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Computer-aided Determination of Lifetime of Pasteurized Whole-Milk via Casein Degradation Kinetics

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Abstract

Maintaining food quality is a priority due to it is the basis of products acceptability from the consumer. In this regard, the lifetime of full-cream pasteurized milk stored under refrigeration at different temperatures (7, 15, 20 and 28 °C) was calculated using computer-aided tools, applying the chemical kinetics of casein degradation and a mathematical model based on the Arrhenius equation. During a period of time, pH values were monitored until sample rejection was corroborated by a sensory panel. The information collected allowed calculating kinetic parameters (k, E_A, Q_{10} and pre-exponential factor) by lineal regression using Statgraphics Centurion XV. Monitoring pH and casein concentration variables through time showed a negative impact on the quality and durability of full-cream pasteurized milk as the temperature was increased. It was found that both models give an appropriate approach to predict the lifetime of full-cream pasteurized milk, with an average variation of16.2 % at 7, 15 and 28°C. In this sense, at 4 °C pasteurized whole milk has a lifetime of 13.83 days.

Keywords: Lifetime, Pasteurized milk, Casein, CAPE, Kinetics, Arrhenius Equation

1. Introduction

In recent years the world's milk production has grown significantly because of milk has become a major component of human diet. In Colombia, this chain is composed of two main links: production of raw milk and a wide range of dairy products, where the principal is the pasteurized milk [1]. This represents an important source of nutrients needed for growth and infant health care in adults [2]; however, it is affected by many factors involved in the loss of their original quality [3]. Therefore, it is vital to determine the lifetime of dairy products, in order to know the time period during which the food remains suitable for consumption from the health point of view, maintaining its sensory characteristics, functional and nutritional above quality limits previously established as acceptable [4] [5]. Commonly, the lifetime determination is based on subjecting the product at accelerate deterioration under controlled storage conditions to use these results to project its behavior under actual distribution conditions [6]. However, the advance of science has made possible to implement a series of models that can represent the real environment [7], and predict the lifetime, due to they provide objective ways to measure quality and determine the use limits of food, based on the knowledge of deterioration mechanisms [8]. Among these mechanisms is found the predictive modeling of casein degradation. This last one is a quality indicator because of it precipitates in the milk causing acidification and enzymatic coagulation due to different reactions with acidic agents [9]. In addition, casein micelles are primarily responsible for the physical stability of dairy products during heat treatment, concentration and storage [10] [11]. Therefore, this work presents a comparison of the lifetime of full-cream pasteurized milk under four storage conditions based on the kinetic model of casein degradation and the Arrhenius equation.

2. Materials and Methods

Sample collection

The full-cream pasteurized milk was donated by the company Colechera, located in the city of Cartagena, Colombia; under the following quality parameters: Acidity between 0.13 – 0.17 %m/v, 3.0 %m/v fat content, density between 1.030 – 1.033 g/cm^3, 11.30 %m/m of total solids and minimum 29 % of casein content. 48 samples of 200 ml each of them were taken and stored in a bag of low density polyethylene in four refrigerators with integrated temperature control system at 4 °C in order to preserve their sensorial quality.

Experimental

An experimental 4x4 design was made using statistical software Statgrafics Centurion XV v.15.214, where temperature and time were varied in order to observe the behavior of the casein concentration and pH as response variables. Table 1 shows the experimental conditions for the 4 tests performed.

Table 1. Experimental conditions to determinate the lifetime of full-cream pasteurized milk

Test Number	Temperature, °C	Time, days
1	7	7
2	15	4
3	20	2
4	28	1

Lifetime Modelling

The lifetime of pasteurized milk was determined by the kinetic model of casein degradation and the Arrhenius equation. From the first, the reaction constant K for each storage temperature was calculated by linear regression graphing Ln C/C_0 versus t, parameters found in Equation 1. On the other hand, the lifetime was calculated by Equation 2, where the initial concentration of casein C_0 is equal to 0.3450 g/L and C corresponds to the casein concentration at the pH where sensory rejection occurs.

