Представлено кінетичну модель процесу формоутворення крапель капсульованих рідин, починаючи від етапу формування зародка краплі до моменту її відриву під дією фізичних сил та технологічних параметрів. Одержані рівняння являються теоретичним описом процесу капсулоутворення та обґрунтовують тривалість процесу, розмірні характеристики кінцевого продукту та потужність конструктивних машин для одержання капсул

Ключові слова: ліпіди, капсулювання, кінетика відриву краплі, оболонка альгінат кальцію, відрив краплі, перемичка краплі, зародок краплі

Представлена кинетическая модель процесса формообразования капель капсулированных жидкостей, начиная от этапа формирования зародыша капли до момента ее отрыва под действием различных физических сил и технологических параметров. Полученные уравнения являются теоретическим описанием процесса капсулообразования и обосновывают продолжительность процесса, размерные характеристики конечного продукта и мощность конструктивных машин для получения капсул

Ключевые слова: липиды, капсулирование, кинетика отрыва капли, оболочка альгинат кальция, отрыв капли, перемычка капли, зародыш капли

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ANALYSIS OF KINETICS PATTERN IN THE FORMATION AND SEPARATION OF A DROP OF FLUID IN THE FORM OF A CAPSULE

V. Potapov
Doctor of Technical Sciences, Professor, Head of Department
Department of trade and refrigeration equipment and applied mechanics*
E-mail: potapov@bigmir.net

O. Neklesa
PhD, Associate Professor
Department of technology of bread, confectionery, pasta and food concentrates*
E-mail: olgapyvovarova52@mail.ru

P. Pyvovarov
Doctor of Technical Sciences, Professor
Department of Food Technology*
E-mail: pcub@ukr.net

*Kharkiv State University of Food Technology and Trade
Klochkivska str., 333, Kharkiv, Ukraine, 61051

1. Introduction

The task on the development of new food and pharmaceutical forms with the use of physical methods of formation is very relevant as the emergence of a new physical shape of a technological product is the driving force behind the development of technologies, processes and equipment.

Capsules, as the shape of an end product, capsulation, including microcapsulation, as the process of occurrence of a new form of commodity, have over recent years become very popular in different areas. More commonly, the capsulation is associated with the sector of production and design of drug delivery systems (DDS) with targeted action [1–3], biologically active substances [4, 5] and structured food products [6] (sauces [7], dessert sweet meals [8], etc.). A common feature for this direction is that the manufactured products are the formed technological systems with new properties, mainly of spherical shape, which can be obtained using the film-like materials.

The scope of application of capsulated products is constantly expanding, and scientists and specialists in appropriate sectors systematically summarize the effectiveness and experience of their use [5–8].

2. Literature review and problem statement

Modern methods for capsule-formation ensure the capsulation of both hydrophilic and hydrophobic materials. The dimensional characteristics define nanocapsules (<1 μm), microcapsules (1–500 μm), and capsules (>500 μm) received by the ratio shell/inner content of 5:95–50:50. In this case, different characteristics of the shell are provided by thickness, structure, permeability, strength, elasticity, resistance to external environment and technological parameters.

Most technologies of the capsulation are based on the implementation of the principle of thermodynamic incompatibility between the components of a shell-forming agent and an encapsulant. In order to capsulate hydrophobic substances, including oil and fat raw materials, polar solutions of polymers are employed that are capable, under certain conditions, of controlled film-formation, that is the formation of shell of a capsule. The given principle forms the base for the implementation of processes of capsulation and it is based on the surface phenomena that occur at the interface of phase separation of liquids that are not mixed [9].

One of the first methods studied in detail for capsulating the hydrophobic fluid systems was the method that applied gelatin as a film-forming thermotropic material. Gelatin is able to form a solid-like surface of the capsules by the extrusion in the medium of non-polar substances (oils) [10]. A presence of the oil receiving medium is a mandatory condition, as it ensures the lack of affinity with the molten gelatin and, as a result, the formation of a spherical shape of seamless capsules.

From a colloidal point of view, it is the limited capability of the system "oil and fat raw materials – water" to mixing that provides the formation of a clear phase separation border, which prevents spreading of a film-forming material on the surface of drops [9–11].

When ionotropic poly-saccharides are used as a film-forming agent, it is necessary to coaxially extrude by the principle of "pipe in pipe" the solution of a film-forming agent (external pipe) and hydrophobic (internal pipe) to the forming medium through the air in the state of formed quasi-stable capsules. When entering the receiving medium, the chemical potentials are implemented and a capsule with texture becomes marketable.

A general character of the process of formation and separation of drops under gravity force is well explored experimentally and takes practically the same form for all fluids (Fig. 1) [12]. Initially, there forms a germ of a drop, which has the shape of a cone, then, as a result of leaking the fluid from a germ under the action of capillary pressure and gravity, a drop of a roughly spherical shape starts to form. There occurs a bridge between it and the germ, which decreases over time until the moment the drop is torn. This current is by gravity, that is, the shape of the bridge retains its shape – it remains the same as in the earlier point in time, only at a different spatial scale, which was established in many experiments [13–15].

At the same time, the theory of this phenomenon has not been described in full until now, since the classic equations of hydrodynamics describe a fully deterministic process while kinetics of the bridge between a germ and a drop refers rather to the catastrophe theory and bifurcation phenomena, in other words nonlinear processes with a feedback [16].

