THEORETICAL AND PRACTICAL ASPECTS OF THE THERMOGRAPHIC METHOD FOR MILK COAGULATION RESEARCH

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Abstract: The precise and objective estimation of the beginning of gelation in milk is topical for both laboratory studies and industrial dairy production. In this work, the principles of the thermographic method of monitoring milk coagulation are formulated. This method has evolved from the well-known hot-wire method; it is based on the measurement of the temperature difference between two thermometers, one of which is heated. Unlike the hot-wire method, the thermographic method can even be used in processes that require significant changes in milk temperature, for example, during heat–acid milk coagulation. Two basic designs of thermographic systems, using as thermometers either differentially connected thermocouple junctions or two identical thermistors connected as two legs of a bridge circuit, are described. In both cases, the temperature difference between the heated and unheated thermometers at about 0.5 W of thermal power supply is about 3°C for incoagulated milk and 8–10°C after clot formation. The qualitative agreement of the results of rheological and thermographic methods has been demonstrated. A thermographic research technique for heat–acid or heat–calcium milk coagulations has been developed. Within the effective viscosity model, the numeric solution of the problem of temperature field simulation in the vicinity of the heated thermometer has been obtained. On the basis of the simulation results, the possibility of studying structure formation in milk during its coagulation has been analyzed using the thermographic data. Experimental results obtained during thermographic research of milk coagulation are presented.

Keywords: milk coagulation control, heat convection, thermographic method

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INTRODUCTION

It is common knowledge that the process of milk coagulation represents the transition of a micellar colloidal system of caseins to a gel-like state. This process underlies many dairy technologies, particularly, cheese making, largely predetermining cheese quality [1]. The latter circumstance makes the coagulation of milk proteins the subject of thorough research for scientists specializing in the properties of milk and dairy products.

The estimation of the beginning of gelation in milk is topical both for scientific research and for process monitoring in industry. Suffice it to note that the exact estimation of the beginning of coagulation directly in the cheese vat makes it possible, in principle, to adjust automatically the process schedule as the physic-chemical indicators of milk change (for example, the protein content) in order to economize on both milk-clotting preparations and cheese production times. Very important is also the correct and unambiguous determination of the duration of the main coagulation stages for research purposes, in particular, for building adequate models of the coagulation process.

Despite the very long history of dairy technology, the methods of objective monitoring of the milk coagulation process appeared relatively recently. We may say that the main method of determining the time of coagulation was visual observation using a cheesemaking knife or a cheesemaker's finger practically until the mid-20th century. Note that the first experience of objective observation over the rennet clotting of milk with a viscometer dates back to 1932 [2].

At present, there are a large number of various methods for objective monitoring of milk coagulation. They all may conventionally be divided into several groups characterized by the choice of milk parameters that undergo changes during coagulation [3–5]. Basically, these are certainly rheological and optical methods, based on observing changes in milk structure during its coagulation. In addition, the rheological methods record structural changes by the system's response to applied mechanical stresses or deformations, and the optical methods, by the change in the absorption or dissipation of visible light, as well as in the emission of the infrared band. The wide use of these two methods depends, primarily, on the possibility of their use directly online. Moreover, these methods ensure obtaining well-correlated data [6–8].

Another quite widespread method to monitor milk coagulation due to the possibility to use it online is the hot-wire method, developed in 1985 [9]. Its essence is that the temperature of an electric current–conducting wire placed in milk increases during coagulation because of a decrease in a convective heat sink resulting from the formation of a structure in milk. This method is indirect rheological in essence; therefore, the results obtained with it correlate well with data obtained both rheologically and optically [10]. Thanks to its simplicity and possibility to be used online, this method continues to be topical nowadays [11].

A disadvantage of the hot-wire method is the dependence of the sensor temperature not only on convective heat exchange in milk but also on milk temperature, which can change, for example, as a result of various production processes. Therefore, the purpose of this work is the development of a simple universal method for the objective monitoring of milk coagulation based on the hot-wire method but without the above disadvantage. In addition, the work has also analyzed a number of theoretical models that describe the operation of the presented method.

OBJECTS AND METHODS OF RESEARCH

The object of research was reconstituted fat-free milk. In order to obtain it, 90 g of instant fat-free milk powder (Milk Factory, Kemerovo, Russia) were dissolved in 910 mL of distilled water and stirred thoroughly. Into the resulting reconstructed milk, 4 cm^3 of a 10% medical solution of $CaCl_2$ (Shenlu Pharm, China) were added, after which it was aged for 12 hours at 6±2ºC.

For rennet clotting, microbially derived chymosin, Maxiren® (DSM, the Netherlands), was used. In order to prepare the solution, 0.1 g of enzyme powder was dissolved in 100 cm^3 of distilled water.

During the simulation of acid clotting, a 10% solution of lactic acid was slowly introduced into milk and stirred thoroughly. The solution was obtained by diluting a 40% nutritive solution of lactic acid (Univerkhim, Chelyabinsk, Russia).

Milk coagulation was carried out in a thermostatted cell of 200 mL.

