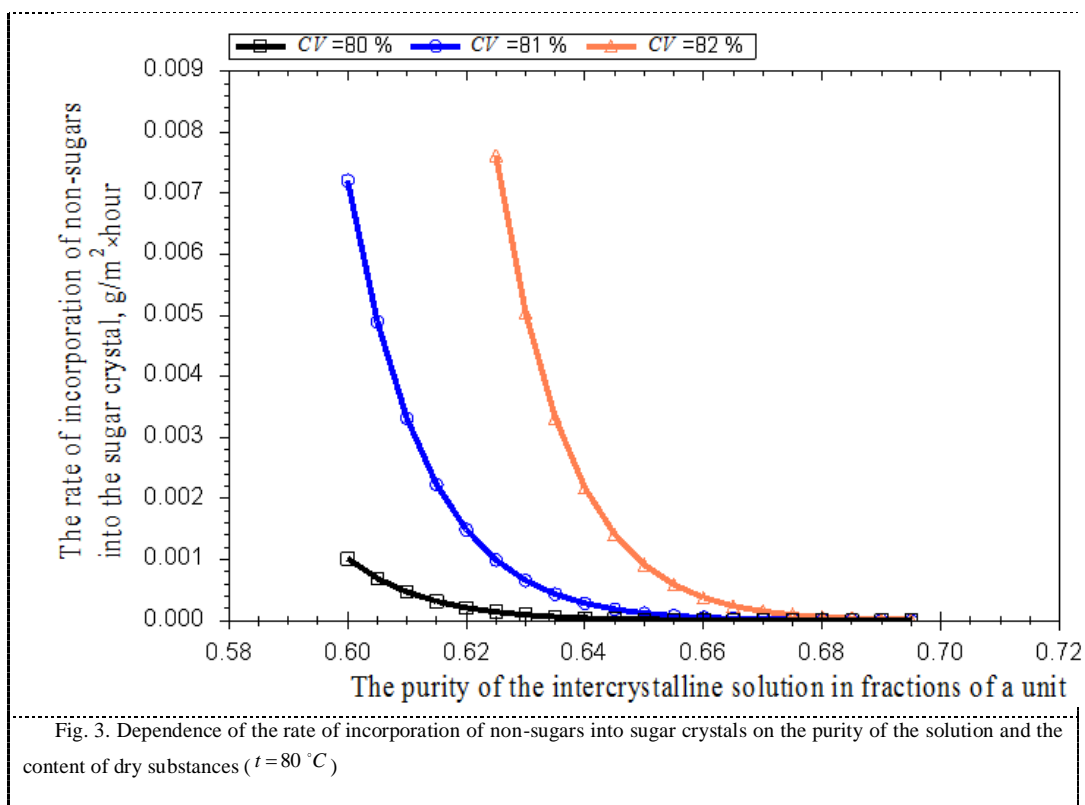

Fig. 3. Dependence of the rate of incorporation of non-sugars into sugar crystals on the purity of the solution and the content of dry substances ($t = 80\ ^{\circ}C$)

4. Conclusion

Thus, a mathematical model has been developed for the inclusion of non-sugars and water of a multicomponent solution into a growing sugar crystal. The model can be used to assess the quality of industrial sugar crystals by calculating the mass of non-sugar and water that have passed from solution to crystal.

_____

5. References

[1] Bugaenko I.F. (2006) Sugar crystallization schemes and their analysis (Moscow: Ltd Aveda)

[2] Tuzhilkin V.I., Balykhin M.G., Lukin N.D. and Kovalyonok V.A. (2018) New technologies of crystallization of sucrose as fundamental factor of increase in economic efficiency of sugar branch. *Journal of Advancements in Food Technology,* **1,** 1. https://doi.org/110.24411/0235-2451-2018-11223

[3] Ovsyannikov V.Yu., Toroptsev V.V., Berestovoy A.A., Lobacheva N.N., Lobacheva M.A. and Martekha A.N. (2021) Development and research of new method for juice extracting from sugar beet with preliminary pressing. *IOP Conf. Series: Earth and Environmental Science,* **640,** 052011. https://doi.org/10.1088/1755-1315/640/5/052011

[4] Gromkovskii A.I., Gromkovskii A.A. and Gromkovskaia N.A. (2021) Economic and mathematical model of the profit of sugar production from beets. *IOP Conf. Series: Earth and Environmental Science,* **640,** 052005. https://doi.org/10.1088/1755-1315/640/5/052005

[5] Arapov D.V., Kuritsyn V.A., Petrov S.M., Podgornova N.M. and Zaitseva M.A. (2021) Specific mass growth rate of sugar crystals: probabilistic modeling. *Food processing: Techniques and Techn*ology, **51,** 39. https://doi.org/10.21603/2074-9414-2021-1-39-52

[6] Arapov D.V., Kuritsyn V.A., Tichomirov S.G. and Denisenko V.V. (2019) Simulation of solubility by the example of a sugar solution. *Sugar Industry,* **144,** 660. https://doi.org/10.36961/si23792

[7] Dmitrienko A.U., Brenman S.A. (1992) Conditions for the Inclusion of non-sugars in growing sugar crystals. *Sugar Industry,* **5,** 13.

[8] Tuzhilkin V.I., Balykhin M.G., Petrov S.M., Podgornova N.M., Lukin N.D. and Kovalyonok V.A. (2021) Mathematical description of the isobaric vaporizing crystallization of sucrose. *Journal of Food Engineering,* **306,** 110614. https://doi.org/10.1016/j.jfoodeng.2021.110614

[9] Kobozev N.I. (1968) Adsorption catalysts and the theory of active centers. *Modern Issues of Physical Chemistry,* **III,** 3.

[10] Kreger F. (1969) The chemistry of imperfect crystals (Moscow: Mir)

[11] Panchenkov G.M., Lebedev V.P. (1974) Chemical Kinetics and Catalysis (Moscow: Chemistry)

[12] Singh S., Felavier H. (1974) Die verteilung von nichtsukrosestoff in sukrosekristallen. *Zuckerindustrie,* **11** 575; **12,** 639.

[13] Slavyansky A.A., Glazieva I.V. (2011) Physicochemical properties of solutions and crystals of sucrose. Sugar, **1,** 39.

_____