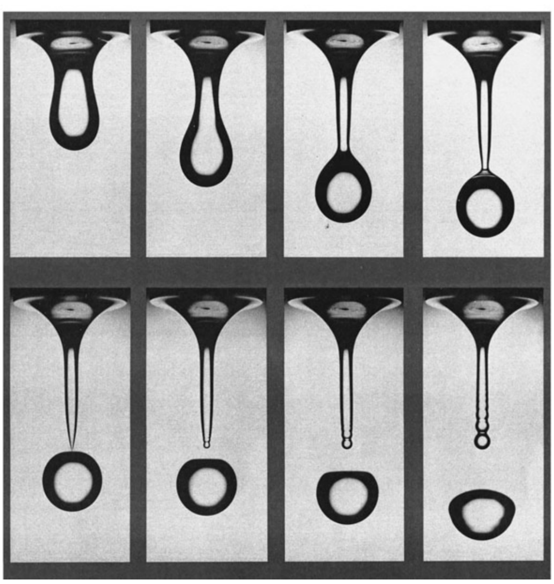

Fig. 1. Stages of separation of a real water drop: time between shots is 0.1 s. Images are taken from article [12]

One of the first attempts at describing the kinetics of tearing a bridge was made by authors in [17]. Underlying the theory is the model, according to which, regardless of the viscosity of fluid flow by gravity, the area around the bridge is controlled only by the forces of inertia and surface tension. Radius of the bridge varies over time by the step law with the same indicator for all fluids.

$$r_{br} \sim \left(\frac{\sigma}{\rho}\right)^{1/3} \times (\tau)^{2/3}, \qquad (1)$$

where r_{br} is the bridge radius; σ is the coefficient of surface tension; ρ is the fluid density; τ is the current time.

This law of "two-thirds" is confirmed by numerical experiments for different liquids, including the solutions of surface-active substances (SAS), rare metals for drops in a wide range of radii, all the way to nanoscale [18, 19].

At the same time, there remains an unsolved issue of the initial size of the bridge itself, which appears at the first stage of shape-formation and depends both on the quality of the fluid and geometric parameters of a capillary. In the absence of these values, equation (1) does not make any sense. Another still unanswered question is the time of the formation of spherical drop out of a germ, which is not described by equation (1).

Even more difficult is the task on the kinetics of shape-formation (a process of the germ formation, bridge and its tearing) for the capsulated fluids, which consist of a liquid shell and a liquid core with different physical characteristics.

3. The aim and tasks of the study

The aim of present work is to obtain an elementary kinetic model of the process of shape-formation of capsulated fluids. This model will allow us to describe all stages of the process (from the formation of a germ to the tearing of the drop) and should qualify for the experimental verification.

To achieve the set aim, the following tasks had to be solved:

– to develop a model of the shape-formation of a capsulated fluid;

– to model a stage of the formation of germ of a drop;

– to model a stage of the formation of a spherical drop and a bridge;

– to model a stage of tearing the bridge and the formation of a quasi-stable drop.

4. Materials, objects and research methods

The solutions of sodium alginate (AlgNa) were received by dispersing the batch of examined substance in drinking demineralized water at t=18...20 °C, with subsequent exposure for (3...4)×60^2 s at t=4...6 °C. The resulting solution was placed into a vacuum desiccator and exposed to degassing for (30...60)×60 s.

The salt $CaCl_2$ was used as a source of Ca^{2+}. In order to prepare a solution of $CaCl_2$, the estimated amount of the substance was dissolved in drinking water at t=18...20 °C for τ=(8...10)×60 s, and the resulting solution was filtered.

Gels of calcium alginate (AlgCa) were received by the introduction of AlgNa solutions to the calculated amount of the $CaCl_2$ solution, as a result of which we obtained gels with different texture and structural-mechanical properties [6].

Details of the authors' technique of the extrusion formation of a capsule "through the air", as well as of the research into kinetics of the formation of capsulated fluids, can be found in article [20].

5. Results of research of elementary kinetic model of the process of shape-formation of capsulated fluids

5. 1. Initial provisions and assumptions for the model of shape-formation of capsulated fluids

The basic provisions for the model are formulated based on the facts and assumptions observed during experiments that allow us to use the elementary equations of fluid mechanics:

– the shape-formation process consists of three stages: the first stage is the formation of the conical germ of a drop, the second stage is the formation of a spherical drop and a bridge between the germ and the drop, the third stage is the flow of the fluid by gravity in the area of the bridge and its tearing (breakaway moment);

– a capsulated system consists of a core and a thin shell from two different fluids. All the physical properties of fluids (density, coefficient of surface tension) do not change in the process of shape-formation. Losses on the viscous friction are absent;

– the problem is axisymmetric – the germ and the drop form at the end of supply pipe with radius r_0 (Fig. 2);

– the shape of a drop is a sphere of radius R, which is to be found. The shape of a conical germ shall be defined as a function r=f(x). The bridge with initial radius r_{br} corresponds to the intersection of the sphere and a conical germ;

– resulting equations should allow us to calculate the duration of all stages of the process.

