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RHEOMETRIC MONITORING OF THE FORMATION OF MILK–PROTEIN BLOBS

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Abstract: This paper presents the results of the theoretical and experimental studies of newly designed devices, namely, the VRSh-1 ball rheometer and the Sgustok-1S dual-range rotary viscometer, for the continuous automatic monitoring of structure formation processes in milk–protein blobs. Each type of rheometers is studied to substantiate and select their geometric and kinematic parameters and the shape of measuring elements. It has been shown that the mechanical actions on the structure of milk–protein blobs during the rheometric monitoring of their formation must be minimal to obtain reliable data on their readiness. It has been proven that the monitoring of the formation of blobs by the method of the low-amplitude dynamic oscillations of a ball does not necessitate the measurement of the phase shift of its oscillations, and the total force of the resistance of a strengthening clot to the displacements of a ball inside it should be selected as a control parameter, which is in direct proportion to the amplitude of linear displacements of a ball in a viscoelastic medium (blob). Such a solution simplifies the design of a rheometer and makes it possible to obtain a similar rheogram, which precisely and reliably describes the coagulation of a milk mixture. The possibility of switching the rigidity ranges of force indicators without stopping the electrical drive, the design of which prevents a formed blob from dynamic impacts, thus providing the precision of monitoring and the preservation of the structure of a blob, has been designed for the method a cylinder rotating in a formed blob. The algorithm of the computer approximation of rheometric monitoring results for the formation of milk–protein blobs with the possibility of correcting its consistence at the terminal stage of coagulation is described.

Keywords: milk blobs, process rheometers, monitoring, quality, image identification, approximation

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INTRODUCTION

Milk and dairy products hold a specific place among the most popular foods, which help a human organism to adapt to deteriorating environmental conditions [1]. The principal stage of the production of any cultured dairy product is the coagulation of proteins and the formation of a blob of desired consistency, the main characteristic of which is the strength and mechanostructural properties [2]. The readiness of a milk–protein blob in the production of cheeses was estimated visually at most enterprises until now [3]. The reliability of the results of such a monitoring depends to a considerable degree on the experience of an operator and its sensory sensitivity. In parallel, the active acidity pH in the production of rennet blobs and the Turner titrable acidity (°T) in the production of cultured dairy product blobs are measured.

Instrumental monitoring is performed using different laboratory instruments (rheometers). For example, there is the known laboratory rheometer used to improve the recipe of dairy products and the technology of their production, namely, the Barkan geleometer [4], on which the "crushability" of a rennet blob at the moment of its readiness is measured via the cyclic indentation of a cone. Elastograms are obtained using a thromboelastograph, which does not give the precise kinetic picture of the formation of blobs due to the partial destruction of their structure.

A non-destructive method and a laboratory instrument for studying the coagulation of milk have been developed. The instrument consists of a temperature-controlled bath, inside which vessels filled with a milk mixture are placed on the axis connected with the electrical drive. The surface of the milk mixture in each vessel is radiated with a laser beam, which is fixed on the scales of a special screen after reflection with a photo camera fastened immovably on the instrument. The locations of reflected beams are changed proportionally to the change in the mechanostructural (rheological) properties of formed blobs upon the cyclic inclination of the vessels by the electric driver. The obtained results are used to plot "conditional rheological parameter–process duration" rheograms [5, 6].

There exist the Scott–Blair rotary elastometers and the torquemeters that are applied in the bulk method of production to monitor the structural strength of formed blobs via the rotation of a cylinder submerged into a milk mixture. In this case, the process is stopped immediately after a desired blob strength and active acidity pH = 4.5–4.7 are attained.

The common shortcoming of all the above listed devices for the monitoring of the readiness of milk–protein blobs is the absence of a control signal, which would allow these instruments to be included into an automatic process control system for monitoring the formation of milk blobs and their readiness for subsequent process operations.

The quality of cultured dairy product blobs in the process of their production is provided by meeting a number of conditions, such as the quality of initial raw materials and cultures and the adherence to technical regulations and process parameters. The readiness of blobs is determined at the end of their coagulation stage by measuring the Turner titrable acidity of samples (ºT) [7]. In particular, it has been shown [8] that the relation between the active and titrable acidities is more or less clearly visible only for raw milk.

For these reasons, the development of scientifically substantiated methods and devices for the continuous automatic rheometric monitoring of the structure formation of milk–protein blobs in the production of dairy products by the bulk method and corresponding software for the implementation of this monitoring is a topical scientific problem of great research and practical interest for not only the food industry, but also for the other industries, in which structured liquid media are produced or used.

The objective of this work is to scientifically substantiate and develop a methodology, equipment, and software for the automatic rheometric monitoring of the formation of milk–protein blobs.

OBJECTS AND METHODS OF STUDY

Studied medium. To study the formation of rennet and acid clots, a standard milk mixture was prepared using dry skim milk of the same batch. This eliminated the effect of the heterogeneity of raw materials on experimental results. Reconstituted skim milk was obtained by dissolving dry milk (100 g) in distilled water (1 dm^3). For proteins to swell, the milk was allowed to stand for 12 h at a temperature of 4 ± 2°C. The obtained milk was pasteurized at a temperature of 80 ± 2°C and cooled to a temperature of 32 ± 2 °C. In particular, dry skim milk is also used at enterprises in the production of cheese products in the inter-season period, when the production of raw milk is abruptly reduced [9].

The Maxiren®, KG-50, and Fromase 2200® milk-coagulating preparations were used for the coagulation of milk.

To intensify the acid–rennet coagulation of milk and improve the mechanostructural (rheological) properties of blobs, ripened milk (20–40%) was added to the reconstituted skim milk [10]. The ripening of milk was performed as follows: fresh milk was pasteurized at a temperature of 63ºC and, after a culture (0.1 %) and calcium chloride ($10 \cdot 10^{-3}$ kg/100 kg) were added, held at a temperature of 12ºC for 6–12 h until a required titrable acidity of 22–25ºT was attained [11]. In compliance with the cheese production technology, the milk mixture in a cheese vat must be stirred after the addition of coagulating preparations and allowed to stand in a quiescent state until the formation of a blob with a required strength (density). This is why it is necessary to provide minimal mechanical actions on the structure of a blob, especially at the stage of its flocculation, to obtain a rheogram, which reliably describes the process of its formation.