Thermographic method

Milk coagulation was monitored by the change in its effective viscosity with the help of temperature-sensing viscosity sensors of in-house design, attached to a computer. The principle of their operation is in measuring the temperature difference between two thermometers stationed in milk at a short distance from each other, one of which being heated. This method is similar to the hot-wire method, but, unlike the latter, it is not sensitive to changes in the environmental temperature, because it links the rheological parameters of milk not with the absolute temperature of the heated thermometer but with temperature difference between the heated and unheated thermometers.

The amount of heat fed to the heated thermometer per time unit depends on the capacity of the electric heater. In our devices, it was 400–600 mW. Heat is removed from the thermometer through heat exchange and convective transfer. As a result of heat equilibrium established between heat release and its removal, the temperature difference between the two thermometers placed in milk takes on a certain value rather quickly. In our experiments, a typical temperature difference value for incoagulated milk was 3–4°C, depending on the heat-release capacity. As a result of milk coagulation, the increased effective viscosity hinders convection, causing the growth of temperature difference between the thermometers. Finally, the structure emerging in milk ceases the convective flow practically altogether, and the heat equilibrium changes. The temperature difference established after coagulation depended in our experiments mainly on the power of heat release and on the quality of the clot formed, being approximately 7–10°C.

We developed two principal circuits that implemented the above method. In the first case, two junction points of a differentially connected thermocouple, one of which was glued directly to the heating resistor, served as thermometers. In the second case, two thermistors connected as two legs of a bridge circuit were used as thermometers. In the latter case, the heating element was a thin wire wound directly on one of the cylindrical thermistors. In both cases, the thermometers are positioned in thin leakproof stainless-steel tubes filled with a dielectric heat-conducting paste at a distance of 2–3 cm from each other. Both ways of implementing our method yield identical results and differ only in the manner they transform the output signal for connection with the personal computer.

As was noted above, the described method is indirectly rheological, characterizing a change in the effective viscosity of milk during coagulation. In order to substantiate this statement, Fig. 1 shows the comparison of a typical rheogram of rennet clotting, obtained with a Brookfield rotary viscosimeter (a) [12], and a typical curve of temperature difference between the heated and unheated thermometers placed in milk under rennet clotting (b).

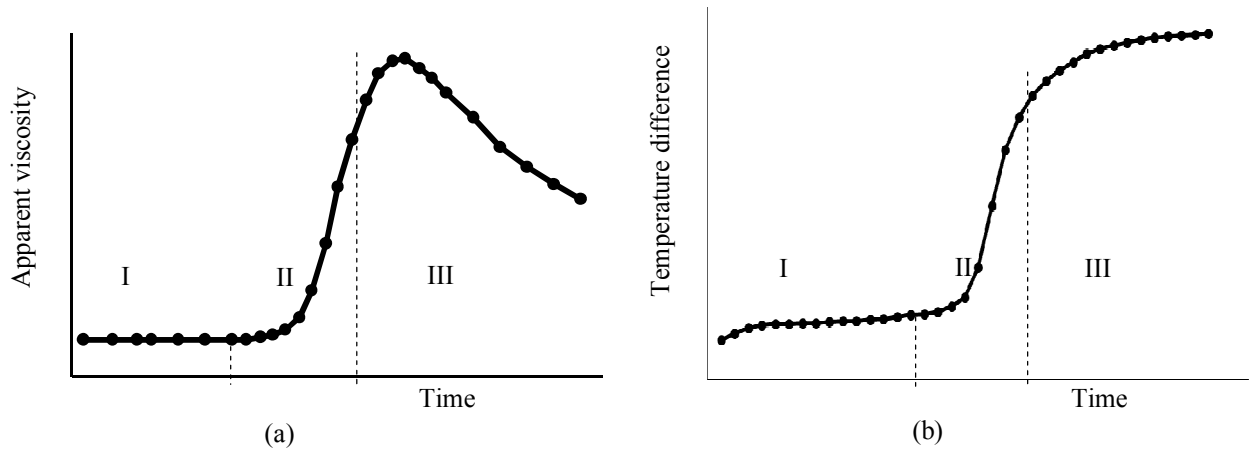


Fig. 1. Comparison of (a) a typical rheogram and (b) thermogram of rennet coagulation.

As is seen from the figure, informationally, the thermogram is practically equivalent to the rheogram. Both curves show distinctly the stages of latent (I) and explicit (II) coagulation. However, stages (III) in Figs. 1a and 1b differ noticeably. Stage III in Fig. 1a corresponds to the syneretic layering of the clot, which results in a decrease in its observable viscosity. As is known, a mechanical impact on the clot is necessary for intensive whey separation to begin, which, in the case of a rotary viscosimeter, is ensured by the moving elements of a measuring cell. There were no mechanically moving parts in our method, which led to a delay in the metastable equilibrium stage. In addition, a higher temperature of the heated thermometer contributed to the further strengthening of the clot around it and, consequently, to the further slow growth of the temperature difference.

On the other hand, the absence of moving parts makes it possible to use easily our sensor to monitor gelation directly in the cheese vat (online), and the simplicity of the design ensures a high reliability at a relatively low cost.

Hereinafter, the curves, obtained with the help of the thermal viscosity meter, that characterize the change in the effective viscosity of milk during coagulation, will be called thermograms (by analogy with rheograms), and the method of deriving them will be called the thermographic method.