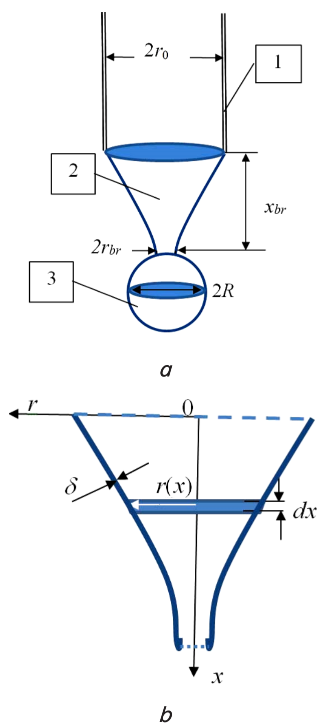

Fig. 2. Schematic of geometry of germ-drop: 1 – fluid supply pipe; 2 – germ of a drop, 3 – drop; *a* – scheme of the geometry of germ-drop; *b* – scheme of the geometry of a conical germ

Fig. 3 shows a photographic monitoring of the formation of a quasi-stable capsule. We used vegetable oil as the encapsulant. We employed the aqueous solution of ionotropic poly-saccharide as a film-forming agent.

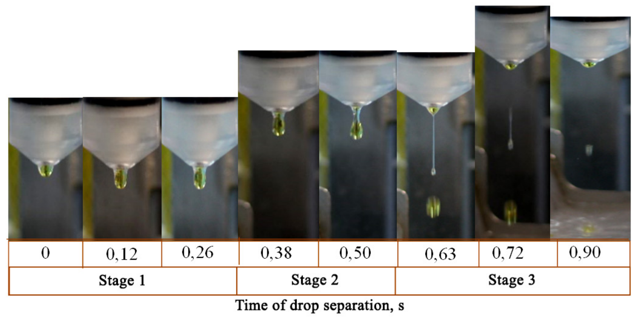

Fig. 3. Stages of the formation of a quasi-stable drop of vegetable oil in a polymer solution: time of leaking the fluid from the germ of a drop until the breakaway moment – 0.63 s: I – formation of the germ of a drop; II – formation of a spherical drop and a bridge; III – tearing of the bridge and the formation of a quasi-stable drop

The above photographic monitoring represents a real process of the formation of a capsule by the ratio film-forming agent/oil as 5:95 to 50:50 by volume.

5. 2. Modeling the stage of the formation of germ of a drop

The purpose of this stage is the calculation of shape of the germ of a drop, since its geometry will define the capillary potential under whose action a transition of the fluid into a spherical drop starts. As this stage, according to known experimental data, occurs rather quickly compared with the formation of a drop, then the task comes down to determining the static stresses arising in the germ of a drop.

Joint action of gravity and surface tension defines the shape of germ of a drop – hydrostatic pressure $p_g=\rho_{gx}$ in any cross-section of the germ is balanced by capillary pressure $p_{cap}=2\sigma/r$ (Fig. 3).

$$dp_{cap}=\rho g dx. \quad (2)$$

Given that this capillary pressure consists of capillary pressure of the shell and inter-phase pressure shell-core, we obtain:

$$-2\left[\frac{\sigma_\delta}{(r+\delta)^2}+\frac{\sigma-\sigma_\delta}{r^2}\right]dr=\rho g dx, \quad (3)$$

where σ is the coefficient of surface tension of liquid of the core; σ_δ is the coefficient of inter-phase tension shell-fluid core ($\sigma>\sigma_\delta$); δ is the thickness of the shell; g is the free fall acceleration; ρ is the given density of liquid system shell-core.

$$\rho=\rho_\delta\cdot c_\rho+\rho_c\cdot(1-c_\rho), \quad (4)$$

where ρ_δ is the density of the shell; ρ_c is the density of the core; c_p is the volumetric share of shell in the volume of a capsulated system.

A solution of differential equation (3) with initial condition $r(x)\big|_{x=0}=r_0$ takes the following form:

$$\left(1-\frac{r}{r_0}\right)\left[\frac{\sigma-\sigma_\delta}{\sigma_\delta}\frac{r_0}{r}+\frac{1}{\left(\frac{r}{r_0}+\frac{\delta}{r_0}\right)\left(1+\frac{\delta}{r_0}\right)}\right]dr=\frac{\rho g r_0}{2\sigma_\delta}x. \quad (5)$$

Let us simplify this expression, taking into account the minimum thickness of the shell, with regard to δ<r0, after which we receive:

$$\frac{x}{r_0}=\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\left(\frac{r_0}{r}-1\right), \quad (6)$$

$$\frac{r}{r_0}=\frac{1}{2Bo\frac{\sigma}{\sigma_\delta}\frac{x}{r_0}+1}, \quad (7)$$

$$\frac{dx}{dr}=-\left(\frac{r_0}{r}\right)^2\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}, \quad (8)$$

where $Bo=\frac{r_0^{\ 2}}{l_{cap}^{\ 2}}$ is the Bond number, which shows the ratio of gravity force to the forces of surface tension; l_{cap} is the capillary length; $l_{cap}=\sqrt{\frac{\sigma}{\rho\cdot g}}$ is the typical size at which a force of the surface tension becomes equal to the force of gravity.

Equations (6)–(8) describe initial geometry of the germ of a drop, that is, a change in the radius of germ on its height and vice versa.