$$- \ln \frac{C}{C_0} = Kt \quad (1)$$

$$t = -\frac{Ln\frac{C}{C_0}}{K} \quad (2)$$

Regarding the second model, Equation 3 presents the linearized Arrhenius equation, from which (Ln K versus 1/T) the pre-exponential factor parameters K_A and Activation Energy E_A were determined. Calculation of the lifetime t_s at normal storage temperature (4 °C) was performed by Equation 4.

$$\ln K = \ln K_A - \frac{E_A}{R}\left(\frac{1}{T}\right) \quad (3)$$

$$t_s = t_{ref}\ e^{-E_A/R[T_s]} \quad (4)$$

Another parameter frequently used to describe the relationship between temperature and reaction constants is the value Q_{10}, which depends on E_A and the absolute temperature T. This parameter is obtained from the definition of reaction rate and the Arrhenius equation and it is expressed by Equation 5.

$$Q_{10} = e^{-\frac{E_A}{R}\left(\frac{10}{T(T+10°C)}\right)} \quad (5)$$

3. Results and Discussion

pH variation as a function of time and temperature

Table 2 shows the pH variation respect to time for each temperature condition studied. It is observed that at high temperatures, the pH decreases in a shorter time due to the lactic acid production by the bacteria present in the milk is positively influenced by temperature. Furthermore, based on these results and those obtained from the sensory test, it was determined that once the milk reached pH 6.0, sensory product rejection occurs because of flocculation of the casein micelles [4]. As the milk approaches the pH of the isoelectric point of caseins, the bonds between the phosphate groups and the calcium ion are broken, the repulsions between the micelles are reduced and the caseins are added forming a little mineralized curd.

Table 2. pH range of variation over time based on storage temperatures

	7 °C	**15 °C**	**20 °C**	**28 °C**
Tiempo, h	0 - 255	0 - 90	0 - 53	0 - 41
pH	6.04 – 6.89	5.23 – 6.89	4.85 – 6.95	4.45 – 6.83

Casein variation as a function of time

Based on the above results and the sensory test, the time taken for the pH reach values of 6.00 to 6.83 was calculated under each storage temperature. The casein concentration was also determined for this pH range, as can be seen in Table 3.

Table 3. Casein concentration at different pH

pH	**Casein, g/L**
6.00	0.2585
6.37	0.2870
6.45	0.3156
6.56	0.2852
6.67	0.3335
6.77	0.3363
6.83	0.3450

Figure 1 shows the declining trend of casein over time. It is observed that change rate is higher at high temperatures than at low, possibly due to the action of lactic acid on the stability of casein micelles. On the other hand, after performing an ANOVA variance analysis a value of $P < 0.05$ was obtained, indicating that there is a statistically significant relationship between casein concentration and time with a 95 % confidence level.