Insensitivity of the thermographic method to milk temperature changes during coagulation allows us to use it in production processes accompanied by such changes. Heat–acid milk clotting, which underlies the production of well-known cheeses, is a good example of this. For instance, Quesco Blanco, which was brought from Spain, is quite popular in South and Central Americas. Paneer is well known in South Asia. Adygei cheese is popular on the territory of the CIS. Heat–acid milk coagulation is based of the settling of milk proteins under the action of an acid and high temperature. The main merit of this method of milk clot is a high degree of deproteinization of raw milk by settling whey proteins together with casein. In addition, compared with casein, whey proteins within the heat–acid clot have a more balanced amino acid composition, improving the biological value of products produced on the basis of heat–acid coagulation.

The direct use of the thermographic method to study the heat–acid coagulation process is complicated by the fact that the application of an acid to heated milk is accompanied by intensive stirring, which hinders structure formation. As a consequence, no strongly marked change in the temperature difference between the heated and unheated thermometers occurs. In order to resolve this problem, we developed the following technique of studying heat–acid milk coagulation. Acid agents are introduced preliminarily into milk, as well as additive substances that are able to affect heat–acid clotting in amounts that admittedly do not cause coagulation at room temperature. The prepared samples are then heated under control until gel appears, which is recorded thermographically. In our opinion, this method allows us to obtain objective data for the analysis of physicochemical specifics of destabilization of the milk protein system under high temperatures. The obtained data may be the basis for the standardization of conditions for the high-temperature coagulation of milk proteins in the production of heat–acid cheeses in the dairy industry.

A mathematical model of the thermographic method

According to Archimedes' law, in a liquid in a gravitational field, the local area of a less density generates a buoyancy force directed upward. This force leads to the emergence of convective flows in liquids whose density ρ depends on temperature T.

Fluid flow equations may be written on the basis of general physical principles: the equation of continuity, which states that a change in fluid density at a given point may only depend on its expansion or compression; the balance of impulses (Newton's second law), which is written as the result of equalizing inertial forces and viscous forces; and the balance of energy, which takes into account, along with other energy types, the diffusive and convective transfer of heat energy. Usually, the equations of motion of a viscous fluid in this form are called the Navier–Stokes equations [13]:

$$\begin{aligned} &\frac{d}{dt}\rho(\mathbf{r},t)+\rho(\mathbf{r},t)\nabla\cdot\boldsymbol{\upsilon}(\mathbf{r},t)=0,\\ &\rho(\mathbf{r},t)\frac{d}{dt}\boldsymbol{\upsilon}(\mathbf{r},t)=-\nabla p(\mathbf{r},t)+\nabla\cdot\mathbf{T}(\mathbf{r},t)+\mathbf{f}(\mathbf{r},t), \qquad (1)\\ &\frac{d}{dt}w(\mathbf{r},t)=-p\nabla\cdot\boldsymbol{\upsilon}(\mathbf{r},t)+\Phi(\mathbf{r},t)-\nabla\cdot q(\mathbf{r},t)+e(\mathbf{r},t). \end{aligned}$$

The values given in this system of equations are set in a point determined by radius vector $\mathbf{r}$ at time point t and have the following meaning:

ρ is a fluid density;

$\boldsymbol{\upsilon}$ is a fluid velocity vector liquid;

P is a pressure created by external forces;

$\mathbf{T}=\mu(\nabla\boldsymbol{\upsilon}+(\nabla\boldsymbol{\upsilon})^{\mathrm{T}})+\mu^{*}(\nabla\cdot\boldsymbol{\upsilon})$ is the viscous part of the stress tensor, where μ is the shear (usual) viscosity coefficient, and μ^{*} is an additional viscosity coefficient related to the fluid's volume deformation;

$\mathbf{f}$ is the density of volumetric forces within the fluid; in our case, $\mathbf{f}=\rho\mathbf{g}$, where $\mathbf{g}$ is the free fall acceleration;

w is the density of the fluid's internal (heat) energy; in our case, we may take that $dw=\rho cdT$, where c is the fluid's specific heat capacity;

$\Phi=\mathrm{tr}(\mathbf{T}(\nabla\boldsymbol{\upsilon})^{\mathrm{T}})$ is a dissipative function that describes the amount of mechanical energy that turns into heat in a unit time in the fluid's' unit volume;

$q=\kappa\nabla T$ is the heat flow vector, where κ is the coefficient of heat conductivity and T is temperature;

e is the density of the volume sources of heat; and

the full time derivative is determined by the expression

$$\frac{d}{dt}\equiv\frac{\partial}{\partial t}+\boldsymbol{\upsilon}\cdot\nabla.$$

Thus, we have at least three simultaneous equations that determine flow parameters: velocity, pressure, and temperature. In addition, we need some equations that link state parameters, in particular, equation $\rho=\rho(T)$.

We also have to know the coefficients of molecular transfer: viscosity μ for Newtonian fluid, coefficient of thermal conductivity κ, and some other coefficients for special flow cases.

