

Thermodynamic evaluation of the stabilization indicators of milk quality as influenced by a complex protector

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Abstract. In the present article the authors discuss the possibility of increasing of the suitability of milk as a raw material for cheese production through preservation of native properties of milk proteins, in the first place biologically complete whey proteins as well as the weight ratio of total and ionic calcium. For thermodynamic evaluation of the biosystem we used activation energy (E_a), chemical, physical and organoleptic characteristics. As a result: a methodology has been developed for determination of foodstuffs activation energy; it was determined that with increase in the proportion of the pectin introduced the activation energy and structuredness of the biosystem also increases, when the proportion of pectin is 0.5% the activation energy is 1.788 kJ/mol, when the proportion of pectin is 3% the activation energy is 2.241 kJ/mol, which means the increase by 25%; in the studied pasteurization standard, the maximum content of calcium is observed at 85°C and is equal to 133.8 mg%, in the control sample of milk the content of calcium is 130 mg%; addition of a complex food additive as a protector makes it possible to preserve native properties of the biosystem and guarantees formation of a denser protein coagulum which allows producing high-quality fermented milk products and cheeses.

1 Introduction

The problem of improving coagulating property of milk proteins (the suitability of milk as a raw material for cheese production) and the search for ways of its solution is of importance for researchers and specialists. One of these ways is preservation of native (original) properties of milk proteins and calcium content during thermal processing. The optimal proportion of calcium and phosphorus, required in the manufacturing process of fermented milk products, hard cheeses and cheese analogues is also very important.

The condition of protein phase of milk is linked to calcium salts. Active acidity, the increase in the proportion of ionic (active) calcium in the milk is the evidence of calcium caseinate-phosphate complex decomposition and passing of part of the protein into soluble form [5].

Therefore conducting the research in stabilization (preservation) of milk protein native properties is a high-priority objective. In this connection we see as a prospective one a research in preservation of milk native properties through addition of polysaccharides pectins that possess high stability to temperatures and acids, which makes them preferable under the conditions of technological process in combination with an ingredient that contains calcium.

It must also be mentioned that pectines manifest high chemical activity with calcium, stabilize milk protein, increase milk viscosity, lower the possibility of syneresis in the product. Pectins are used in the production of sour

cream, yoghurts other fermented dairy products. They allow solving the problem of a “flabby curd” which is primarily connected to the quality of milk as a raw material. The curd becomes denser and more homogeneous.

2 Objective

The objective of the article is to study the influence of a complex food additive containing a protector on the preservation of native properties of milk as a thermodynamic system, and also to determine the optimal amount of JNJ type polysaccharide of GENU pectin and the best pasteurization standard of milk on the basis of the combination of properties: chemical ones (titrated, active acidity), physical ones (relative viscosity – flow rate, dynamic viscosity), organoleptic ones.

3 Materials and methods

Milk and JNJ type polysaccharide of GENU pectin (further on denoted as pectin) were used as the objects of the research. The amount of the pectin introduced varied from 0.5 to 3 weight% and the pasteurization temperatures were 75, 85 and 95 °C.

The amount of calcium L-lactate was calculated on the basis of the results obtained after the first stage of the studying of influence of pasteurization on the calcium weight ratio. At the pasteurization temperature of milk (85±2) °C the decrease in calcium weight ratio by

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(21.12±0.11)% and in absolute terms by 23...24 mg%. Taking into the consideration the fact that 100 g of calcium L-lactate contain 13.8 g of the basic element i.e. calcium, it is necessary to compensate the loss of calcium and to provide a “supplementary” amount for cooperative action with pectin aimed at the stabilization of milk proteins. The estimated amount of calcium L-lactate food additive is 363 mg per 100 g of the raw material, or 3.6 kg per 1000 kg of the raw material (milk). It was constant.

As a means of the experiment control we studied the influence of the thermal treatment (pasteurization) of milk without introduction of the food additive. The experiments were repeated 3-5 times.

Mathematical processing of the measurement data and building of regression equations were carried out with the help of statistical methods and using MS Excel software. 3D modeling was done using Table Curve mathematic system.

To prove the suggested hypothesis we processed the experimental data in order to determine the thermodynamic properties of the biosystem (milk + pectin) using various amounts of pectin and pasteurization standards.

Thermodynamic evaluation of a biosystem is an important characteristic of foodstuffs condition. One of the thermodynamic characteristics is the energy of activation (E_a) which characterizes the energy potential directed at breaking intermolecular bonds. The amount of the energy characterizes the rate (dynamics) of biochemical, microbiological processes and the structuredness of the product in the course of fermentation. Transition of a molecule from one state of balance into another is a transition through a potential barrier as high as the energy of activation. The molecule acquires the energy for the transition through a potential barrier from the thermal motion of adjacent molecules [1,3,5].