The rheogram of a strengthened blob in the coordinates “compressing force F–absolute linear strain Δl” is shown in Fig. 1. It has the three specific regions:

(1) Region AB is nearly linear and is typical for the materials obeying the Hooke’s law. In this region, the change in the compressing force F produces proportional elastic strains Δl;

(2) Region BC is characterized by the violation of proportionality between the compressing force and the absolute linear strains due to the appearance of some plastic strains, which slightly grow until the maximal compression force F_{max} is attained at point C; and

(3) Region CD corresponds to the brittle destruction of a blob with a resulting decrease of its resistance to load.

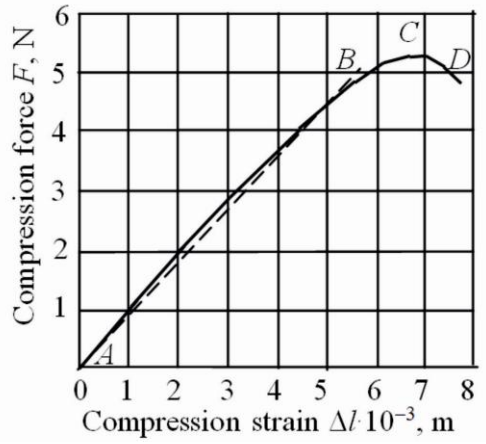


Fig. 1. Absolute compression strain of a strengthened acid–rennet blob versus compression force.

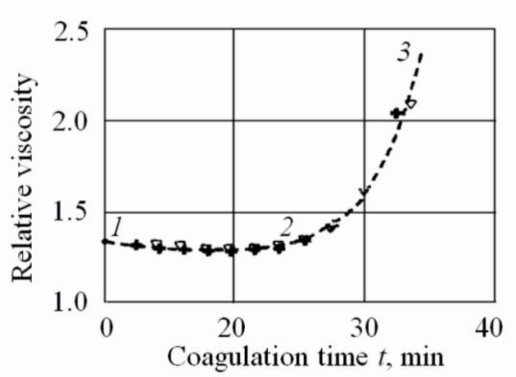


Fig. 2. Relative viscosity of a rennet blob versus time: (*1, 2*) primary coagulation stage, (*2, 3*) secondary coagulation stage, (▽) experiment, (+) calculation.

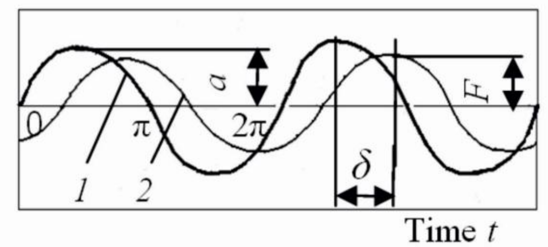
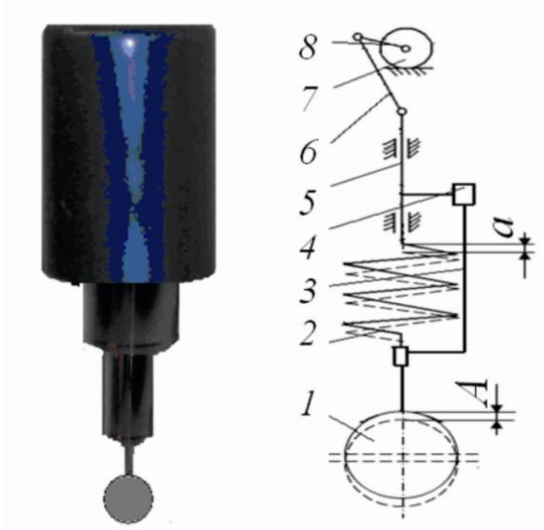


Fig. 3. Oscillations of a ball in a continuous medium.



(a) (b)

Fig. 4. VRSh-1 ball oscillatory rheometer: (a) general view, (b) principal circuit, (*1*) ball, (*2*) spring, (*3*) rod, (*4*) displacement indicator, (*5*) plunger, (*6*) shaft, (*7*) gear motor, (*8*) crank.

From the analysis of this rheogram it can be concluded that a strengthened acid–rennet blob may be classified as a viscoelastic body.

The coagulation of milk was studied by rheological methods on the new developed rheometers:

(1) The VRSh-1 ball low-amplitude oscillatory rheometer [12] (Fig. 4); and

(2) The Sgustok-S1 dual-range rotary rheometer at a constant revolution speed of the fluted measuring cylinder [13, 14] (Fig. 8).

Comparison studies were performed using a Rheotest-2 certified rotary viscometer (Germany). The active acidity of a milk–protein blob was measured on a pH-150M laboratory instrument, and its titrable acidity was estimated on an ATP-1 semi-automatic potentiometric analyzer (Russia).

According to the literature data, it is customary to divide the coagulation of milk into the two stages (Fig. 2): (1) the primary coagulation stage (region *1–2*) is called the latent (inductive) coagulation stage and characterized by the gradual reduction of the stability of casein micellae under the action of milk-coagulating preparations. In the opinion of *de Kruif* et al. [15], a slight decrease in the viscosity of a milk mixture (~0.01 Pa s) is produced by the reduction of the size of micellae as a result of cutting the *κ*-casein hairs from their surface by the rennet enzyme. In the opinion of *Lomholt* et al. [16] and *Marchin* et al. [17], the growth of viscosity after slight decrease is due to the aggregation of micellae with a simultaneous increase in the effective hydrodynamic radius of particles, i.e., their volumetric content [16, 17]. Some other hypotheses are also proposed. For example, *El'chaninov* [18, 19] has concluded from the detailed analysis of the contemporary Russian and foreign literature that the moment of the attainment of an initial viscosity value should be considered as the beginning of *evident* coagulation, i.e., the gel point of the process.

The secondary coagulation stage (region *2–3*) is characterized by the active formation of the spatial structure of a gel (flocculation stage), its strengthening, and the appearance of the viscoelastic properties of a blob. The precise determination of the beginning and terminal time moments of the evident formation of a gel during the coagulation of milk is a topical problem for the control of technological processes in the production of various dairy products, as it enables the automatic correction of the behavior of an technological process upon the fluctuation of the physicochemical parameters of milk, e.g., the content of protein in raw materials. A process engineer must "see" the changes occurring in the milk during its coagulation, i.e., "know" his milk and operatively manage it [20, 21].