The main difficulty in solving the above equations arises owing to a possible change in transfer parameters μ and κ, as well as density ρ. Since μ and κ mainly depend on temperature, they change substantially in processes with large temperature differences. In other cases, these parameters may often be assumed as constant. However, in order to obtain motion, we should always take into account changes in pressure.

Let us first note that, at low temperature differences and, consequently, at small flow rates, there is a stationary limit to the solving system (1), which corresponds to conditions $\frac{\partial \rho}{\partial t} = 0, \quad \frac{\partial \upsilon}{\partial t} = 0, \quad \frac{\partial T}{\partial t} = 0$.

In our case, the stationary condition should also take into account the possible change in viscosity during the milk clotting process. Indeed, if the characteristic time during which the milk viscosity changes noticeably exceeds considerably the time of setting up the stationary flow mode, then the process may be considered quasi-stationary.

Note also that the heat release by the volume sources is the main cause of the fluid temperature change. Then we obtain the following system of stationary equations to determine velocity and temperature distributions in the fluid:

$$\begin{aligned}
&(\boldsymbol{\upsilon}(\mathbf{r})\cdot\nabla)\rho(\mathbf{r}) + \rho(\mathbf{r})\nabla\cdot\boldsymbol{\upsilon}(\mathbf{r}) = 0,\\
&\rho(\mathbf{r})(\boldsymbol{\upsilon}(\mathbf{r})\cdot\nabla)\boldsymbol{\upsilon}(\mathbf{r}) = -\nabla p(\mathbf{r}) + \mu\nabla^2\boldsymbol{\upsilon}(\mathbf{r}) + \lambda\nabla\cdot\boldsymbol{\upsilon}(\mathbf{r}) + \rho\mathbf{g}, \qquad (2)\\
&\rho(\mathbf{r})C_P(\boldsymbol{\upsilon}(\mathbf{r})\cdot\nabla)T(\mathbf{r}) = -\kappa\nabla^2 T(\mathbf{r}) + e(\mathbf{r}).
\end{aligned}$$

The next approximation may be the assumption of the fluid's practical incompressibility. Let us assume that the fluid density is constant in all cases, except for taking into account the buoyancy force when we describe convection (the Boussinesq approximation). In this approximation, the difference of pressure and gravity forces may be represented as

$$\rho\mathbf{g} - \nabla p \approx \mathbf{B} + \nabla p^* = \mathbf{g}(\rho_T - \rho_0) + \nabla p^*,$$

where ρ_T is the fluid density at temperature T; ρ_0 is the fluid density at temperature T_0; and p^* is the nonhydrostatic part of the fluid pressure. Under T_0 we mean the fluid temperature far from the heat source. Using the condition of a small change in density, we may write down the buoyancy force through the temperature coefficient of the fluid volume expansion, β. Indeed, $\rho_T \approx \rho_0(1-\beta(T-T_0))$; therefore,

$$\mathbf{B} = -\mathbf{g}\rho_0\beta(T-T_0).$$

In addition, in system (2), we should set

$$\rho(\mathbf{r}) = \rho_0 = const.$$

In many flows induced by the buoyancy force, there is axial symmetry, since a surface or body near which a flow occurs is symmetrical in relation to the vertical axis. A flow close to axisymmetric should, obviously, also appear in the case of a convective flow formed by a small heat source. Such flows represent jets and rising plumes.

In the Boussinesq approximation, $\nabla\rho = 0$, $\nabla\cdot\boldsymbol{\upsilon} = 0$, and the quasi-stationary equations of system (2) with a point heat source, written in the cylindrical coordinate system, will have the following form:

$$\begin{aligned}
&\frac{1}{r}\frac{\partial(r\upsilon_r)}{\partial r} + \frac{\partial\upsilon_z}{\partial z} = 0\\
&\upsilon_z\frac{\partial\upsilon_z}{\partial z} + \upsilon_r\frac{\partial\upsilon_z}{\partial r} = \nu\left(\frac{\partial^2\upsilon_z}{\partial z^2} + \frac{\partial^2\upsilon_z}{\partial r^2} + \frac{1}{r}\frac{\partial\upsilon_z}{\partial r}\right) - \frac{\partial p_z^*}{\partial z} + g\beta(T-T_0)\\
&\upsilon_z\frac{\partial\upsilon_r}{\partial z} + \upsilon_r\frac{\partial\upsilon_r}{\partial r} = \nu\left(\frac{\partial^2\upsilon_r}{\partial z^2} + \frac{\partial^2\upsilon_r}{\partial r^2} + \frac{1}{r}\frac{\partial\upsilon_r}{\partial r} - \frac{\upsilon_r}{r^2}\right) - \frac{\partial p_r^*}{\partial r} \qquad (3)\\
&\upsilon_z\frac{\partial T}{\partial z} + \upsilon_r\frac{\partial T}{\partial r} = \lambda\left(\frac{\partial^2 T}{\partial z^2} + \frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}\right) + W_h f,
\end{aligned}$$

where $\nu = \frac{\mu}{\rho_0}$ is the fluid's kinetic viscosity; $\lambda = \frac{\kappa}{\rho_0 c}$ is the coefficient temperature conductivity; W_h is the power fed to the point heat source; and $f(z,r)$ is the function of heat source distributions, which in the case of a point heat source has the following form: $f(z,r) = \frac{\delta(z)\delta(r)}{2\pi r}$. The velocity, temperature, and pressure fields are determined from the solution of equation system (6) with the corresponding boundary conditions. The problem was solved numerically by the finite element method in the COMSOL Femlab system.