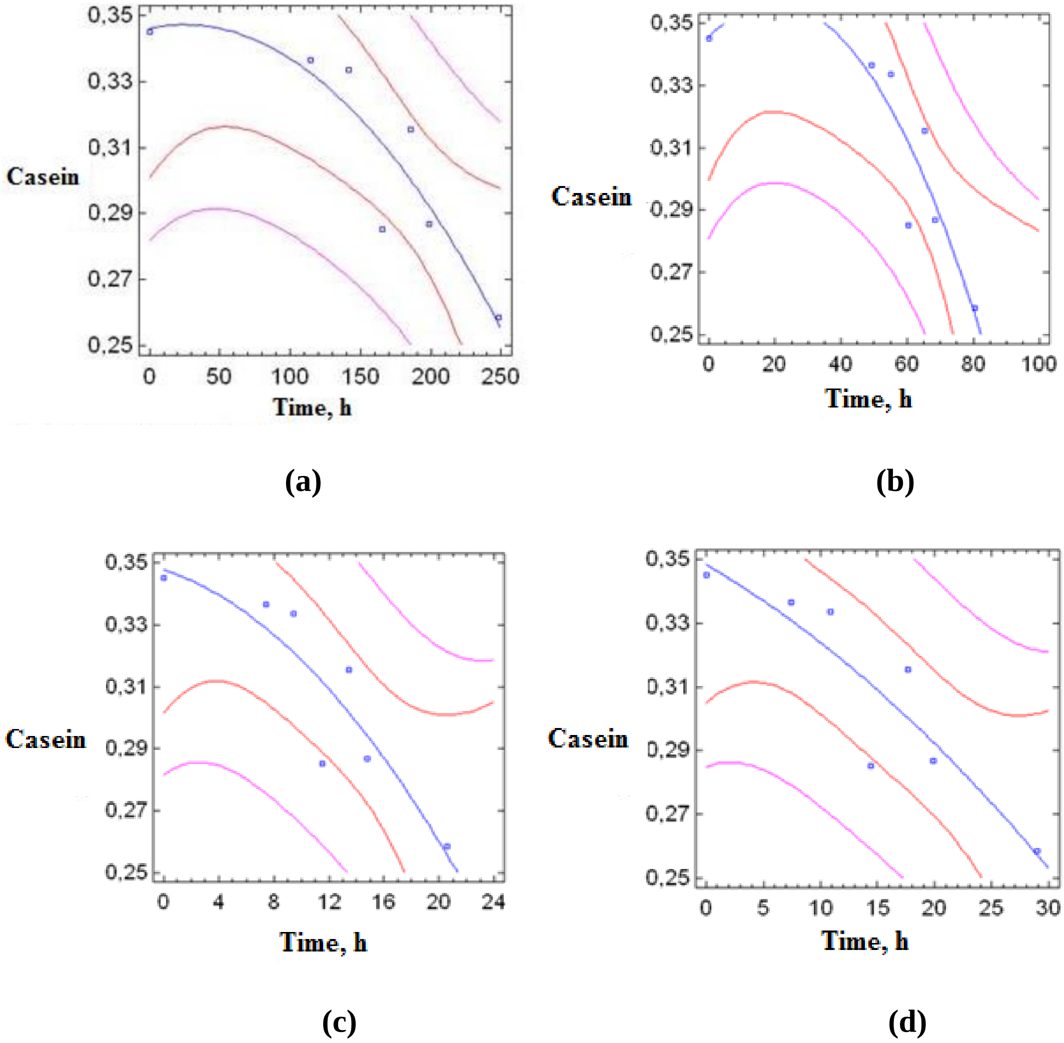

Figure 1. Casein concentration as a function of time at a) 7, b) 15, c) 20 and d) 28°C

Lifetime determination: Kinetic Model and Arrhenius Equation

Table 4 presents the reaction rate constant K for each storage temperature, which was used to determine the lifetime. It is observed that the constant increases as the temperature does so due to the kinetic energy of the particles.

Table 4. Rate constant based on the kinetic model of casein degradation

Storage temperature, °C	**K, h^{-1}**	**R^2**
7	0.0011177	67.56 %
15	0.0030734	54.89 %
20	0.0103527	80.75 %
28	0.0145355	75.92 %

Based on the above results were obtained the data necessary for the linearization of Arrhenius equation. Table 5 presents the values of all parameters of the equation, the lifetime t_s and the Q_{10} value of full-cream pasteurized milk at 4 °C, which means that the reaction rate of deterioration is accelerated by 0.494 times per 10 °C increase in temperature. By comparing this value with others reported in the literature for frozen foods like pork (Q_{10}=8) or fatty fish (Q_{10}=9), it is observed to be relatively low for a quality perishable food such as milk[12].

Table 5. Parameters of Arrhenius equation for milk Pasteurized at 4 °C

$-E_A/R$	10442.80
-EA	20739.40 cal/mol
Ln K_A	32.32
K_A	1.09^{14} h^{-1}
t_{ref}	1.41^{-14} h
Q_{10}	0.494
t_s	13.83 days

Finally, Table 6 shows a comparison between different lifetimes calculated with the Arrhenius equation and the kinetic model of casein degradation for each storage condition. The results show that the percent difference for temperatures of 7, 15 and 28 °C is below 20%, compared to 20 °C which is 34.6%, which indicates that the use of both methods provides an appropriate approximation for the forecast of lifetime of full-cream pasteurized milk.