RESULTS AND DISCUSSION

Theoretical substantiation of the new ball low-amplitude oscillatory rheometer. The scheme illustrating the principle of studying a medium in the case of the forced low-amplitude harmonic oscillations of a sensitive element (ball) is shown in Fig. 3. The phase shift δ between the oscillation amplitudes of the control displacement *a* (curve *1*) and the force *F* (curve *2*) resisting the displacement of the ball is determined by the rheological properties of a formed milk–protein blob.

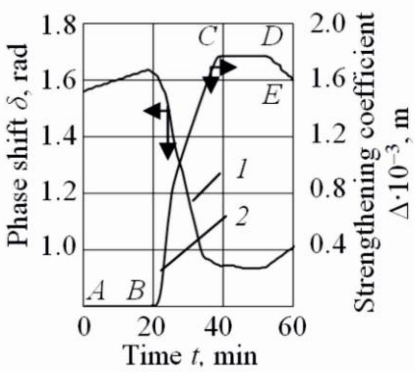


Fig. 5. Blob formation rheograms: (*1*) phase shift, (*2*) strengthening coefficient.

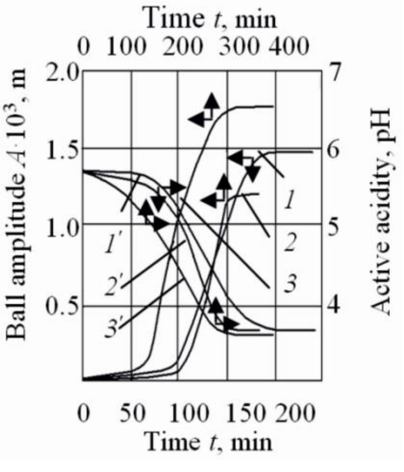


Fig. 6. Monitoring of blobs: rheograms of (*1*) yoghourt, (*2*) soured milk; (*3*) cottage cheese and active acidity of (*1′*) yoghourt, (*2′*) soured milk, and (*3′*) cottage cheese.

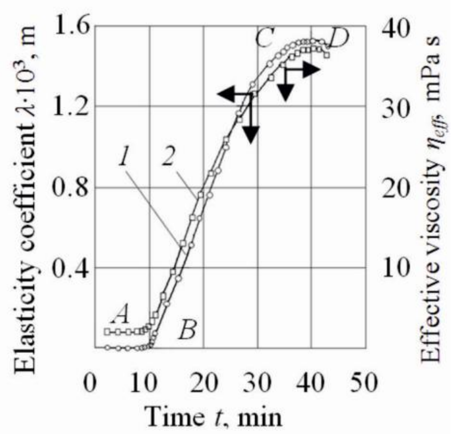


Fig. 7. Comparative rheograms for (*1*) VRSh-1 rheometer and (*2*) Rheotest-2 rotary viscometer.

When the ball harmonically displaces, the forces of elastic F_E and viscous F_V resistance to its motion appear in the formed viscoelastic milk–protein blob. The elastic blob strain force F_E acting on the ball during its harmonic motion is determined as

$$F_E = 2Cx(t) = 2C\cos(\omega t + \phi), \tag{1}$$

where C is the elasticity coefficient, N/m.

The amplitude force of viscous resistance FV to the motion of the ball at $\sin(\omega t + \phi) = 1$ is calculated by the Stokes formula

$$F_V = 3\pi\eta D\upsilon = 3\pi dA\sin(\beta\omega t + \phi), \tag{2}$$

where η is the gel viscosity, Pa s; D is the ball diameter, m, and υ is the ball speed, m/s

$$(\upsilon = dx / dt = A\omega\sin(\omega t + \varphi)).$$

With consideration for Eqs. (1) and (2), the total values of the medium resistance force F have an intermediate oscillation phase, i.e.,

$$\begin{gathered} F(t) = F_E + F_V = 2CA\cos(\omega t + \phi) + \\ + 3\pi\eta DA\omega\sin\ \omega t + \phi\ , \end{gathered} \tag{3}$$

From the analysis of Eq. (3) it follows that the elastic force F_E and the viscous resistance force F_V are directly proportional to the amplitude A of the displacements of the ball in a milk mixture in the case of its oscillations. In this case, there is no need to calculate the total resistance force when monitoring the strengthening of a blob. Obviously, it is sufficient to monitor the change of the ball displacement amplitude A. The validity of such an approach is also mentioned in [22]. Then the total medium resistance force $F(t)$ can be expressed as the difference between the oscillation amplitude $a = x_0(t)$ of drive unit *4* and the current displacement amplitude $A = x(t)$, i.e.,

$$F(t) = C_1\Delta x(t) = [x_0 - x(t)], \tag{4}$$

where C_1 is the rigidity of the spring.

From the analysis of Eqs. (3) and (4) it follows that the force $F(t)$ is directly proportional to the ball displacement amplitude change equal to the increment $\Delta x(t)$, which will grow to its ultimate value during the strengthening of a blob in proportion to its readiness. This increment was selected as a control parameter and called *strengthening coefficient*, m:

$$\Delta = a - A(t) = \Delta x(t), \tag{5}$$

Phase shift δ between a and A is determined on the basis of experiment. If $\varphi[F(t)]$ is the oscillation phase of a specified force, and $\varphi[x(t)]$ is the oscillation phase of ball displacements produced by this force, the phase shift is determined as

$$\delta = \varphi\ \ F(t)\ \ - \varphi\ \ x(t)\ \ , \tag{6}$$

Theoretical analysis and experimental studies have provided the basis for developing the design of the new VRSh-1 ball oscillatory rheometer, the general view of which is shown in Fig. 4a (the bracket for its installation on a vat and the secondary block are conditionally omitted) [12]. Its principal circuit is illustrated in Fig. 4b. The principle used in the rheometer is that the revolution of the shaft of gear motor *7* at an angular speed ω is converted by means of crank *8* and shaft *6* into linear harmonic oscillations with an amplitude a of plunger *5* (control unit), to which spring *2* and hollow ball *1* displacing with an amplitude A are attached. The viscoelastic resistance of a blob to the displacements of ball *1* will grow with the strengthening and formation of its three-dimensional structure, thus producing a corresponding decrease in the amplitude $A = x\ (t)$ of spring *2* elastic strains, which are transmitted by light hollow rod *3* to displacement indicator *4* made in the form of a pulse counter and registered by the secondary block.