RESULTS AND DISCUSSION

Results of numeric calculations

Figure 2 shows the numeric solution of system (3) for a small cylindrical heat source 3 mm long and 2 mm in diameter, in which a constant power of 0.5 W is given out. Milk is considered a fluid with the following parameters: the density, ρ_0 = 1030 kg/m^3; the coefficient of heat conductivity, κ = 0.55 W/(m·K); and the coefficient of volume expansion, $\beta = 10^{-4}$. The viscosity of this fluid can change in very wide limits, as shown in the figure. The absence of radial and axial flows on the region boundaries were selected as the boundary conditions: $r \subset [0, r_{\max}]$; $z \subset [-z_{\max}, +z_{\max}]$.

$$\left.\frac{\partial\upsilon_r}{\partial r}\right|_{r=r_{\max}} = 0; \quad \left.\frac{\partial\upsilon_r}{\partial z}\right|_{z=\pm z_{\max}} = 0; \quad \left.\frac{\partial\upsilon_z}{\partial r}\right|_{r=r_{\max}} = 0;$$

$$\left.\frac{\partial\upsilon_z}{\partial z}\right|_{z=\pm z_{\max}} = 0; \quad \left.\frac{\partial T}{\partial r}\right|_{r=r_{\max}} = 0; \quad \left.\frac{\partial T}{\partial z}\right|_{z=\pm z_{\max}} = 0.$$

In addition, the fluid flow on the boundaries is absent $\upsilon_z(r_{\max}) = 0$; $\upsilon_r(r_{\max}) = 0$; $\upsilon_z(\pm z_{\max}) = 0$; $\upsilon_r(\pm z_{\max}) = 0$, and the temperature is constant $T(r_{\max}) = T_0$; $T(\pm z_{\max}) = T_0$, where T_0 = 30°C. The dimensions of the region for numeric integration were chosen in the following way: $r_{\max}$ = 5 mm; $z_{\max}$ = 10 mm.