In order to check the physical correctness of the obtained expression, let us find the volume of germ V_{emb}. To this end, in accordance with determining the volume of an axisymmetric figure, we write:

$$V_{emb}=\pi\int_0^x r(x)^2dx=\pi\frac{x\cdot r_0^{\ 2}}{1+\frac{Bo}{2}\frac{\sigma_\delta}{\sigma}\frac{x}{r_0}}. \quad (9)$$

Substituting expression for the height of the germ (6) in this formula, we obtain:

$$V_{emb}=2\pi\frac{\sigma}{\sigma_\delta}\frac{r_0-r}{Bo}r_0^{\ 2}. \quad (10)$$

It becomes obvious that within the limits beyond r→0, volume of the germ of a drop V_{emb} approaches value V_{max}:

$$V_{max}=2\pi\frac{\sigma}{\sigma_\delta}\frac{r_0^{\ 3}}{Bo}=2\pi\frac{\sigma^2}{\sigma_\delta}\frac{r_0}{\rho g}. \quad (11)$$

If the shell is missing (fluid in the germ is homogeneous $\sigma_\delta=\sigma$), then the magnitude of V_{max} in equation (11) is exactly the same as the value of maximum volume, which is in balance at the end of the pipe of radius r_0 under the action of gravity force and the force of surface tension, which, as is known, is equal to:

$$\rho g V_{max}=2\pi r_0\sigma. \quad (12)$$

Thus, the resulting equations (6)–(10) are physically correct.

5. 3. Modeling the stage of the formation of a spherical drop and a bridge

A change in the shape of a germ, which forms a spherical drop, occurs under the action of gravity, which is counteracted by the force of surface tension. We shall assume that a drop starts to take shape in a moment when the current radius of the germ is equal to the initial radius of the bridge. Based on the law of conservation of energy, work Ag, which is enabled by the force of gravity while increasing the height of the germ, is equal to work A_σ against the forces of surface tension during the formation of a spherical drop:

$$dA_g=pdV_{drop}, \quad (13)$$

$$dA_\sigma=\sigma dS_{drop}. \quad (14)$$

Let us find the volume of a drop:

$$V_{drop}=\frac{4}{3}\pi R^3. \quad (15)$$

The pressure that is created by the force of gravity by the height of a drop of fluid is equal to:

$$p=p_{br}+2R\rho g, \quad (16)$$

where R is the radius of the drop; p_{br} is the initial hydraulic pressure over the bridge, which, taking into account (6), is equal to:

$$p_{br}=\rho g x_{br}=\rho g r_0\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\left(\frac{r_0}{r_{br}}-1\right). \quad (17)$$

Integrating (13), taking into account these expressions by the radius of the drop, we receive:

$$A_g=4\pi\left(\frac{1}{2}\rho g R^4+\frac{1}{3}p_0R^3\right)+const. \quad (18)$$

The constant of integration is calculated from the initial condition

$$A_g(R)\Big|_{R=r_{br}}=0.$$

Hence, we obtain:

$$A_g=4\pi\left[\frac{1}{2}\rho g(R^4-r_{br}^{\ 4})+\frac{1}{3}p_0(R^3-r_{br}^{\ 3})\right]. \quad (19)$$

Let us find an expression for the calculation of radius of a drop R. It becomes obvious that the total volume of the drop and the volume of the germ is equal to the maximum volume that can be in balance at the end of the pipe with radius r_0. That is why, given (10) and (11), we write:

$$V_{max}=\frac{4}{3}\pi R^3+V_{emb}. \quad (20)$$

Hence, we find a relation between the radius of a drop R and the radius of the bridge r_{br};

$$R=r_0\left(\frac{3}{2}\frac{\sigma}{\sigma_\delta}\frac{1}{Bo}\frac{r_{br}}{r_0}\right)^{\frac{1}{3}}. \quad (21)$$

Substituting into (19) expression for the radius of a drop (21) and the initial hydrostatic pressure (17), we receive the final equation for calculating the gravity work on the formation of a spherical drop.

$$A_g = 2\pi\rho g r_0^{\,4} \times$$
$$\times\left[\frac{4}{3\mathrm{Bo}}\frac{\sigma}{\sigma_\delta}\left(1-\frac{r_{br}}{r_0}\right)\left(\frac{\sigma}{\sigma_\delta}\frac{3}{2\mathrm{Bo}}-\frac{r_{br}^{\,2}}{r_0^{\,2}}\right)+\left(\frac{\sigma}{\sigma_\delta}\frac{3}{2\mathrm{Bo}}\frac{r_{br}}{r_0}\right)^{\frac{4}{3}}-\left(\frac{r_{br}}{r_0}\right)^4\right]. \quad (22)$$

Further, we calculate the work of surface tension force on the formation of a spherical drop. Based on (14), we write:

$$A_\sigma = \int_{S_0}^{S_{drop}} \sigma dS, \quad (23)$$

where S_{drop} is the surface area of a drop; S_p is the surface area of the drop corresponding to the initial radius of bridge r_{br}, considering that the initial radius at the end of a germ is equal to the radius of the bridge, we have

$$S_0 = 2\pi r_{br}^{\,2}, \quad S_{drop} = 4\pi R^2 - 2\pi r_{br}^{\,2}.$$

Given this, we receive:

$$A_\sigma = 4\pi\sigma\left(R^2 - r_{br}^{\,2}\right). \quad (24)$$

Substituting the radius of a drop in this equation (21), we obtain the resulting work of the surface tension force:

$$A_\sigma = 4\pi\sigma r_0^{\,2}\left[\left(\frac{\sigma}{\sigma_\delta}\frac{3}{2\mathrm{Bo}}\frac{r_{br}}{r_0}\right)^{\frac{2}{3}}-\left(\frac{r_{br}}{r_0}\right)^2\right]. \quad (25)$$

