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APPLICATION OF MATHEMATICAL MODELS IN MILK COAGULATION PROCESS DURING LACTIC ACID FERMENTATION

I. RELATION BETWEEN ENZYMATIC AND ACIDIC MILK COAGULATION

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Acidic and enzymatic coagulation of milk are complex processes which proceed in several phases and are dependent upon many different parameters. The formation of coagulum during lactic-acid fermentation is in fact acidic coagulation of milk. It occurs because of an increase in concentration of lactic acid, which causes a decrease in pH. Enzymatic coagulation of milk has been analytically described by means of mathematical models by many authors. Although enzymatic and acidic coagulation of milk do not proceed according to identical physical and chemical rules, it is possible to compare them kinetically.

The aim of this paper was to combine the kinetics of enzymatic and acidic coagulation of milk and to mathematically present the changes that develop during lactic-acid fermentation of milk.

The models presented in this paper enable a more complex mathematical analysis of the coagulation of the protein content of milk during lactic-acid fermentation. Application of the models enables the analysis and comparison of the kinetics of coagulation in different types of milk and various types of fermented dairy products manufactured with lactic acid bacteria. Mathematical combination of coagulation kinetics of the protein complex in milk with reological characteristics of the obtained fermented dairy products enables easier defining of parameters for lactic acid fermentation.

Keywords: enzymatic and acidic coagulation of milk, fermentation kinetics and coagulation kinetics, mathematical models

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Milk coagulation can be enzymatic (production of cheese) and acidic (manufacture of fermented dairy products). Both the acidic and enzymatic coagulation of milk are complex processes that proceed in several phases. Enzymatic coagulation of milk, according to the coagulation theory (VAN HOOYDONK et al., 1984; VAN HOOYDONK & WALSTRA, 1987) proceeds in two phases. In the first phase, the enzymatic one, what occurs is the destabilisation, i. e. delocalization and fission of κ-casein micelles (HYSLOP, 1993; HYSLOP & QVIST, 1996). In the second phase, collision and coagulation of delocalized casein micelles occur (CARLSON et al., 1987). The first phase follows first order rate kinetics rules and is defined as velocity of enzymatic phase (K_1) (VAN HOOYDONK & WALSTRA, 1987). The second phase of casein coagulation in milk follows second order rate kinetics rules and is defined as coagulation rate constant (K_2) (CARLSON et al., 1987).

During the process of coagulation caused by the activity of acid, different physical and chemical changes occur in the protein complex as compared with enzymatic coagulation (MULVIHILL & FOX, 1989; KAIĆ-RAK & ANTONIĆ-DEGAČ, 1996). During the first phase of acidic coagulation, destabilization and desaggregation of casein micelles occur, but not the fission of the casein molecules. In the second phase, physical and chemical changes occur, with a tendency towards repeated fusion of casein micelles. All these changes lead to a firstly metastable casein system and at the isoelectric point (pH=4.6) a stable casein system or coagulum is produced (TRATNIK, 1998).

The velocity and the course of the lactic-acid fermentation is also dependent upon a number of factors which may stimulate or inhibit either the bacterial culture used for fermentation or some of the enzymes which catalyse the transformation of lactose into lactic acid. Numerical values of reaction rate constants K_1 and K_2 as well as kinetics of physical and chemical changes during lactic-acid fermentation depend upon a number of parameters: temperature, pH value, chemical structure of milk, change of ionic power and electrochemical potential, viscosity of milk and other factors (PAYENS, 1989; BRINGE & KINSELLA, 1991; TEO et al., 1996; TRATNIK, 1998; WALSTRA, 1998).

The aim of this paper was, on the basis of the results obtained in previous researches (LOEWENSTEIN et al., 1980; BOŽANIĆ et al., 1996, 1998; NOVAKOVIĆ et al., 1997, 1998), to mathematically present the dependency of the reological parameters of milk upon the course and velocity of fermentation and coagulation. In this, lawfulnesses of several models on enzymatic coagulation of caseins in milk (HYSLOP, 1993; HYSLOP & QVIST, 1996) during lactic-acid coagulation were used.