The calculation of the amount of activation energy of foodstuffs is done with the help of Frenkel-Eyring equation:

$$\eta = A \cdot \exp\left(\frac{E_a}{R \cdot T}\right) \quad (1)$$

where η is the dynamic viscosity of a foodstuff, Pa·s;

A is the preexponential factor, dimension of viscosity, Pa·s;

E_a is the energy of activation, J/mol;

R is the universal gas constant, $R=8.314$ J/(mol·K);

T is the thermodynamic temperature, K.

The equation (1) makes it possible to trace the qualitative changes in the state of the biosystem. The multiplier A in the equation is defined as the product of the bulk modulus by the molecule vibration period at one of its positions [4].

Then we take the logarithm of the equation (1):

$$\ln(\eta) = \ln(A) + \frac{E_a}{R} \cdot \frac{1}{T} \quad (2)$$

We introduce the following designations: $y = \ln(\eta)$, $a = \ln(A)$, $b = E_a/R$; $x = 1/T$

Taking into account the designations introduced we obtain a linear regression equation $y = a + bx$. The linear character of the dependence of the natural logarithm on viscosity $\ln(\eta)$ and the reciprocal of thermodynamic temperature $1/T$ shows that the linear approximation is correct and also allows determination of the amount of activation energy of viscous flow.

The amounts of activation energy of milk with various amounts of pectin introduced were determined on the basis of mathematical processing of experimental dependence of $\ln(\eta)$ on $1/T$.

4 Results and discussion

Table 1 represents the technique of calculation of activation energy of milk with pectin, which was added in the proportion of 0.5 %. Figure 1 graphically represents the linearization of the experimental data of the dynamic viscosity of milk with the addition of 0.5 % pectin within the Arrhenius coordinates.

As a result of the linearization of the experimental data of the dynamic viscosity of milk with the addition of 0.5 % pectin within the temperatures range from 65 to 95°C, we have got a regression equation $y = 0.215 \cdot x - 0.0588$ (Fig. 1). From this equation we deduce the coefficients $b = 0.215$, $a = -0.0588$.

The activation energy is $E_a = b \cdot R = 0.215 \cdot 8.314 \cdot 10^3 = 1.787 \cdot 10^3$ J/mol = 1.797 kJ/mol. The preexponential factor of Frenkel-Eyring equation is $A = \exp(a) = \exp(-0.0588) = 0.943$.

The formula for calculation of variation of the dynamic viscosity of milk with the addition of 0.5 % pectin depending on the temperature is written as:

Table 1. The scheme for calculation of activation energy of milk with the addition of 0.5 % pectin.

| $^{\circ}\text{C}$ | η , mPa·s | T, K | 1000/T, K ⁻¹ | ln(η) | η_p , mPa·s | $(\eta-\eta_p)/\eta$ |
|------------------------------|-------------------|---------|----------------------------|--------------|---------------------|----------------------|
| 65 | 1.78 | 338 | 2.959 | 0.58 | 1.782 | 0.00096715 |
| 75 | 1.75 | 348 | 2.874 | 0.56 | 1.749 | 0.000319283 |
| 85 | 1.72 | 358 | 2.793 | 0.54 | 1.720 | 0.000289958 |
| 95 | 1.71 | 368 | 2.717 | 0.52 | 1.692 | 0.000982241 |
| Error of model prediction, % | | | | | | 0.06 |
| Activation energy E (kJ/mol) | | | | | | 1.79 |
| Preexponential factor | | | | | | 0.943 |

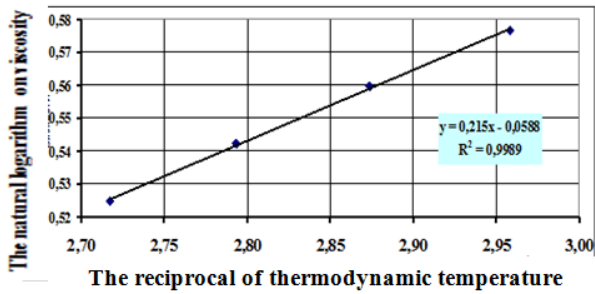


Fig. 1. The linearization of the experimental data of the dynamic viscosity of milk with the addition of 0.5 % pectin within the Arrhenius coordinates.

Table 2 represents the technique of calculation of activation energy of milk with pectin, which was added in the proportion of 3 %. Figure 2 graphically represents the data of the dynamic viscosity of milk with the addition of 3 % pectin.