In comparison with analogues, the VRSh-1 rheometer provides the measurement of the amplitude a of plunger *5* via the adjustment the length of crank *8* and the use of one cylindrical measuring spring *2* and pulse counter *4* as an indicator of ball *1* displacements. This has simplified the design of the rheometer as a whole, reduced the inertia and rigidity of the force indicator and, as a result, increased the accuracy of measurements.

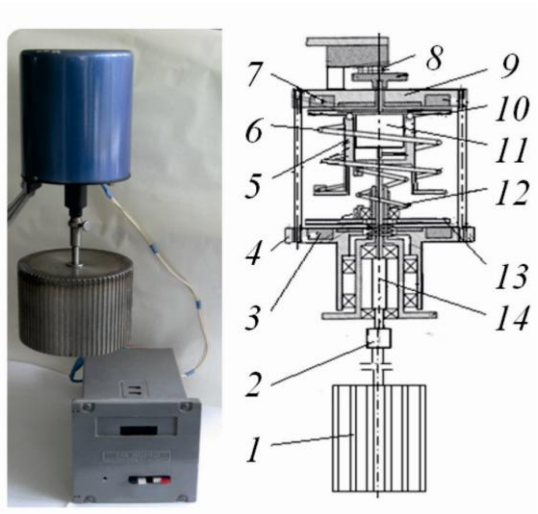
Selection and substantiation of the geometrical and rheometric parameters of the rheometer. On the basis of experimental studies, the following working parameters were selected: ball diameter $D = 60 \cdot 10^{-3}$ m, spring wire diameter $d_R = 2 \cdot 10^{-3}$ m in the production of acid–rennet blobs and $d_C = 1 \cdot 10^{-3}$ m in the production of cultured milk blobs, control unit's amplitude $a = 2 \cdot 10^{-3}$ m, drive unit's oscillation frequency $\nu = 0.0333$ Hz. The Archimedean buoyant force acting onto the ball is compensated by an increase in its weight.

Acid-rennet coagulation of milk. The blob formation monitoring rheograms obtained by measuring the phase shift δ and the strengthening coefficient Δ are plotted in Fig. 5. From their comparison it has been established that rheogram *2* more precisely describes the process of estimating the duration of stages and gives more reliable information on the formation and strengthening of blobs. The strengthening coefficient Δ (m) was finally taken as a control parameter.

Coagulation of cultured milk blobs. The formation of cultured milk beverage blobs was studied by the example of the production of 2.5-% soured milk, 2.5-% yoghourt, and 5-% cottage cheese with the use of standard cultures in compliance with technical regulations. The results at a spring diameter $d = 1.0 \cdot 10^{-3}$ m are plotted in Fig. 6. It has been established that rheograms *1–3* obtained on the VRSh-1 rheometer differ from pH curves $1' – 3'$ in the duration of process stages by less than 2–3%.

Estimating the reliability of blob formation monitoring results. The rheograms obtained for an acid–rennet blob at a temperature of 30±1°C on the VRSh-1 experimental rheometer (curve *1*) and the Rheotest-2 certified laboratory viscometer (curve *2*) are plotted in Fig. 7. From the analysis of the rheograms it follows that the relative deviation of the duration of stages is 2.36–2.74%, and the total process times differ by 2.16%. It may be concluded that the VRSh-1 rheometer can be applied for the industrial monitoring of the formation of acid–rennet and cultured milk blobs.

Method of rotary rheometry. At the following stage, the formation of acid–rennet blobs was studied by the method of the rotation of a cylinder in a working vat at a minimum angular velocity ω. The general view and principal circuit of the new Sgustok-1S dual-range rotary rheometer are shown in Fig. 8. [13, 14].



(a) (b)

Fig. 8. Sgustok-1S rotary rheometer: (a) general view, (b) principal circuit, (*1*) cylinder, (*2*) lock, (*3*, *7*) electromagnets, (*4*) cogwheel, (*5*) sleeve, (*6*) soft spring, (*8*) current-conducting brushes, (*9*) disk, (*10*, *13*) ferromagnetic rings, (*11*) resistive transducer, (*12*) hard spring, (*14*) shaft.

The rheometer is equipped with two torque indicators, namely, "soft" spring *6* and "hard" spring *12*. To turn spring *6* (or *12*) on, voltage is applied to electromagnet *7* (or *3*), which will fix ferromagnetic ring *10* (or *13*) attached to spring *6* (or *12*). The other ends of the springs are fastened to sleeve *5* installed on shaft *14* attached to measuring cylinder *1*.

To perform the monitoring of the formation of a blob, cylinder *1* is submerged into a milk mixture and, for example, spring *6* is turned on, thereupon voltage is applied to the driver, which begins to rotate cogwheel *4*. As a blob is formed, the torque moment M_T appears on the cylinder. It twists spring *6* via shaft *14* and sleeve *5* at a proportional angle, which is registered by resistive transducer *11* and transferred to the processing block. "Hard" spring *12* is used in the production of cheeses, and "soft" spring *6* is used in the production of cultured dairy products. A novelty in the rheometer's design is the possibility of the simultaneous or separate turn-on of springs *6* and *12*. When the springs are turned off, cylinder *1* is stopped instead of being turned back to the initial position, while the driver is running. This makes it possible to preserve the already formed structure and continue the monitoring of the process after the springs are switched.

The studies on the substantiation of a control parameter and the geometric and kinematic characteristics of measuring cylinders schematized in Figs. 9 and 10 with the dimensions listed in the table were performed at the first stage.

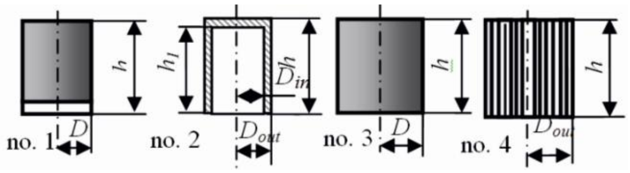


Fig. 9. Schemes of measuring cylinders.