1. Materials and methods

1.1. Mathematical models of enzymatic coagulation of caseins in milk

Collision and coagulation velocity constant K_2, according to the kinetic theory of enzymatic coagulation of casein, is directly dependent upon reaction velocity constant by which the first (enzymatic) phase of milk coagulation K_1 is defined (Carlson et al., 1987). Namely, following the destabilization of κ-casein micelles, their collision and aggregation proceed with or without activation energy and depends on the diffusion rate of the destabilized milk micelles, i.e. on viscosity of milk and concentration of destabilized micelles in milk suspension (Van Hooydonk et al., 1984; Van Hooydonk & Walstra, 1987; Dalgleish & Holt, 1988). The initial phase of enzymatic milk coagulation is defined by a general equation (Hyslop, 1993):

$$\mu_n = \sum_{k=1}^{\infty} k^n C_k \tag{1}$$

where μ_n is the nth moment of the aggregate creation, k is the number of particles (monomers) in the aggregate and C_k is the molar concentration of created aggregates. The degree of aggregation, i.e. accumulation of destabilized micelles in the constantly increasing agglomerates is defined by an average weight degree polymerisation:

$$\bar{x}_w = \mu_2 / \mu_1 \tag{2}$$

It is taken that if n=0, μ_0=C_0, i.e. all micelles are intact (the beginning of fermentation). In the case when κ-kasein micelles must be hydrolysed first so that the process of coagulation can begin, Payens (1977) suggested the following expression for an average weight degree polymerisation:

$$\bar{x}_w = 1 - \left\{ \left(M_0^2 - M_2^2 \right) \mu_1 - M_1^2 \mu_2 \right\} / m_0 M_0 \tag{3}$$

where M_0 is the molecule mass of unhydrolysed micelles, M_1 is the molecule mass of hydrolysed micelles, M_2 is the molecule mass of casein macropeptides in micelles and m_0 is the total concentration of casein expressed in mass units per total milk volume. There is also a proteolysis degree expressed in this, which proceeds simultaneously with enzymatic hydrolysis of Phe-Met connections in κ-casein, and which causes retardation of coagulation of milk. In the Payens equation (3), the expression $(M_0^2 – M_2^2)\,\mu_1$ represents the proteolysis velocity and causes the decrease in the average weight degree polymerization. On the other hand, $M_1^2\,\mu_2$ stands for the molar mass of hydrolysed micelles ready for aggregation, i.e. the condition of the increase in the average weight degree polymerisation. For increase in molar concentration of the produced aggregates (C_k), DRAKE (1972) uses the Von Smoluchowski expression:

$$\frac{dC_k}{dt} = \frac{1}{2} K_{\alpha\beta} \sum_{i+j=k} C_\alpha C_\beta - K_{\chi\beta} C_\chi \sum_{j=1} C_\beta \tag{4}$$

where constants $K_{\alpha\beta}$ and $K_{\chi\beta}$ mean the velocity of collision of partially created aggregates which contain α, β and χ integrated subunits, whilst C_α, C_β and C_χ represent molar concentration of these created aggregates. DRAKE (1972) offered an expression on the basis of which it is possible to monitor the kinetics of increase in the size of the κ-casein particles in the second phase of milk coagulation:

$$\frac{d\sum\limits_{k=1}^{\infty} k^n C_k}{dt} = \frac{d\mu_n}{dt} = \nu + \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} \left\{ (i+j)^n - i^n - j^n \right\} K \cdot C_\alpha C_\beta \tag{5}$$

where K is the coagulation velocity constant (concentration of coagulated particles/time) and ν represents the velocity of primary (i.e. enzymatic) phase of hydrolysis of κ-casein. The equation (5) represents the basis of the theory of the so called diffusion controlled process of coagulation of milk, according to which the velocity of coagulation of casein in milk in the first phase depends on the velocity of enzymatic hydrolysis of κ-casein, whilst the second phase proceeds without activation energy and is exclusively dependent upon the velocity of diffusion of destabilized micelle particles through milk as a medium. The expression of the beginning of coagulation (first moment) results from equation (5):

$$\mu_1(t) - \mu_0 = \int_0^t \nu(t)\, dt \tag{6}$$

Since the primary (enzymatic) phase of coagulation follows the first order kinetics law, the velocity of enzymatic reaction of κ-casein hydrolysis will be:

$$\nu = K_1 C_0 e^{-K_1 t} \tag{7}$$

K_1 is the first order reaction velocity constant and C_0 is the initial concentration of intact casein micelles. By insertion of expression (7) into (6), this is obtained:

$$\mu_1 = C_0 \left(1 - e^{-K_1 t} \right) \tag{8}$$

By developing the expression (8) in Maclauren order, we obtain:

$$\mu_1 = K_1 C_0 t(1 - K_1 t / 2! + K_1^2 t^2 / 3! - ...) \tag{9}$$

Equations (1–9) represent the basis of the kinetic theory of enzymatic casein coagulation. The further deduction depends upon the number of other conditions such as relative position of enzymes in relation to the surface of micelles, surface activity of κ-casein micelles, ability to detain or release water from pores of expanded calcium – caseinate – complex – network, concentration and influence of ions in the casein micelle environment, viscosity of milk and a number of other factors. HYSLOP (1993) and HYSLOP and QVIST (1996) state, among others, four possible mathematical interpretations for enzymatic casein coagulation in milk:

Collision and aggregation rate constant retains the same value during the entire coagulation process

$$K_{\alpha\beta} = K_0 \;\; (K = K_{\alpha\beta}) \tag{10}$$

DRAKE (1972), for the second moment suggests the expression:

$$\mu_2 = \mu_1 + K_0 \int_0^t \mu_1^2 dt \;\; (\mu_0 = 0) \tag{10a}$$

Insertion of expression (10a) in Payens equation (3) and integration result in:}

$$\begin{aligned}\bar{x}_w = 1 - 2\delta(1-\delta)(1-e^{-K_1 t}) + (1-\delta)^2 K_0 C_0 \{t - (2/K_1)\\ ((1-e^{-K_1 t}) + (1/2K_1)(1-e^{-2K_1 t}))\}\end{aligned} \tag{10b}$$

where $\delta = M_2/M_0$ is the molecule mass of micelles disintegrated and delocalized by the enzymes.

Equation (10b) represents the initial expression for experimental definition and calculation of values of average weight degree polymerisation.

Collision and aggregation rate constant is proportional to the number of subunits in the coagulating particles

$$K_{\alpha\beta} = \alpha\beta K \tag{11}$$

Collision and aggregation rate constant depends on the energetic barrier of the first and second coagulation phases

The concept of energy barrier in the theory of enzymatic casein coagulation was stated by DARLING and VAN HOOYDONK (1981). The aggregation rate constant defined here is based on Arrhenius equation:

$$K_{\alpha\beta}(t) = A \cdot \exp\left(\frac{-\phi(t)}{k_B T}\right), \tag{12}$$

where $\phi(t)$ is the energy barrier as a function of time, expressed by means of the size of barrier for enzymatic (proteolytic) phase (ϕ_δ) and later coagulation phase without the proteolytic influence (ϕ_∞):

$$\phi(t) = \phi_\delta\,(1-\alpha(t))+\phi_\infty \tag{12a}$$

where k_B is the Boltzman constant. T is the absolute temperature and A is the coagulum creation rate without energy barrier and is expressed by this formula:

$$A = 8k_B T/3\eta_{rel} \tag{12b}$$

in which η_{rel} represents the relative viscosity of the solution. By coefficient $\alpha(t)$ the intensity of proteolysis, i.e. destabilization of κ-casein molecules in the first phase, is represented. The initial energy barrier value (for t=0), before the beginning of each reaction, will therefore be as follows:

$$\phi_0 = \phi_\delta + \phi_\infty \tag{12c}$$

Insertion of the Arrhenius expression (12) into Drake's equation of increment of coagulated particles (5) results in a final kinetic equation for the case when the enzymatic hydrolysis rate and casein coagulation rate depend on the energy barrier value:

$$\frac{d\mu_2}{dt} = \nu + A\exp\left(\frac{-\phi_\delta \exp(-K_1 t) + \phi_\infty}{k_B T}\right)\mu_1^2 \tag{12d}$$

This model was used by HYSLOP (1989) and by a number of other authors who were engaged in the problems of enzymatic coagulation of milk (CARLSON et al., 1987); VAN HOOYDONK & WALSTRA, 1987; DALGLEISH & HOLT, 1988).