Table 2. The scheme for calculation of average prediction error, activation energy and preexponential factor of milk with the addition of 3 % pectin.

| °C | η , mPa·s | T, K | 1000/T, K ⁻¹ | ln(η) | η_p , mPa·s | $(\eta - \eta_p)/\eta$ |
|------------------------------|----------------|------|-------------------------|--------------|------------------|------------------------|
| 65 | 1.38 | 338 | 2.959 | 0.32 | 1.383 | 0.002181552 |
| 75 | 1.35 | 348 | 2.874 | 0.30 | 1.352 | 0.001243009 |
| 85 | 1.33 | 358 | 2.793 | 0.29 | 1.323 | 0.005452823 |
| 95 | 1.29 | 368 | 2.717 | 0.25 | 1.296 | 0.004619837 |
| Error of prediction, % | | | | | 0.34 | |
| Activation energy E (kJ/mol) | | | | | 2.241 | |
| Preexponential factor | | | | | 0.623 | |

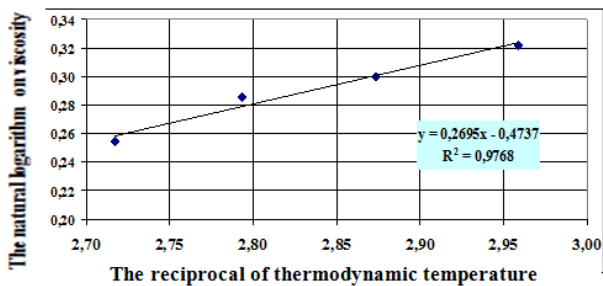


Fig. 2. The linearization of the experimental data of the dynamic viscosity of milk with the addition of 3 % pectin within the Arrhenius coordinates.

The results of the research have shown, that the increase of the proportion of pectin added into milk from 0.5 to 3 % leads to the increase in activation energy from 1.788 to 2.241 kJ/mol, i.e. by 25%.

Comparative summary table of the values of activation energy of dairy products, prediction errors and mathematical models determination (approximation) coefficients is given in table 3.

Table 3. The energy of activation of milk and dairy products flow.

| Foodstuff (temperatures range) | Activation energy, (kJ/mol) | Prediction error, % | Mathematical models determination coefficients |
|---------------------------------------|-----------------------------|---------------------|------------------------------------------------|
| Milk (75...95 °C) | 1.341 | 0.06 | 0.998 |
| Milk with 0.5 % of pectin (75...95°C) | 1.788 | 0.06 | 0.999 |
| Milk with 1 % of pectin (75...95 °C) | 1.825 | 0.12 | 0.985 |
| Milk with 2 % of pectin (75...95 °C) | 1.875 | 0.22 | 0.987 |
| Milk with 3 % of pectin (75...95°C) | 2.241 | 0.34 | 0.977 |

Mathematical processing of the experimental data was carried out and 3D models of the influence of the pectin introduced and the temperature of pasteurization on the variation of the dynamic viscosity (Fig. 3) and calcium contents in the biosystem (Fig. 5) were developed to substantiate the pasteurization standards of the biosystem. The experimental data is represented in tables 4 and 5.

Table 4. The variation of the dynamic viscosity (mPa·s) of milk depending on the proportion of the pectin introduced and the temperature of pasteurization.

| The temperature of pasteurization, °C | The proportion of pectin, % | | | | |
|---------------------------------------|-----------------------------|------|------|------|------|
| | 0 control values | 0.5 | 1.0 | 2.0 | 3.0 |
| 75 | 1.76 | 1.75 | 1.72 | 1.58 | 1.38 |
| 85 | 1.74 | 1.72 | 1.71 | 1.50 | 1.34 |
| 95 | 1.70 | 1.71 | 1.70 | 1.46 | 1.29 |

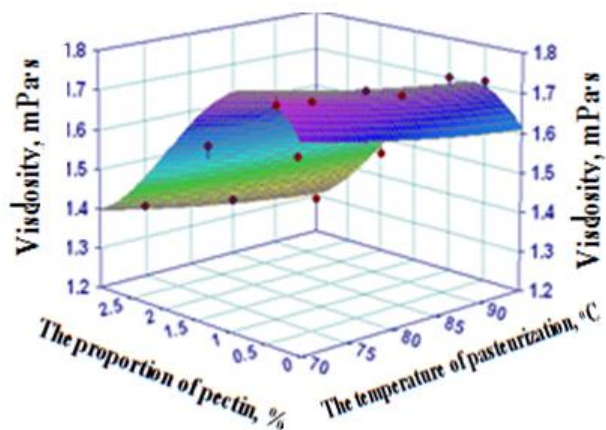


Fig. 3. The response function of the variation of the dynamic viscosity of milk with pectin.

When analyzing the influence of the proportion of pectin on the variation of the dynamic viscosity of milk it must be pointed out that the reaction activity of milk proteins and pectin with the use of calcium is growing up to a definite proportion. That means the activity of

stabilization process decreases in the case of excessive proportion of pectin (more than 1%). Table 5 gives the data on the variation of total calcium content depending on the proportion of the pectin introduced and the pasteurization standard (test samples).