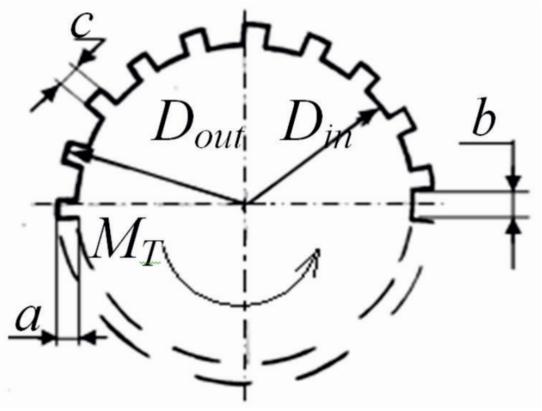


Fig. 10. Calculation scheme of the fluted cylinder no. 4.

Table 1. Geometric parameters of the cylinders

Geometric parameters of measuring cylinders	Notation	Numbers of measuring cylinders			
		1	2	3	4
Outer diameter, m	$D_{out} \cdot 10^3$, m	39.2	39.2	80.0	80
Inner diameter, m	$D_{in} \cdot 10^3$, m	–	15.0	–	–
Cylinder height, m	$h \cdot 10^3$, m	72.0	78.0	80	80
Groove depth, m	$a \cdot 10^3$, m	–	–	–	2.0
Groove width, m	$b \cdot 10^3$, m	–	–	–	3.0
Rib width, m	$c \cdot 10^3$, m	–	–	–	0.8
Number of grooves	n	–	–	–	66

Selection of a control parameter. Only *ultimate shear stress* θ_0 can be taken as a control parameter in the monitoring of the formation of a blob by the method of submerging a rotating cylinder into a vat.

The values of θ_0 on the surface of measuring cylinders will induce torque moments M_T. For known torque moments and cylinder dimensions, the following formulas for the calculation of ultimate shear stresses were obtained:

no. 1:

$$\theta_0 = \frac{2M_T}{\pi D^2 (h + 0.167D)}, \tag{7}$$

no. 2:

$$\theta_0 = \frac{2M_T}{\pi \left[D_{out}^2 \; h + 0.167 D_{out} \; + D_{in}^2 \; h_1 + 0.167 D_{in} \; \right]}, \tag{8}$$

no. 3:

$$\theta_0 = \frac{2M_T}{\pi D^2 (h + 0.333D)}, \tag{9}$$

no. 4:

$$\theta_0 = \frac{2M_T}{\pi D_{out} - cn \;\; hD_{out} + 0.667 \pi D_{out}^3}, \tag{10}$$

Selection of the geometric parameters of cylinders. The studies of the effect of the angular speed ω of measuring cylinders on the parameter θo of ready blobs within a range of 0.058–0.750 s^{-1} on the Sgustok-1S rheometer have resulted in the rheograms shown in Fig. 11. On the basis of these rheograms, measuring cylinder no. 4 and the angular speed ω = 0.262 s^{-1}, at which the parameter θ_0 took maximum values, were selected as working conditions.

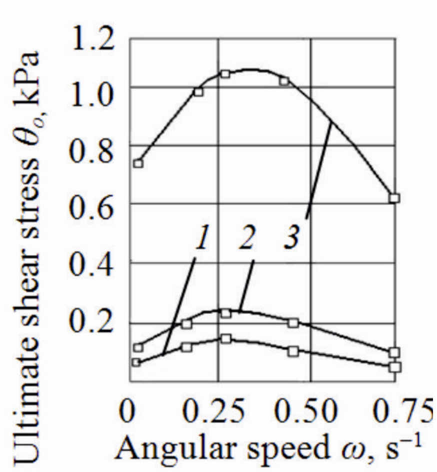


Fig. 11. Ultimate shear stress θ_0 versus angular speed of cylinders: (*1*, *2*) no. 1, (*2*) no. 3, (*3*) no. 4.

The results of studying the formation of acid–rennet and cultured milk blobs are given below. At first, the effect of the shape and geometrical dimensions of measuring cylinders on the character of acid–rennet blob formation rheograms and the parameter θo was studied, and the results were plotted in Fig. 12. In these studies, a "soft" spring with a wire diameter d_S = 0.9·10–3 m and a "hard" spring with $d_H = 1.5 \cdot 10^{-3}$ m were used at a spring rigidity ratio of ≈ 1 : 9.72. The average diameters of the springs $d_{S.av} = 38 \cdot 10^{-3}$ m and $d_{H.av} = 48 \cdot 10^{-3}$ m were taken at the same number of turns n = 10.

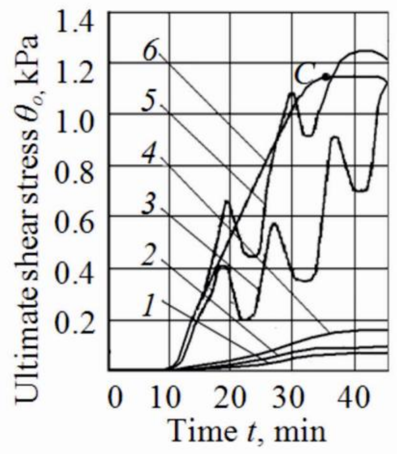


Fig. 12. Dependence of the ultimate shear stress θ_0 on the shape of cylinders and the rigidity of springs:
(1, 2) cylinders nos. 1 and 2 (soft force indicator), (3) cylinder no. 3 (soft force indicator), (4) cylinder no. 3 (hard force indicator), (5) cylinder no. 4 (soft force indicator), (6) cylinder no. 4 (hard force indicator).

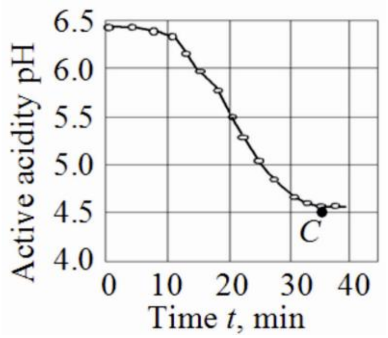


Fig. 13. Souring pH curve (cylinder no. 4).