Table 6. Lifetime of pasteurized milk at different storage temperatures based on the Arrhenius equation and casein degradation kinetic model

Storage temperature, °C	**Lifetime, days**		**Percent difference, %**
	Arrhenius equation	**Kinetic Model**	
7	9.2	10.9	15.6
15	3.3	3.8	15.5
20	1.7	2.7	34.6
28	0.7	0.8	17.5

4. Conclusions

In this work the lifetime of full-cream pasteurized milk at different storage temperatures was calculated using the Arrhenius equation and a mathematical model that represents the casein degradation kinetics, which was obtained experimentally at laboratory level. Monitoring the variables pH and casein concentration over time showed a negative impact on the quality and durability of full-cream pasteurized milk as the temperature it was increased. The Q_{10} value obtained of 0.494 compared with other values of Q_{10} reported in the literature indicates that it is low for a quality perishable food such as milk. The Arrhenius model provided the quantitative basis for the relationship between the activation energy and the rate at which the reaction is carried out. In this sense, it was found that the minimum energy required for the kinetic degradation of casein under storage conditions exposed in this work is 20739.40 cal/mol. Finally, when comparing the two models, it was found that both provide an appropriate approximation for the lifetime of full-cream pasteurized milk, with an average variation of 16.2 % at 7, 15 and 28°C.

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References

[1] F. Organización Mundial de la Salud, Leche y Producos Lácteos 2da Edición, 2011.

[2] M. J. Cardador and M. Gallego, Origin of haloacetic acids in milk and dairy products., *Food Chemistry*, **196** (2016), 750–756. https://doi.org/10.1016/j.foodchem.2015.10.011

[3] S. N. Masiello, N. H. Martin, A. Trmčić, M. Wiedmann, K.J. Boor, Identification and characterization of psychrotolerant coliform bacteria isolated from pasteurized fluid milk., *Journal of Dairy Science*, **99** (2016), 130–140. https://doi.org/10.3168/jds.2015-9728

[4] C. S. Ranadheera, W. S. Liyanaarachchi, J. Chandrapala, M. Dissanayake, T. Vasiljevic, Utilizing unique properties of caseins and the casein micelle for delivery of sensitive food ingredients and bioactives, *Trends in Food Science & Technology*, **57** (2016), 178–187. https://doi.org/10.1016/j.tifs.2016.10.005

[5] P. Kalmus, T. Kramarenko, M. Roasto, K. Meremäe, A. Viltrop, Quality of raw milk intended for direct consumption in Estonia, *Food Control*, **51** (2015), 135–139. https://doi.org/10.1016/j.foodcont.2014.11.018

[6] A.E.C. Antunes, A.T. Silva e Alves, D.A. Gallina, F.K.H.S. Trento, P.B. Zacarchenco, A.G.F. Van Dender, I. Moreno, R.C.S.C. Ormenese, L.M. Spadoti, Development and shelf-life determination of pasteurized, microfiltered, lactose hydrolyzed skim milk, *Journal of Dairy Science*, **97** (2014), 5337–5344. https://doi.org/10.3168/jds.2014-8020

[7] V. Ivanovna, The Kinetics Model of Coverings' Properties with Consideration of the Heredity Factor, *Contemporary Engineering Science*, **8** (2015), 85–89. https://doi.org/10.12988/ces.2015.412257

[8] I. Garkina, Modelin of Kinetic Processes in Composite Materials, *Contemporary Engineering Science*, **8** (2015), 421–425. https://doi.org/10.12988/ces.2015.5258

[9] N. Sun, Y. Liang, B. Yu, C. Tan, B. Cui, Interaction of starch and casein, *Food Hydrocolloids*, **60** (2016), 572–579. https://doi.org/10.1016/j.foodhyd.2016.04.029

[10] T. Huppertz, I. Gazi, H. Luyten, H. Nieuwenhuijse, A. Alting, E. Schokker, Hydration of casein micelles and caseinates: Implications for casein micelle structure, *International Dairy Journal*, **74** (2017), 1–11. https://doi.org/10.1016/j.idairyj.2017.03.006

[11] D. S. Horne, A balanced view of casein interactions, *Current Opinion in Colloid & Interface Science*, **28** (2017), 74–86. https://doi.org/10.1016/j.cocis.2017.03.009

[12] B. Fu and T. Labuza, Shelf life testing: Procedures and prediction methods for frozen foods, 2000.

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