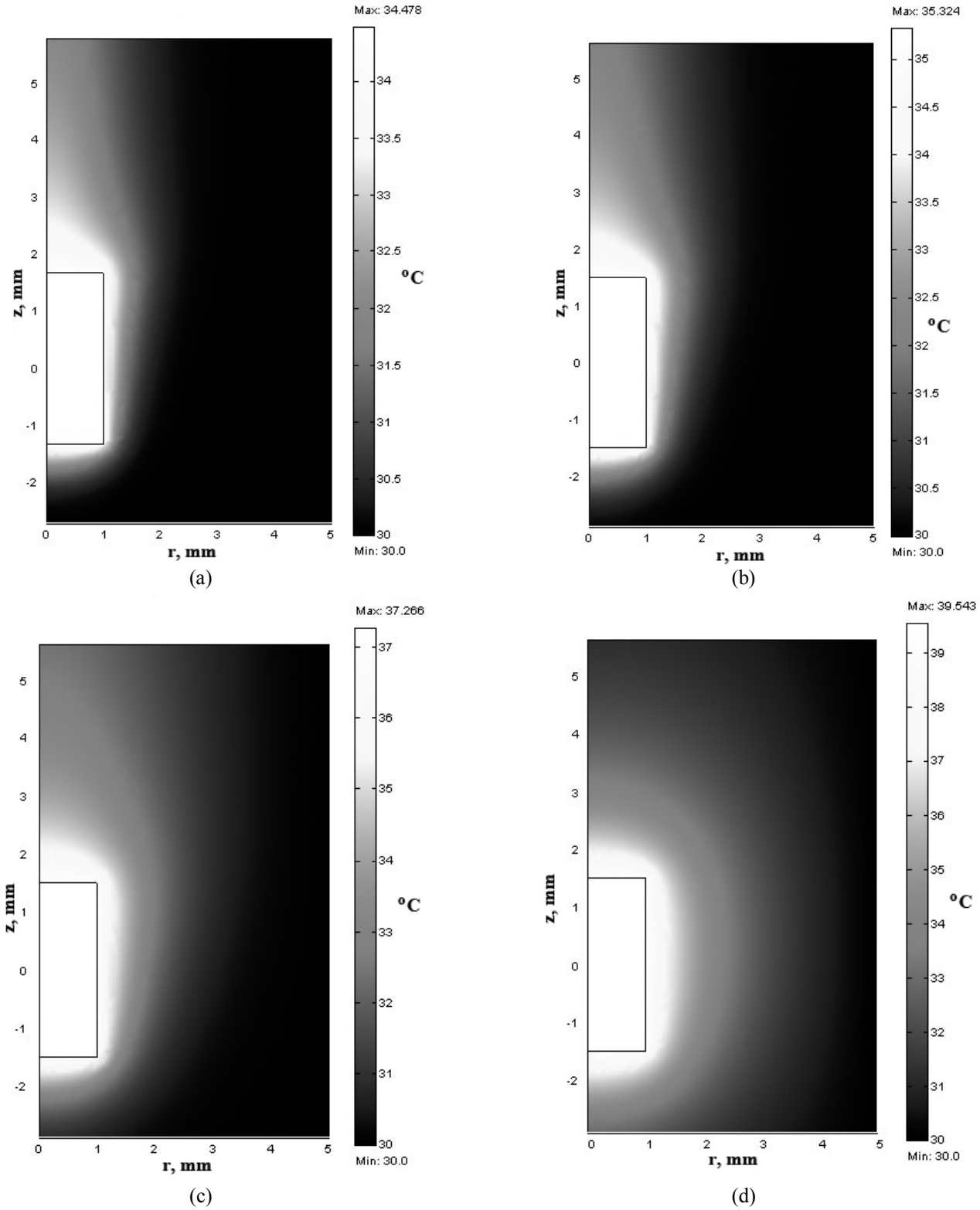


Fig. 2. Temperature distribution in milk with different apparent viscosities around the heated resistor. (a) $\mu = 1.5 \cdot 10^{-3}$ Pa·s, (b) $\mu = 1.0 \cdot 10^{-2}$ Pa·s, (c) $\mu = 1.0 \cdot 10^{-1}$ Pa·s, and (d) $\mu = 1.0$ Pa·s.

As is seen from the figure, the change in the temperature difference between the heated resistor and the main part of milk in an interval from $\Delta T \approx 4$°C to $\Delta T \approx 10$°C, which corresponds to the thermographic findings, occurs as the fluid viscosity changes by about 1000 times.

Obviously, in this case we are speaking about a certain effective viscosity of milk, which is an analog of the apparent viscosity, recorded with a rotary viscometer. Figure 3 shows the dependence of the thermographic temperature difference on the effective viscosity of milk, derived from the results of numeric simulation.

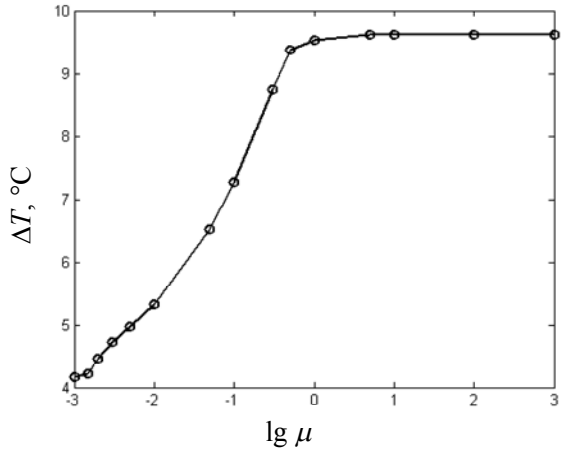


Fig. 3. Dependences of thermographic temperature difference on log of apparent milk viscosity as a result of numeric simulations.

The real dynamic viscosity of milk changes only by several times at the initial stage of flocculation, after which the main resistance to the convective flow comes from the hydrodynamic interaction of the fluid with the forming gel structure. Therefore, the analysis of the numeric estimation data may become the basis for the quantitative study of the forming structure of the milk clot. Roughly speaking, a change in effective viscosity by three orders of magnitude, according to Poiseuille's law for the flow of a viscous fluid through a capillary tube, should correspond to a decrease in the mean pore diameter in the clot by about 5–6 times.

Let us assess the relationship between the permeability of the porous structure of the milk gel and the thermographic temperature difference using Darcy's law:

$$U = \frac{k}{\mu}\operatorname{grad} p \,. \qquad (4)$$

where U is the convective flow's velocity and k is the coefficient of permeability of the medium.

After the formation of a structure in milk, we may ignore the hydrodynamic part of the pressure owing to the practical absence of flows. Then the fluid at depth z amounts to $p = -\rho g z$. Consequently:

$$\operatorname{grad} p = \frac{\partial p}{\partial z} = g\frac{\partial(\rho z)}{\partial z} = g\left(z\frac{\partial \rho}{\partial z} + \rho\right) = g\left(z\frac{\partial \rho}{\partial T}\frac{\partial T}{\partial z} + \rho\right). \qquad (5)$$

As was noted above, the milk density depends on the local temperature according to the law: $\rho = \rho_0(1 - \beta\Delta T)$, then:

$$\frac{\partial \rho}{\partial T} = -\rho_0\beta \,. \qquad (6)$$

Expression (5) with account for (6) will look as follows:

$$\frac{\partial p}{\partial z} = g\left(\rho - z\rho_0\beta\frac{\partial T}{\partial z}\right). \qquad (7)$$

The first summand in (7) represents the density of the pressure force that equalizes the gravity force in a stationary fluid, and the second represents a component of the density of forces that cause the convective transfer of the fluid owing to the temperature difference. It follows from expression (7) that the mean density of these forces is $\left\langle\frac{\partial p}{\partial z}\right\rangle = \rho_0 g\beta\Delta T$.