Collision and aggregation rate constant depends on the number of free (reactive) sites on the particles which polymerise

The aggregation rate constant value is deducted from the Flory-Stockmayer theory (STOCKMAYER, 1943):

$$K_{\alpha\beta} = 4B + 2B(f-2)(\alpha+\beta)+B(f-2)^2\,\alpha\beta \tag{13}$$

where B is the proportionality coefficient and f is the number of functional sites ready for polymerisation. Although the equation (13) was originally used with polymerisation of linear and short-chain polymers, HYSLOP (1989) applied it to spherical particles such as casein micelles. Namely, by parameter f the importance of the enzymatic phase, in which micelles are destabilized and conditions suitable for coagulation are created, has been emphasized. Therefore, parameter f can be expressed as the product of functional sites at the end of proteolysis (f_∞) and that of proteolysis intensity (α):

$$f = f_\infty \alpha(t) \tag{13a}$$

Such a model is also suitable for comparison of two types of milk because it emphasizes the structural characteristics of milk.

1.2. Rheological characteristics of fermented dairy products

Fermented dairy products (beverages) are Newtonian liquids. All fermented dairy beverages have characteristics of a liquid, typical of the pseudoplastic (thixotropic) type of liquids (ROVEDO et al., 1991; STEVENTON et al., 1995). Pseudoplastic liquids are those which are driven to motion at arbitrarily low shear stress, but rapidly increase the shear rate when shear stress reaches a certain value. At infinitely high shear stress, the pseudoplastic liquid acts in the Newtonian way. To these liquids, the Ostwald-Reiner degree rule ("power law") applies (ROVEDO et al., 1991):

$$\tau = m \cdot D^n \tag{14}$$

$$\eta_{app} = m \cdot D^{n-1} \tag{15}$$

where τ = shear stress (Nm^{-2}), D = shear rate (s^{-1}), η_{app} = apparent viscosity (Pas), m = consistency coefficient ($Ns^n m^{-2}$), and n = flow index. Exponent n varies between 0 and 1. By decreasing the value of n, the difference in flow of pseudoplastic in relation to Newtonian liquids is increased (STEVENTON et al., 1995).

Viscosity of thixotropic liquids changes in the course of time so that a certain shear rate in the beginning corresponds to an equal value of shear stress and after a certain period of time, the shear stress for the same shear rate is changed. In liquids, shear rate gradually increases from zero to a certain value and it goes back to zero. Thixotropic material, if not exposed to strain, in the course of time destroys its structure and its viscosity decreases. The velocity of this destruction depends on the number of connections capable to break, which is very important in terms of dairy fermented products. Thixotropic liquids may at any time be considered pseudoplastic and therefore rheological characteristics of dairy products are often regarded as pseudoplastic. Thixotropy is a reversible process and after a certain period of time the structure is gradually rebuilt (AMEMIYA & SHOEMAKER, 1992).

1.3. Mathematical models of acidic coagulation of milk

The above mentioned models refer to enzymatic casein coagulation by addition of rennin (HYSLOP, 1993; HYSLOP & QVIST, 1996). As well as in cheese production, during manufacture of fermented dairy products coagulation kinetics is of the utmost importance for the texture of the product (VAN HOOYDONK et al., 1984; VUJIČIĆ, 1985; STEVENTON et al., 1995). Since the coagulation of the protein system in milk follows precise physical and chemical rules (TRATNIK, 1998), it is possible by modification of the above mentioned models of enzymatic coagulation to express mathematically the dynamics of structural changes during lactic acidic fermentation. Instead of rate constant K_1 of enzymatic casein hydrolysis, in the case of lactic acidic fermentation a destabilization rate constant of casein micelles K_A may be introduced; and instead of collision and aggregation rate constant K_2 during coagulation, for lactic acidic fermentation a repeated connection rate constant and coagulation of destabilized micelles in acidic coagulum K_B may be introduced.