Equating the work that is carried out by the force of gravity (22), and the work of surface tension force (25), we receive equations for determining the initial radius of the bridge r_{br0} under condition:

$$A_g(r_{br0}) = A_\sigma(r_{br0}). \quad (26)$$

It is obvious that this condition of the equality of works can be performed in the defined cross-section of a germ, which depends on physical parameters that are included in (22) and (25) and characterize the given process. Equation (26) is transcendental relative to the original initial radius of the bridge r_{br0}, which is why its numerical value is given in the form of a dimensionless dependence in Fig. 6.

Being aware of the initial radius of the bridge, and using equation (21), it is possible to calculate the radius of a drop in the breakaway point. Thus, the obtained equations (21) and (26) characterize the geometry of a germ and a drop.

5. 4. Modeling the stage of tearing the bridge and the formation of a quasi-stable drop

Let us determine the time required for the formation of a germ and a drop. We shall follow the proposed model and confine ourselves to the estimation of appropriate time based on the equations received above for calculating the work of gravity and surface tension forces.

Based on the law of conservation of energy, work of the forces per time unit to form a germ and a drop is equal to the power of supply source (parameters of fluid supply into the feeding pipe). We shall assume that the parameters of supply in the process of forming a germ and a drop do not change, then the initial time of the formation can be calculated as follows:

$$\Delta\tau_1 = \frac{\Delta A}{p_0 Q_V}, \quad (27)$$

where $\Delta\tau_1$ is the duration of germ and drop formation (duration of the first and second stages); ΔA is the total work of forces of gravity and surface tension; p_0 is the pressure in the supply pipe; Q_V is the volumetric consumption of fluid in the supply pipe.

Total work ΔA consists of the work to form a drop, which we determined previously (23), and the work to form the germ of a drop, which can be calculated in a similar way.

$$dA_{emb} = p dV_{emb} = \rho g x dV_{emb}. \quad (28)$$

Substituting here the expressions for the height of a germ (6) and its volume (10), one obtains:

$$dA_{emb} = 4\pi\rho g r_0^{\,3}\left(\frac{1}{\mathrm{Bo}}\frac{\sigma}{\sigma_\delta}\right)^2\left(1-\frac{r_0}{r}\right)dr. \quad (29)$$

Integrating this equation by the radius in the range from r_0 to r_{br}, we obtain:

$$A_{emb} = 4\pi\frac{\sigma r_0^{\,2}}{\mathrm{Bo}}\left(\frac{\sigma}{\sigma_\delta}\right)^2\left[\ln\left(\frac{r_0}{r_{br}}\right)+\frac{r_{br}}{r_0}-1\right]. \quad (30)$$

Thus, if one knows the total work of the forces of surface tension (25) and gravity (30), it is possible to calculate the time of the formation of a germ and a drop:

$$\Delta\tau_1 = \frac{4\pi\sigma r_0^{\,2}}{p_0 Q_V} \times$$
$$\times\left[\left(\frac{\sigma}{\sigma_\delta}\frac{3}{2\mathrm{Bo}}\frac{r_{br}}{r_0}\right)^{\frac{2}{3}}-\left(\frac{r_{br}}{r_0}\right)^2+\frac{1}{\mathrm{Bo}}\left(\frac{\sigma}{\sigma_\delta}\right)^2\left[\ln\left(\frac{r_0}{r_{br}}\right)+\frac{r_{br}}{r_0}-1\right]\right]. \quad (31)$$

If one knows parameters for supplying the fluid in the forming pipe (pressure and consumption), as well as the initial radius of the bridge, by using equation (31) it is possible to calculate the total duration of the first and second stages of the formation of a drop.

Kinetics of thinning the bridge, as already stated, is described in theory in article [17]. By following their model, we shall also assume that in the area of the bridge the flow is fast enough, while the gradients of velocity are small, so viscous friction will be neglected. A crucial role in this case is played by the force of inertia and the force of surface tension. However, in contrast to the model described in [17], we shall take into account the expression for the initial radius of a bridge and the condition of flow by gravity. We shall also assume that the thickness of the shell of a capsulated drop is much smaller than the radius of supply pipe δ<<r0.

Based on these considerations, we write the equation for the process participants near the bridge:

$$\frac{\rho\upsilon^2}{2}=\frac{2\sigma}{r}, \qquad (32)$$

where υ is the fluid flow velocity in the area of the bridge.