As a result of studying the formation of acid–rennet blobs, it has been established that the values of θ_0 obtained for cylinders no. 1 or 2 and the spring d_S are small and do not provide the plotting of reliable rheograms (curves *1* and *2*). The rheogram for cylinder no. 3 and the spring d_S (curve *3*) has a saw-tooth shape explained by an insufficient rigidity of the force indicator's spring [23]; the values of θ_0 for the same cylinder and the spring d_H were small due to the slipping of the cylinder (curve *4*). The rheogram for fluted cylinder no. 4 with the spring d_S has a saw-toothed shape (curve *5*) similarly to rheogram *3*. The rheogram, which objectively reflects the blob formation process, was obtained for fluted cylinder no. 4 and the spring d_H (curve *6*).

To estimate the reliability of rheogram *6*, the parallel measurements of the active acidity pH plotted in Fig. 12 were performed. From the analysis of the curves shown in Figs. 11 and 12 it follows that cylinder no. 4, the characteristics of which are given in the table, is reasonable to use for the monitoring of the formation of acid–rennet blob.

The study of the effect of a mixture recipe and principal technological process parameters on the control parameter—ultimate shear stress θ_0 of an acid–rennet blob—with the purpose of revealing the factors for the correction and control of the process of their formation is of scientific and practical interest. The studies were performed on a Rheotest-2 certified rotary viscometer. The varied factors were the pasteurization temperature X_1 (70–90ºC), the coagulation temperature X_2 (20–40ºC), the mass content of rennet enzyme X_3 ($(0.8–1.8)\cdot 10^{-3}$ kg/100 kg), the culture content X_4 (1.5–4.5%), the mass content of calcium chloride X_5 ($(25–55)\cdot 10^{-3}$ kg /100 kg); the mechanical action intensity (angular cylinder rotation speed) X_6 (0.058–0.750 s^{-1}), the fat content in milk X_7 (1–4%), and the ripe milk amount X_8 (20–40%).

To solve the formulated problem, the full factorial experiment (full-FFE) represented by two plans FFE 2^4 was performed. For the first plan, the parameters $X_{1,}$ $X_{2,}$ $X_{3,}$ and X_4 were varied, and the other factors were fixed at the center of their variation range. Similarly, $X_{5,}$ $X_{6,}$ $X_{7,}$ and X_8 were varied for the second plan. After the computer-aided processing of the obtained dependences, their verification for adequacy, and the elimination of insignificant factors, the resulting regression equations have the following form:

$$\begin{aligned}\theta_0 = 1.221 + 0.127X_1 + 0.136X_2 + 0.116X_3 - \\ -0.0751X_4 + 0.0132X_3X_4 + 0.0113X_2X_3X_4 + \\ +0.0151X_1X_2X_3X_4,\end{aligned} \tag{11}$$

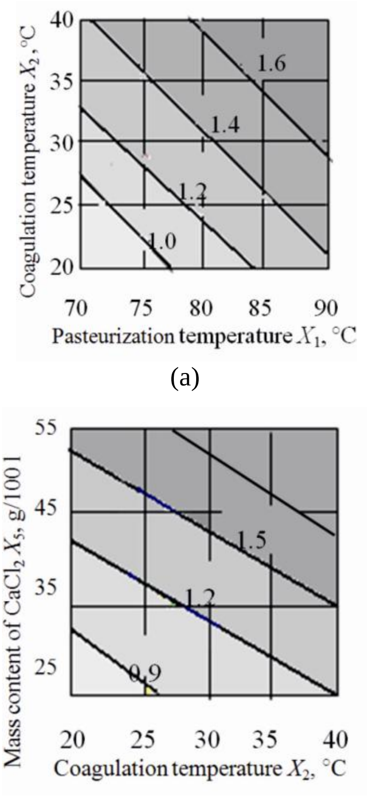
$$\begin{aligned}\theta_0 = 1.219 + 0.258X_5 - 0.0541X_6 - 0.162X_7 - \\ -0.101X_8 + 0.0182X_5X_7 + 0.0226X_6X_8 - \\ -0.0214X_5X_7X_8 + 0.0125X_5X_6X_7X_8.\end{aligned} \tag{12}$$

The analysis of regression model (11) shows that θ_0 is 1.58 and 1.65 kPa at a pasteurization temperature $X_1 = 90$°C, a coagulation temperature $X_2 = 40$℃, a mass content of introduced enzyme $X_3 = 1.8\cdot 10^{-3}$ kg/100 kg, and a culture content X_4 of 1.5 and 4.5%, respectively. The growth of the pasteurization temperature X_1 from 70 to 90°C increases θ_o by 1.17–1.23 times, and the growth of the coagulation temperature X_2 from 20 to 40°C increases θ_0 by 1.18–1.28 times.

The isolines of the dependences of θ_0 on the pasteurization temperature X_1 and the coagulation temperature X_2 at constant contents of enzyme X_3 and culture X_4 are plotted in Fig. 14a. These dependences enable the selection of a combination of process parameters for the production of a blob of optimal strength.

From the analysis of regression model (12) it follows that the growth of the mass content of calcium chloride X_5 from $25\cdot 10^{-3}$ to $55\cdot 10^{-3}$ kg/100 kg increases θ_0 by 1.25–1.36 times. Conversely, the growth of the fat content X_7 from 1 to 4% and the ripe milk amount X_8 from 20 to 40% decreases θ_0 by 1.18–1.28 and 1.13–1.15 times, respectively. The maximum values of θ_0 = 1.63 kPa were obtained at a mass fraction of calcium chloride X_5 of $55\cdot 10^{-3}$ kg/100 kg and a mechanical action intensity X_6 of 0.33 s^{-1}.

The isolines reflecting the change in θ_0 at varied calcium chloride content X_5 and coagulation temperature X_2 (and fixed introduced enzyme content X_3 and mechanical action intensity X_6) are plotted in Fig. 14b. It has been established that the mass content of *calcium chloride* X_5 produces a much more considerable effect on the blob strength θ_0 than *any other* factor. The second factor producing the strongest effect on strengthening ability is the mass content of fat in milk X_7, but the content of fat in a product is determined by the recipe of a produced cheese. The coagulation temperature X_2 is the third factor by the intensity of its effect on the blob strength θ_0. From the analysis of the performed experiment it can be concluded that the formation of acid–rennet blobs is reasonable to be controlled by varying the mass content of calcium chloride and the coagulation temperature.