Taking into account all the transformations, expression (4) will take the form:

$$\langle U\rangle = \frac{k}{\mu}\left\langle\frac{\partial p}{\partial z}\right\rangle = \frac{k}{\mu}\rho_0 g\beta\Delta T \,. \qquad (8)$$

where $\langle U\rangle$ is the mean velocity of the flow.

Expression (8) determines the relationship between the coefficient of permeability and the thermographic temperature difference:

$$k = \frac{\langle U\rangle\mu}{\rho_0 g\beta\Delta T} \,. \qquad (9)$$

The analysis of velocity fields derived from model calculations at various viscosities allowed us to obtain a dependence of the mean flow velocity, $\langle U\rangle$, on the temperature difference (Fig. 4).

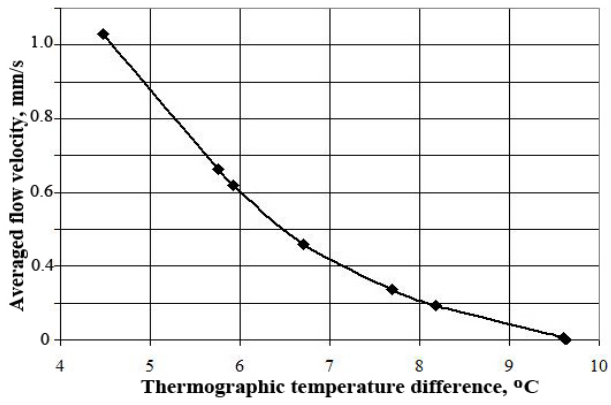


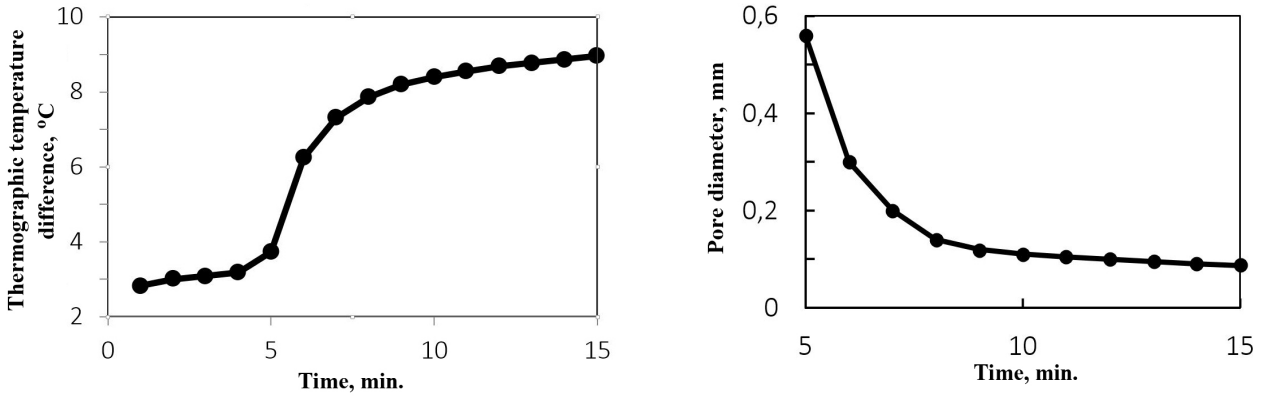
Fig. 4. Dependences of averaged flow velocity on thermographic temperature difference as a result of numeric simulations.

Using formula (9) and the diagram in Fig. 4, we can establish a relationship between the coefficient of permeability and the thermographic temperature difference for the chosen thermogram.

Experimental results

Fig. 5a shows a thermogram of the rennet clotting of milk, and Fig. 5b shows the result of its processing in accordance with the procedure described above. When plotting dependence 5b, we assumed that the coefficient of permeability was related to the mean size of pores formed during coagulation by the simplest dependence $k \approx \delta^2$, where δ is the pore diameter. As is seen from the figures, the mean pore size in the milk gel decreases from about 0.6 mm at the very beginning of clotting to about 0.1 mm after the actual completion of structure formation.

Figure 6 shows thermograms of the rennet clotting of reconstituted fat-free milk into which different amounts of calcium chloride were added. As was expected, the introduction of soluble calcium into milk has reduced significantly the duration of the inductive stage of coagulation. The experimental findings have served as the basis for the development of a phenomenological model of milk coagulation, which explains the role of calcium in this process [14].



(a) (b)

Fig. 5. A thermogram of reconstituted skim milk rennet coagulation (a) and (b) estimation of mean pore diameter in this process.