This rate consists of the longitudinal υ_x and transverse υ_r components:

$$\upsilon=\sqrt{\upsilon_x{}^2+\upsilon_r{}^2}=\sqrt{\left(\frac{dx}{d\tau}\right)^2+\left(\frac{dr}{d\tau}\right)^2}. \qquad (33)$$

By changing the order of differentiation, we write:

$$\upsilon=\sqrt{\left(\frac{dr}{d\tau}\right)^2\left(\frac{dx}{dr}\right)^2+\left(\frac{dr}{d\tau}\right)^2}. \qquad (34)$$

Next, let us take into account that the current is by gravity, that is, the shape of the bridge does not change over time. Mathematically, this means stability of derivative from the shape of a germ. Given expression (8), we receive:

$$\frac{dx}{dr}=\text{const}=-\left(\frac{r_0}{r_{br0}}\right)^2\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}. \qquad (35)$$

Substituting the last expression in (34), one obtains a relation between the speed of flow and the radius of bridge:

$$\upsilon=\frac{dr}{d\tau}\sqrt{\left[\left(\frac{r_0}{r_{br0}}\right)^4\left(\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\right)^2+1\right]}. \qquad (36)$$

Next, substituting this velocity in (21), we obtain the following differential equation of the kinetics of radius of a bridge:

$$\frac{dr}{d\tau}\sqrt{\left(\frac{r_0}{r_{br0}}\right)^4\left(\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\right)^2+1}=\frac{2}{\sqrt{r}}\sqrt{\frac{\sigma}{\rho}}. \qquad (37)$$

The solution of this equation at initial condition $r(\tau)|_{\tau=0}=$ $=0$ takes the form:

$$\tau=\frac{1}{3}\sqrt{\frac{\sigma\cdot r^3}{\rho}}\sqrt{\left(\frac{r_0}{r_{br0}}\right)^4\left(\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\right)^2+1}. \qquad (38)$$

Note that the received equation differs from equation (1), proposed in [17], by a constant coefficient, given the initial radius of the bridge, and, in contrast to equation (1), allows us to calculate the duration of thinning of the bridge from the initial value r_{br0} to zero. Thus, the duration of the third stage (bridge breakaway time) is equal to:

$$\Delta\tau_2=\frac{1}{3}\sqrt{\frac{\sigma\cdot r_{br0}{}^3}{\rho}}\sqrt{\left(\frac{r_0}{r_{br0}}\right)^4\left(\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\right)^2+1}. \qquad (39)$$

Based on the conducted theoretical research, we developed a kinetic model of the formation of capsulated fluids. To verify the proposed model, it is necessary to confirm the correctness of calculations in order to adapt them to the actual technological process.

6. Discussion of results of examining the kinetic model for the shape-formation of capsulated fluids

In order to confirm correctness of the obtained theoretical calculations of the kinetics of forming a quasi-stable capsule, we shall conduct an analysis of the obtained results. Fig. 4 shows a dimensionless initial radius of the bridge, computed as a result of numerical solution of equation (26) and a dimensionless initial radius of a drop (21) depending on the dimensionless radius of the feed pipe (in fractions of capillary length l_{cap}).

Based on the dependences presented in Fig. 4, 5, the initial radius of the bridge and the radius of the drop decreases with decreasing radius of the feed pipe, while an increase in the relative coefficient of surface tension core-shell (σ/σ_δ) leads to the increase in the corresponding radii.

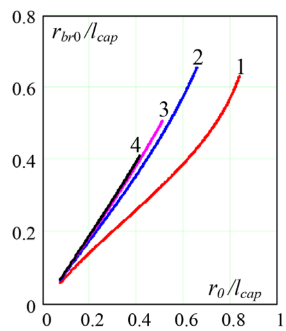

Fig. 4. Initial radius of the bridge depending on the radius of supply pipe and relative coefficient of surface tension: 1 – σ/σ_δ=1; 2 – σ/σ_δ=2; 3 – σ/σ_δ=3; 4 – σ/σ_δ=4

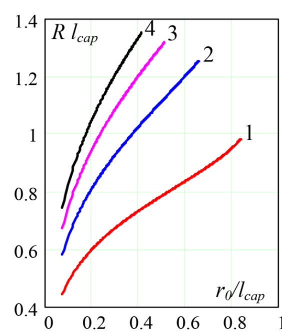

Fig. 5. Initial radius of the drop depending on the radius of supply pipe and relative coefficient of surface tension: 1 – σ/σ_δ=1; 2 – σ/σ_δ=2; 3 – σ/σ_δ=3; 4 – σ/σ_δ=4

Thus, for relative radius of the supply pipe $r_0=0.4l_{cap}$, while increasing the relative coefficient of surface tension by 3 times, the radius of the drop increases by 1.7 times (Fig. 5).

This result is a consequence of the fact that the presence of a shell increases the resultant force of surface tension that acts on the core of a drop (inter-phase force of molecular interaction is directed inside the drop – $\sigma>\sigma_\delta$). There occurs so to speak the "reinforcing" of the drop surface, which in this case can withstand larger pressure from the force of gravity.

However, in order to obtain a larger radius of the drop, it is necessary to reduce the radius of the feed pipe. Thus, in order to receive a drop with radius $R=1.3l_{cap}$, radius of the feed pipe must not exceed $0.4l_{cap}$ (Fig. 5). This constraint is caused by the fact that at large radii of the feed pipes, gravity force is larger than the force of surface tension, so a drop is not formed, the laminar mode of the flow sets in instead. Within the framework of the proposed model, this means that the condition of equality between the forces of gravity and surface tension (26) is not satisfied.

Let us analyze obtained dependences for the duration of forming the germ of a drop (31) and bridge breakaway period (39). Since these equations include two unknown magnitudes (parameters of fluid supply in the feed pipe), we shall represent equations (31) and (39) in the dimensionless form.