The change in consistency coefficient value (m) during lactic acid fermentation depends, like the change in average polymerisation weight degree ($\bar{x}_w$) in the case of enzymatic coagulation, on enzyme concentration substrate concentration. pH of the environment, temperature and other factors influence the quality of coagulum of fermented dairy products as follows: used culture of lactic acid bacteria (KRŠEV, 1989), fermentation kinetics (NOVAKOVIĆ et al., 1997) and the entire milk system and structure (JOHNSON, 1991). Therefore, instead of average polymerisation weight rate in Payens equation (3), for lactic acid fermentation the term average change in consistency coefficient value (m_p) may be introduced as a rheological parameter which indicates the coagulum quality of fermented dairy products.

2. Results

2.1. Relation between consistency coefficient and average polymerisation weight degree

It is assumed that coagulation rate constant of destabilized casein micelles (K_B) in milk is actually not changed during the entire fermentation process, as is suggested by expression (10). According to JOHNSON (1991), the average polymerisation weight degree is approximately identical to the relative viscosity of milk:

$$\overline{x}_w = \eta_{rel} \tag{16}$$

In this case, the increase in average value of consistency coefficient ($\overline{m}_p$) is in proportion to the average weight polymerisation degree and expressions (2) and (3) being used, it may be expressed as:

$$\overline{m}_p = \zeta \cdot \overline{x}_w = \zeta \cdot \frac{\mu_2}{\mu_1} = \zeta - \left\{\left(M_0^2 - M_2^2\right)\mu_1 - M_1^2 \mu_2\right\}\zeta / m_0 M_0 \tag{16a}$$

where ζ = proportionality coefficient.

If expression (16a) is presented in the form of:

$$\overline{m}_p = \zeta - \left(\frac{M_0^2 - M_2^2}{m_0 M_0}\right) \cdot \mu_1 \zeta - \left(\frac{M_1^2}{m_0 M_0}\right) \mu_2 \zeta \tag{16b}$$

and if we take that

$\frac{M_0^2 - M_2^2}{m_0 M_0} = A_1$, $\frac{M_1^2}{m_0 M_0} = A_2$, $\mu_1 \zeta = x$ and $\mu_2 \zeta = y$,

the expression (16b) may be expressed in the following linear form:

$$Z = \zeta – A_1 \cdot x – A_2 \cdot y \tag{16c}$$

with $Z = \overline{m}_p$. This problem can be solved by the method of the least squares, i.e. multiple regression. Therefore, determining the molecule mass of uncoagulated and coagulated proteins at a certain moment of fermentation and the consistency coefficient by a rheometer, we can calculate the parameters which report the coagulation kinetics ($\mu_1 \zeta(t)$, $\mu_2 \zeta(t)$).

2.2. *Relation between enzymatic reaction rate constant and viscosity*

The linear relation between constant K_1 and reciprocal value of milk viscosity was presented by TOMASSONE and co-workers (1983) by regression equation:

$$K_1 = –0.1073 \cdot 10^{–3} + 3.6984 \cdot 10^{–3}\ (1/\eta_{rel}) \tag{17}$$

If the dependence of the destabilization rate constant of casein micelles (K_A) on viscosity during fermentation is to be expressed, the following formula can be used:

$$K_A(t) = -a+b(1/\eta_{rel}(t)) \tag{17a}$$

or for apparent viscosity:

$$K_A(t) = -a+b(1/\eta_{app}(t)) \tag{17b}$$

or:

$$K_{A1} = -a+b(1/\eta_{rel(1)}),$$

$$K_{A1} = -a+b(1/\eta_{app(1)}),$$

$$K_{A2} = -a+b(1/\eta_{rel(2)}),$$

$$K_{A2} = -a+b(1/\eta_{app(2)}),$$

....

....

$$K_{An} = -a+b(1/\eta_{rel(n)}), \tag{17c}$$

$$K_{An} = -a+b(1/\eta_{app(n)}), \tag{17d}$$

Expression (17b), according to the theory of acidic coagulation of milk (TRATNIK, 1998), remains valid until pH of milk reaches 5.4 and numerical values of constants a and b depend on the intensity of decrease in pH of milk from the initial value (approx. 6.7) to 5.4.