(a)

(b)

Fig. 14. Isolines of the effect of the principal control factors on the ultimate shear stress at fixed (a) $X_3 = 1.8\cdot 10^{-3}$ kg/100 kg, $X_4 = 1.5$% and (b) $X_3 = 1.8\cdot 10^{-3}$ kg/100 kg, $X_6 = 0.262$ s^{-1}.

Computer-aided approximation of the milk coagulation process. To perform the control of the technological process of the production of a milk–protein blob, it is important for a process engineer to obtain the information about its behavior to have a real opportunity of its correction with the purpose of the production of a high-quality finished product. The results of developing a procedure for the identification of *rheological images of milk–protein blobs* on the basis of pronounced process *stadiality* are considered below. As has already been proven above for the monitoring of the formation of blobs on the ball and rotary rheometers, any characteristics of the product in direct relationship with its rheological (mechanostructural) properties, namely, the strengthening coefficient Δ (m), the ultimate shear stress θ_0 (Pa), the effective viscosity η_{eff}

(mPa s), etc., may be used as a control rheological parameter.

A typical milk protein coagulation rheogram looks as shown in Fig. 15. Dashed-line rheogram segments *AB* and *DE* are straightened, as this simplification does not almost influence on the identification of the basic milk protein coagulation stages.

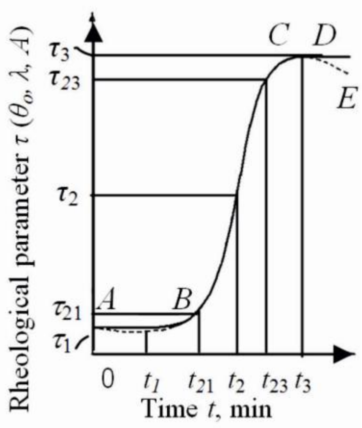


Fig. 15. Milk protein coagulation rheogram.

Recognition method. Rheological data are automatically registered with a time discreteness $\Delta t << t_3$. The discretization step Δt was taken $\approx$ 10 s for acid–rennet milk coagulation and 60 s for traditional acid milk coagulation. The data collection device forms three two-dimensional arrays of values (t_k, τ_k), (t_k, τ_κ'), and (t_k, τ_κ''), where $\tau'_k = (\tau_{k+1} - \tau_k)/\Delta\tau$, and $\tau''_k = (\tau'_{k+1} - \tau'_k)/\Delta t$.

The analysis of these arrays allows the unique identification of all the principal process stages:

(1) At induction stage *AB*, the point (t_1, τ_1) corresponds to the maximum dispersion of casein micellae, i.e., the minimum value $\tau_1 = \tau_{\min}$. This point can be analytically characterized by the zero values of the first and second time derivatives of the function $\tau = f(t)$:

$$\tau(t) = \tau_1 \approx \tau_{\min}, \quad \frac{d\tau}{dt}\bigg|_{t=t_1} = 0, \quad \frac{d^2\tau}{dt^2}\bigg|_{t=t_1} \approx 0, \tag{13}$$

(2) At flocculation stage *BC*, the program traces the behavior of the function, determining its extrema. The positive maximum corresponds to the time t_{21} (point *B* (t_{21}, τ_{21})) and characterizes the development of the evident coagulation stage. Its essential feature is the growth of τ at a maximum rate:

$$\frac{d\tau}{dt}\bigg|_{t=t_{21}} \rangle 0, \quad \frac{d^2\tau}{dt^2}\bigg|_{t=t_{21}} = \left(\frac{d^2\tau}{dt^2}\right)_{\max} \rangle 0. \tag{14}$$

The maximum rate of the growth of the control parameter τ is attained at the point (t_2, τ_2), when its second time derivative becomes equal to zero, i.e.,

$$\frac{d^2\tau}{dt^2}\bigg|_{t=t_2} = 0; \qquad \frac{d\tau}{dt} = \tau'_{\max,} \tag{15}$$

The termination of the evident coagulation stage of a blob is determined from the negative minimum of the function $\tau = \tau''(t)$ at the time moment t_{23} (point *C* (t_{23}, τ_{23})), where the deceleration rate of the growth of τ is maximal:

$$\frac{d\tau}{dt}\bigg|_{t=t_{23}} \rangle 0, \quad d^2\tau \frac{d^2\tau}{dt^2}\bigg|_{t=t_{23}} = \left(\frac{d^2\tau}{dt^2}\right)_{\min} \langle 0, \tag{16}$$

(3) At metastable equilibrium stage *CD*, the control rheological parameter τ_3 attains its maximum at the point (t_3, τ_3), i.e.,

$$\tau(t_3) = \tau_3 \approx \tau_{\max} \quad \text{at} \quad \frac{d\tau}{dt}\bigg|_{t=t_3} \approx 0, \quad \frac{d^2\tau}{dt^2}\bigg|_{t=t_3} \approx 0, \tag{17}$$

The process termination is determined by the attainment of a preliminary specified small positive value by the first derivative τ_κ' after the point t_{23}. In this work, it has been established that the strengthening of a blob is almost stopped, if $\Delta\tau \leq \tau'(t_{23})/10$.

After the time moment t_{23} is determined, the information system gives a message about the coming termination of the process. For rennet blobs, the beginning of their syneretic stratification on segment *CD* is diagnosed by a preliminary specified negative value of the second derivative τ'', i.e., its decrease. The blob is ready for further processing, if the difference between τ_3 and its reference value τ_{ref} for a given technological process is less than $\Delta\tau$ specified by quality standards.

Analytical identification of the rheological image of a blob. The rheogram shown in Fig. 14 is plotted on the basis of the analytical approximation of the Heaviside "step" function

$$H(x) = \lim_{a\to\infty} \frac{1}{1+e^{-ax}},$$

where

$$H(x) = \left\{\begin{matrix} 0, x < 0 \\ 1, x > 0 \end{matrix}\right\}.$$

It was used as a basis to obtain the approximating dependence for milk–protein blobs

$$\tau(t) = \tau_1 + \frac{\tau_3}{1+e^{-a(t-t_2)}}, \tag{18}$$

where a is the parameter characterizing the blob strengthening rate, min^{-1}.