A characteristic time for the processes that are controlled by the forces of gravity and surface tension is the magnitude $\sqrt{l_{cap}/g}$. Taking it into account, we shall introduce dimensionless time $\tau\sqrt{g/l_{cap}}$ and, hence, equation (39) takes the dimensionless form:

$$\Delta\tau_2^* = \frac{1}{3}Bo^{\frac{3}{4}}\sqrt{\frac{r_{br0}^{\ 3}}{r_0^{\ 3}}}\sqrt{\left(\frac{r_0}{r_{br0}}\right)^4\left(\frac{2}{Bo}\frac{\sigma}{\sigma_\delta}\right)^2+1}, \qquad (40)$$

where $\Delta\tau_2^* = \Delta\tau_2\sqrt{g/l_{cap}}$ is the dimensionless time.

Equation (40) shows that the time of a bridge breakaway is a function of only two variables: the Bond number (as the initial radius of the bridge also depends on number B_o) and the relative coefficient of surface tension (σ/σ_δ).

Let us bring equation (31), which describes duration of the germ and drop formation, to the dimensionless form. In this equation, there are two unknown magnitudes – parameters of pressure in the feed pipe (p_0, Q_V). We consider that the pressure p_0 is of the order of capillary pressure, that is $p_0=2\sigma/r_0$ and the volumetric fluid consumption is associated with the velocity of flow in the feed pipe as $Q_V=\pi r_0^2\cdot\upsilon_0$. Then, taking into account the dimensionless time, equation (31) takes the following form:

$$\Delta\tau_1^* = \frac{2\sqrt{Bo}}{\sqrt{Fr}}\times$$

$$\times\left[\frac{1}{Bo}\left(\frac{\sigma}{\sigma_\delta}\right)^2\left[\ln\left(\frac{r_0}{r_{br0}}\right)+\frac{r_{br0}}{r_0}-1\right]+\left(\frac{3}{2Bo}\frac{\sigma}{\sigma_\delta}\frac{r_{br0}}{r_0}\right)^{\frac{2}{3}}-\frac{r_{br0}^{\ 2}}{r_0^{\ 2}}\right], \qquad (41)$$

where $\Delta\tau_1^* = \Delta\tau_1\sqrt{g/l_{cap}}$; $Fr=\upsilon_0^2/(g\cdot l_{cap})$ is the Froude number; υ_0 is the rate of fluid supply in the feed pipe.

As follows from equation (39), dimensionless time of the germ and drop formation is a function of three variables: the Bond number, the Froude number and the relative coefficient of surface tension – σ/σ_δ.

Fig. 6 shows dimensionless time of the bridge breakaway depending on the Bond number. Fig. 7 shows the time of the germ and drop formation depending on the Bond number.

It follows from the above dependences that the impact of relative coefficient of surface tension core-shell (σ/σ_δ) is much stronger than that of the Bond number. Reduction in the Bond number by 3 times leads to an increase in the time of drop separation by 25.0 %, while the corresponding increase by three times in the coefficient of surface tension increases the time of drop separation by 2.5 times (Fig. 7).

It is clear that the change in the parameters of fluid supply in the feed pipe (Froude number) proportionally changes the time of the germ and drop formation. Thus, for example, reducing the Froude number by 30.0 %, which corresponds to the reduction in the flow velocity in the feed pipe by 16.0 %, increases duration of the stage of germ and drop formation by 16.0 % (Fig. 7).

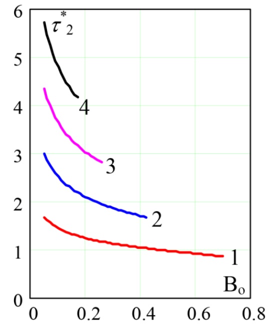

Fig. 6. Dimensionless time of the bridge breakaway: 1 – σ/σ_δ=1; 2 – σ/σ_δ=2; 3 –σ/σ_δ=3; 4 – σ/σ_δ=4

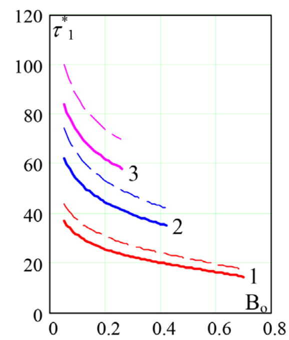

Fig. 7. Dimensionless time of the germ and drop formation: 1 – σ/σ_δ=1; 2 –σ/σ_δ=2; 3 – σ/σ_δ=3; solid lines – Fr=0.01; dotted lines – Fr=0.007

Important is the fact that the time of germ and drop formation is much longer than the time of the bridge breakaway (by about 20 times). Thus, the main factor that limits the time of formation and tearing of a drop is exactly the stage of germ and drop formation, rather than the time of bridge breakaway. This means that the operational speed of a device for manufacturing the capsules on the principle of collapse by gravity defines performance efficiency of the capillary by capsule-formation. Let us perform assessment of these times for the case of the formation of a drop of clean water. For values ρ=1000 kg/m^3; $\sigma=\sigma_\delta$=0.071 N/m; $r_0=1\times10^{-3}$ m, the initial radius of a bridge is $r_{br0}=1.37\times10^{-3}$ m, drop radius $R=2.45\times10^{-3}$ m and, if we take the value of number Fr=0.01 (water supply rate 1.7 cm/s), then we receive, accordingly, the time of germ and drop formation 0.47 s and the time of bridge breakaway 0.022 s. These results are in good agreement with data [12], shown in Fig. 1, where one can clearly see that the most of the time until a drop separates is spent on the germ and bridge formation. For complex fluids and multi-component extrusion, using the design by the principle "pipe in pipe", these magnitudes need to be determined experimentally, because the fluctuations in values may be possibly determined by the degree of complexity of a fluid, as well as technological factors, parameters of the process, etc.