Table 5. The variation of total calcium content (mg%) in the test samples depending on the pasteurization temperature and the proportion of the pectin introduced.

| The temperature of pasteurization, °C | The proportion of pectin, % | | | | |
|---------------------------------------|-----------------------------|-------|-------|-------|-------|
| | 0 control values | 0.5 | 1.0 | 2.0 | 3.0 |
| 75 | 104.0 | 125.6 | 131.6 | 131.8 | 132.0 |
| 85 | 93.3 | 134.2 | 135.6 | 135.8 | 136.0 |
| 95 | 89.2 | 132.9 | 133.0 | 133.1 | 133.8 |

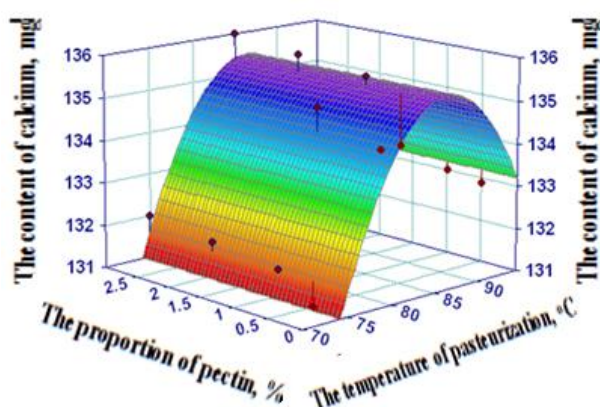


Fig. 4. The response function of the variation of total content (mg%) in the test sample.

The analysis of the data represented in table 5 shows that a compensative protector (pectin + calcium lactate) provides the weight ratio of calcium not less than 133 – 135 mg%, which is very important for the characteristics of the suitability of milk as a raw material for cheese production. At the pasteurization temperature of 85°C the content of calcium is at maximum value within the considered temperatures range of the pasteurization standard.

Table 6 present the data on total protein content depending on the pasteurization temperature and the proportion of the pectin introduced.

Table 6. The variation of total protein content (%) depending on the pasteurization temperature and the proportion of the pectin introduced.

| The temperature of pasteurization, °C | The proportion of polysaccharide – pectin, % | | | | |
|---------------------------------------|----------------------------------------------|------|------|------|------|
| | 0 control values | 0.5 | 1.0 | 2.0 | 3.0 |
| 75±2 | 3.18 | 3.52 | 3.51 | 3.51 | 3.51 |
| 85±2 | 3.08 | 3.54 | 3.54 | 3.54 | 3.54 |
| 95±2 | 3.04 | 3.50 | 3.49 | 3.48 | 3.48 |

The tabular data represent the response function of the total protein content variation where the content of

protein is at maximum value at the pasteurization temperature of 85°C. The proportion of pectin has no influence on the variation of protein content, but it must be pointed out that the total protein content is higher than in the control sample by 15%.

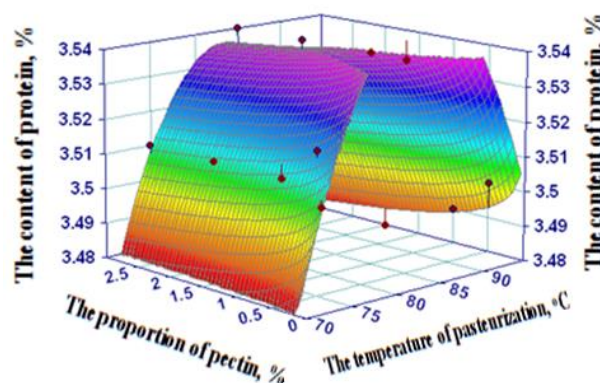


Fig. 5. The response function of the total protein content in the biosystem.

The developed mathematical models represented in Fig. 3,4,5 give an adequate description of the objects of study.

5 Conclusion

1. A methodology has been developed for determination of foodstuffs activation energy with the help of MS Excel software.
2. With increase in the proportion of the pectin introduced the activation energy and structuredness of the biosystem also increases, when the proportion of pectin is 0.5% the activation energy is 1.788 kJ/mol, when the proportion of pectin is 3% the activation energy is 2.241 kJ/mol, which means the increase by 25%.
3. In the studied pasteurization standard, the maximum content of calcium is observed at 85oC and is equal to 133.8 mg%. In the control sample of milk the content of calcium is 130 mg%.
4. Addition of a complex food additive as a protector makes it possible to preserve native properties of the biosystem and guarantees formation of a denser protein coagulum which allows producing high-quality fermented milk products and cheeses.

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