Equation (19) is convenient for the prediction of changes in the rheological parameter τ with time for a number of reasons: first, the characteristic time point t_2 and the values of τ_1 and τ_3 are its explicit parameters and, second, the maxima of the first and second derivatives of this function can be determined analytically. For example, the maximum of the first derivative is really found at the time point t_2 and equal to

$$\frac{d\tau}{dt}\bigg|_{t=t_2} = \frac{a\tau_3}{4}, \tag{19}$$

To determine the extrema of the second derivative of Eq. (19), the third derivative is found as

$$\frac{d^3\tau}{dt_3}=a^3\tau_3\left[\frac{e^{-a(t-t_2)}}{\left(1+e^{-a(t-t_2)}\right)^2}-\right.$$
$$\left.-\frac{6e^{-2a(t-t_2)}}{\left(1+e^{-a(t-t_2)}\right)^3}-\frac{6e^{-2a(t-t_2)}}{\left(1+e^{-3a(t-t_2)}\right)^4}\right]=0, \qquad (20)$$

With the notation

$$y=e^{-a(t-t_2)}, \qquad (21)$$

Eq. (20) can be written as

$$1-\frac{6y}{(1+y)}+\frac{6y^2}{(1+y)^2}=0, \qquad (22)$$

The roots of Eq. (22) are $y=2\pm\sqrt{3}$. The simultaneous solution of Eqs. (21) and (22) gives

$$t=t_2+\ln\left(2\pm\sqrt{3}\right)/a\ .$$

Taking into account that $\ln\left(2-\sqrt{3}\right)=-1.317$, and $\ln\left(2+\sqrt{3}\right)=1.317$, the times t_{21} и t_{23} are finally obtained to have the following values

$$t_{23}=t_2+1.317/a, \quad t_{21}=t_2-1.317/a, \qquad (23)$$

Hence, Eqs. (19) and (23) allow both the process duration t_3 and the probable value of the rheological parameter τ_3 at the blob readiness moment to be predicted as early as by the time moment t_2 using an available experimental database (for the rheological function itself and its first and second derivatives).

The results of the approximation of the effective viscosity η_{eff} for the ripening of 25-% sour cream by model Heaviside function (18) are shown in Fig. 16. The model function (solid line) has the following parameters: a = 0.028 min^{-1}, $\tau_1 = \eta_{eff1}$ = 1.45 mPa s, t_2 = 352 min, $\tau_3 = \eta_{eff3}$ = 9.15 mPa s. From the analysis of the computer-aided approximation in the working window in Fig. 17 it can be concluded that the described method rather adequately approximates the acid coagulation of milk.

In conclusion, it should be noted that the principles of the rheological monitoring of structure formation processes in continuous media can successfully be applied in the automatic control and management systems in the production of cheeses and cultured dairy products. The complex studies of the rheological properties of different milk–protein blobs, the development and study of new rheometers and methods of their application, and the organization of the computer-aided processing and identification of the rheological images of formed blobs will allow the quality of finished milk products to be improved.

On the basis of studying the kinetics of the formation of an acid–rennet blob, the mathematical models estimating the effect of the composition of a milk mixture and process factors on the finite strength of rennet blobs, i.e., the ultimate shear stress θ_o, were obtained.

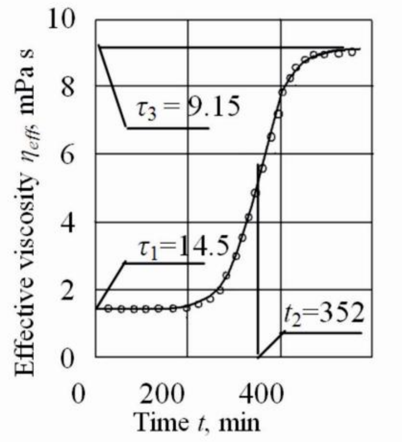
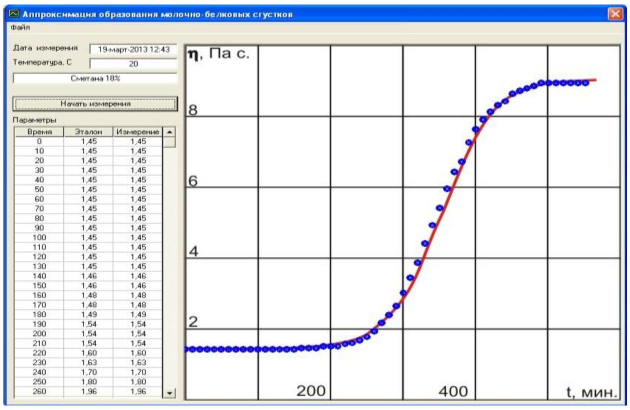


Fig. 16. Approximation of the sour cream ripening rheogram: (○) experiment, (–) model.



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Параметры

Время	Эталон	Измерение
0	1,45	1,45
10	1,45	1,45
20	1,45	1,45
30	1,45	1,45
40	1,45	1,45
50	1,45	1,45
60	1,45	1,45
70	1,45	1,45
80	1,45	1,45
90	1,45	1,45
100	1,45	1,45
110	1,45	1,45
120	1,45	1,45
130	1,45	1,45
140	1,46	1,46
150	1,46	1,46
160	1,48	1,48
170	1,48	1,48
180	1,49	1,49
190	1,54	1,54
200	1,54	1,54
210	1,54	1,54
220	1,60	1,60
230	1,63	1,63
240	1,70	1,70
250	1,80	1,80
260	1,96	1,96

Fig. 17. Main window of the program for the identification of the rheological image of a 25-% sour cream blob.

The factors enabling the control of the terminal blob formation stage and the production of milk–protein blobs of specified consistency—*calcium chloride content* and *coagulation temperature*—were determined.

The method and algorithm allowing the monitoring of blob formation kinetics, the application of required corrective actions at a blob formation time moment τ_2, and the prediction of a blob readiness time moment on the basis of the computer-aided approximation of the Heaviside step function were developed for the identification of the rheological images of milk–protein blobs.

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