If we refer to Fig. 6 again, we shall note the impact of surface tension on the process duration: an increase in the difference of coefficients of surface tension core-shell ($\sigma-\sigma_\delta>0$) increases the time of bridge breakaway but reduces the formation of germ of a drop.

It is clear that the time of the formation of germ is inversely proportional to the velocity of fluid supply, but, for obvious reasons, it may not be arbitrary as it agrees with the capillary flow mode.

7. Conclusions

Here we proposed an elementary kinetic model of the process of shape-formation of drops of fluid (including the capsulated ones – liquid core inside a liquid shell) that describes all the stages of the process, from the formation of a germ to the separation of a drop:

1. Based on the developed assumed models of the shape-formation of capsulated fluid, we carried out theoretical study and received equations, which make it possible to calculate initial radius of the bridge between a germ and a drop, radius of the drop, duration of the germ formation and the time of bridge breakaway.

2. The equations received are in good agreement with the available experimental data and the theory of flow by gravity in the area of a bridge and they refine the known equations due to the existence of initial radius of the bridge, which is a mandatory condition when modeling the stage of formation of germ of a drop.

3. In the course of modeling the stage of the formation of a spherical drop and a bridge, it is demonstrated theoretically that the main factor that limits the process of formation and separation of a drop is exactly the stage of the germ and, in particular, drop formation. Time of the germ and drop formation is much longer (by about 20 times) than that of the bridge breakaway.

4. When modeling the stage of bridge breakaway and the formation of a quasi-stable drop, it was found that the presence in capsulated fluids of shells (increase in the relative coefficient of surface tension core-shell) significantly affects both the dimensions of a bridge and a drop and the time of the processes of formation of a drop and its separation. In this case, an increase in the relative coefficient of surface tension by 3 times increases the radius of a drop by 1.6 times, and the overall time of the formation and separation of a drop by 2.5 times.

Resulting equations might be applied in the future for experimental verification of the proposed model of the formation and separation of a drop of fluid, as well as when designing the devices for obtaining capsules and substantiating their capacity by the finished product.

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RESEARCH INTO QUALITY OF BEER WITH THE ADDITION OF PINE NEEDLES EXTRACT

N. Penkina
PhD, Associate Professor*
E-mail: penkina-nataliya@rambler.ru

L. Tatar
Assistant**
E-mail: tornado.1972@mail.ru

V. Kolesnyk
Senior Lecturer *
E-mail: vkol240584@gmail.com

T. Karbivnycha
PhD, Associate Professor**
E-mail: tanya280372@rambler.ru

T. Letuta
PhD, Professor
Department of Commodity and Expertise of Goods***
E-mail: Lettanya@ukr.net

*Department of merchandise in customs***
Department of Commodity, quality management and environmental safety*
***Kharkiv State University of Food Technology and Trade
Klochkivska str., 333, Kharkiv, Ukraine, 61051

Обґрунтовано доцільність використання нетрадиційної рослинної сировини для збагачення пива, якою частково замінюють хміль. Досліджено параметри екстрагування (температура, тривалість, гідромодуль) біологічно-активних речовин із хвої сосни звичайної. Оцінено отримані водні екстракти за органолептичними та фізико-хімічними показниками. Розроблено рецептуру пива, до складу якого входить водний екстракт хвої сосни звичайної. Оцінено вплив пива з додаванням хвойного екстракту на антиоксидантну систему організму біологічних об'єктів

Ключові слова: рослинна сировина, антиоксиданти, хвойний екстракт, пивне сусло, математична модель, біологічні об'єкти

Обоснована целесообразность использования нетрадиционного растительного сырья для обогащения пива, которым частично заменяют хмель. Исследованы параметры экстрагирования (температура, продолжительность, гидромодуль) биологически активных веществ из хвои сосны обыкновенной. Оценены полученные водные экстракты по органолептическим и физико-химическим показателям. Разработана рецептура пива, в состав которого входит водный экстракт хвои сосны обыкновенной. Оценено влияние пива с добавлением хвойного экстракта на антиоксидантную систему организма биологических объектов

Ключевые слова: растительное сырье, антиоксиданты, хвойный экстракт, пивное сусло, математическая модель, биологические объекты

1. Introduction

Beer is a rather popular beverage in many countries of the world that enjoys demand due to its flavor and aroma characteristics, especially among young people.

At present, technology of beer production is aimed at developing new varieties with the addition of alternative vegetable raw materials, which give the drink certain taste peculiarities and increases the demand for the produce [1, 2]. In addition, beer, made with the addition of vegetable raw materials, has its advantages: functional directed action, improved organoleptic, physical and chemical parameters, a longer shelf life [3, 4].

By adding antioxidants of vegetable raw materials to the formulation of beer, it is possible to reduce the oxidative and toxic effects of alcohol on the human organism [5]. Harmless