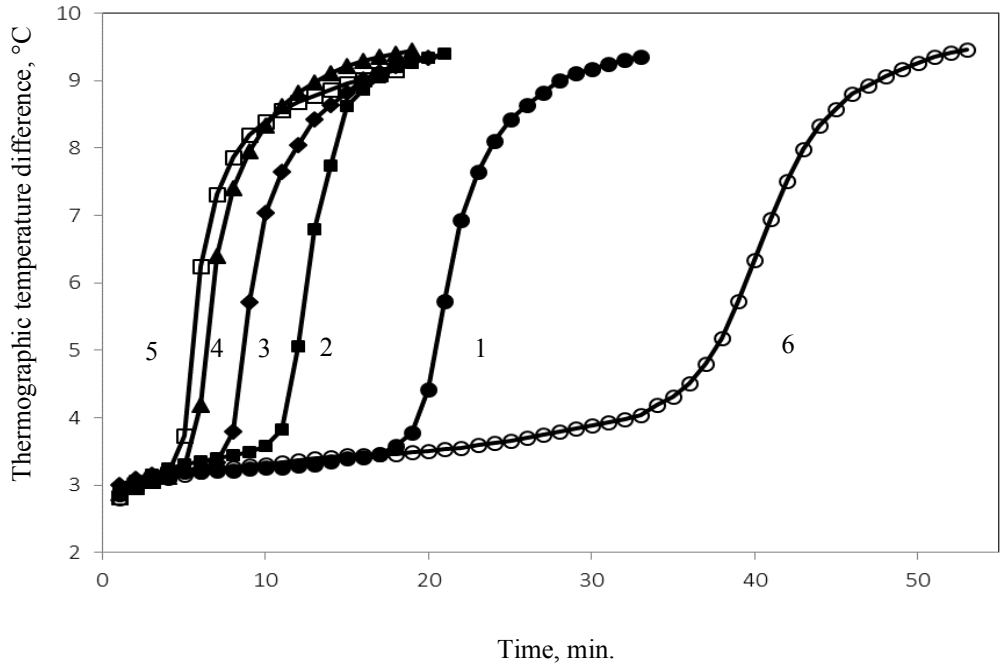


Fig. 6. Thermograms of reconstituted skim milk coagulation by chymosin (25 mg/dm^3) at 30°C with different addition of $CaCl_2$.
Curves: (1) addition of 0.4 g of $CaCl_2$ per 1 dm^3 of milk;
(2) addition of 0.8 g of $CaCl_2$ per 1 dm^3 of milk;
(3) addition of 1.2 g of $CaCl_2$ per 1 dm^3 of milk;
(4) addition of 1.6 g of $CaCl_2$ per 1 dm^3 of milk;
(5) addition of 2.0 g of $CaCl_2$ per 1 dm^3 of milk;
(6) no $CaCl_2$ added to milk.

The data in Fig. 7 exemplifies the application of the thermographic method to processes whose technology is associated with changes in milk temperature, demonstrating the dependence of clotting temperature on the initial milk acidity. Unlike standard thermograms, where the abscissa axis reflects the clotting time, in Fig. 2 the milk temperature is plotted along the abscissa axis. A sharp increase in the thermographic temperature difference corresponds to structure formation, as in a standard case.

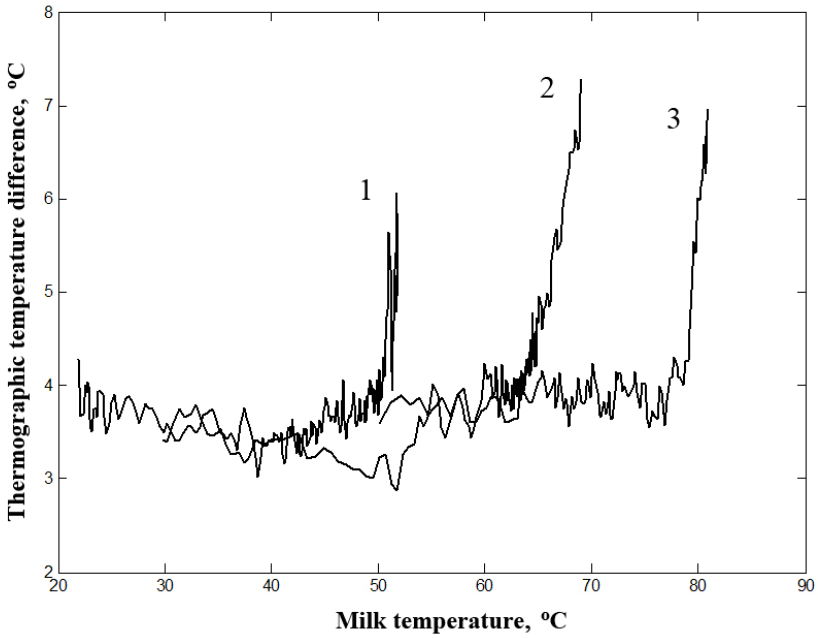


Fig. 7. Dependences of thermographic temperature difference on milk temperature for milk samples with different initial acidity: (1) pH = 5.6, (2) pH = 5.9, and (3) pH = 6.2.

The study of heat–acid heat-calcium milk coagulation by the thermographic method underlay the recently published physicochemical model of these processes, explaining their similarities and differences [15].

CONCLUSION

Thus, we have developed the thermographic method, which combines the simplicity of the hot-wire method and, in addition, allows milk coagulation monitoring even during the production processes related to changes in milk temperature. Hydrodynamic and heat processes that take place in the vicinity of the heated thermometer have been modeled, and the principal possibility to analyze the forming structure of the milk clot has been demonstrated on the basis of the thermographic method. Note that the thermographic sensors that we have developed can easily be combined with other sensors of milk technological parameters, providing thus the possibility of complex monitoring of the cheese production process, as well as the production of other dairy products at the milk coagulation stage both during laboratory research and directly during online production processes.

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