2.3. Relation between coagulum creation rate constant and milk viscosity in relation to energy barriers

According to expression (12b), relation between relative viscosity and coagulum creation rate constant without energy barrier (symbol for lactic acid fermentation is A_f) is expressed by:

$$\eta = \frac{8k_BT}{3A_f} \tag{18}$$

Assuming that viscosity is apparent viscosity at a certain shear rate (D = constant), the consistency coefficient value may be expressed as:

$$m = \frac{8k_B T}{3A_f\, D^{n-1}} \tag{18a}$$

Insertion of constant A_f form expression (18a) in expression (12) results in the following for coagulum creation constant rate:

$$K_B = \frac{8k_B T}{3mD^{n-1}} \exp\left(\frac{-\phi(t)}{k_B T}\right) \tag{18b}$$

If in (18a) constant A_f is expressed as a function of shear rate, an expression is provided by which it is possible to calculate the coagulum creation rate constant without energy barrier based on measurement results obtained by rotation viscometer:

$$A_{if} = \frac{8k_B T}{mD_i^{n-1}};\ \mathrm{i} = 1,2,\ldots 15. \tag{18c}$$

By means of expression (18c) it is possible to calculate the A_f constant or coagulum creation rate constant with the influence of energy barrier at different shear rates based on expressions (18b) and 18c).

Equation (18b) for determined conditions can be solved using the Quasy-Newton nonlinear regression method.

3. Conclusion

By modification, it is possible to apply the mathematical models of enzymatic coagulation of casein in milk to lactic acid fermentation. Since the quality of coagulum of fermented dairy products is greatly dependent upon coagulation kinetics of milk protein systems, the models obtained in such manner connect the coagulation kinetics of casein in milk during lactic acidic fermentation with rheological characteristics of fermented dairy products. Thus it is easier to follow mathematically and to compare the complex changes which occur in milk during lactic acid fermentation.

Symbols

K_1: velocity constant of enzymatic (proteolytic) phase (first-order rate constant) (s^{-1})
K_2: coagulation rate constant (second-order rate constant) (s^{-1})
μ_n: n-th moment for a distribution of aggregated particles
C_k: molar aggregate concentration (mol dm^{-3})
k: number of monomeric units in an aggregate
C_0: total molar concentration of micelles (mol dm^{-3})
$\bar{x}_w$: weight-average degree of polymerisation (g s^{-1}, mol s^{-1})
M_0: molecular mass of unhydrolysed micelles (g mol^{-1})
M_1: molecular mass of hydrolysed micelles (g mol^{-1})
M_2: molecular mass of casein macropeptide found in a micelle (g mol^{-1})
m_0: total casein concentration in unit of mass per unit volume (g dm^{-3})
$K_{\alpha\beta}$, $K_{\chi\beta}$: rate constants for collision between particles having α and β as well as χ and β subunits (s^{-1})
C_α C_β C_χ: molar concentration of α, β and χ particles (mol dm^{-3})
v: velocity of the primary (enzymatic) phase of coagulation (s^{-1})
δ: molecular mass of micelle split off by enzyme (g mol^{-1})
A: the coagulation rate constant without energy barrier (s^{-1})
k_B: Boltzmann constant
T: the absolute temperature (K)
$\alpha(t)$: coefficient of proteolysis intensity
$\phi(t)$: energy barrier as a function of time
ϕ_0: initial energy barrier (for t=0)
ϕ_δ: the amount of energy barrier affected by proteolysis
ϕ_∞: the amount of energy barrier unaffected by proteolysis
f: the number of functional sites that lead to polymerisation
f_∞: the number of functional sites at the and of proteolysis
τ: shear stress (Nm^{-2})
η_{app}: apparent viscosity (Pas)
η_{rel}: relative viscosity (Pas)
D: shear rate (s^{-1})
n: flow index
m: consistency coefficient (Ns^{n}m^{-2})
K_A: rate constant of casein micelle destabilisation (s^{-1})
K_B: rate constant of acidic coagulum release (s^{-1})
$\bar{m}_p$: average change in consistency coefficient value (Ns^{n} m^{-2} s^{-1})
ζ: proportionality coefficient (Ns^{n} mol^{-1} m^{-2})
A_f: rate constant of acidic coagulum relase without energy barrier (s^{-1})

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