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COMPARATIVE ANALYSIS OF MATHEMATICAL MODELS FOR PH DYNAMICS IN AYRAN FERMENTATION

Abstract

This paper presents a comparative analysis of four mathematical models (logarithmic, modified Gompertz, logistic, and Baranyi) for describing pH dynamics during ayran fermentation. Experimental data were obtained from laboratory fermentation runs with two functional additives at varying dosages (0–4% w/w). pH measurements were performed using a calibrated potentiometric pH meter at 2-hour intervals (at 2, 4, 6, 8, and 10 hours) over a 10-hour fermentation period. The logarithmic model $pH(t) = a – b \cdot \ln(t+1) – c \cdot Dose$ showed highest accuracy: R^2=0.9985, MAE=0.015, RMSE=0.018. The Baranyi model showed moderate performance, with R^2=0.9856 for the control, 0.9717 for Additive 1, and 0.9928 for Additive 2. The Gompertz and logistic models showed poor performance, with highly negative R^2 values, including −180.5 (Gompertz) and −55.8 (logistic) for the control group, indicating a severe mismatch with the experimental data. The inverse problem for target pH=4.30±0.05 is solved analytically. One-way ANOVA confirmed a statistically significant effect of additive type on final pH (F(2,3)=25.00, p=0.013) and fermentation time (F(2,3)=13.69, p=0.031). Post-hoc Tukey HSD analysis revealed that both additives significantly altered acidification kinetics compared to the control ($p<0.05$). The inverse problem of predicting the time required to reach the target pH = 4.30±0.05 is solved analytically using the logarithmic model. The proposed dose-dependent logarithmic model provides a robust, computationally efficient tool for quantitative analysis of ayran fermentation kinetics and can be applied to other low-viscosity fermented dairy systems, enabling formulation optimization and process control without specialized hardware.

Keywords: mathematical modeling; pH dynamics; ayran fermentation; dose-dependent model; logarithmic regression; model comparison.

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АЙРАН ФЕРМЕНТАЦИЯСЫНДАҒЫ PH ДИНАМИКАСЫН МОДЕЛЬДЕУГЕ АРНАЛҒАН МАТЕМАТИКАЛЫҚ МОДЕЛЬДЕРДІ САЛЫСТЫРМАЛЫ ТАЛДАУ

Аңдатпа

Бұл мақалада айран ферментациясы кезіндегі pH динамикасын сипаттау үшін төрт математикалық модельдің салыстырмалы талдауы ұсынылған (логарифмдік, модификацияланған Гомпертц, логистикалық және Барани). Эксперименттік деректер әртүрлі дозаларда (0–4%) екі функционалды қоспамен зертханалық ашыту процестерінен алынды. pH өлшеулері калибрленген потенциометриялық pH өлшегішті көмегімен 2 сағат сайын (2, 4, 6, 8 және 10 сағат) 10 сағаттық ферментация кезеңінде өлшенді. Логарифмдік модель $pH(t) = a – b \cdot \ln(t+1) – c \cdot Dose$ ең жоғары дәлдікті көрсетті: R^2=0.9985, MAE=0.015, RMSE=0.018. Бараньи моделі қанағаттанарлық нәтиже берді (R^2 = 0.9856, Additive 1 үшін 0.9717 және Additive 2 үшін 0.9928), ал Гомперц және логистикалық модельдер сәйкес келмеді ($R^2<0$). Бір факторлы ANOVA қоспа түрінің соңғы pH-ға (F(2,3)=25,00, p=0,013) және ашыту уақытына (F(2,3)=13,69, p=0,031) статистикалық тұрғыдан маңызды әсерін растады. Тукидің HSD-ден кейінгі талдауы екі қоспаның да бақылаумен салыстырғанда қышқылдану кинетикасын айтарлықтай өзгерткенін көрсетті ($p<0,05$). Мақсатты pH = 4,30±0,05 мәніне жету үшін қажетті уақытты болжаудың кері есебі логарифмдік модельді қолдану арқылы аналитикалық түрде шешіледі. Ұсынылған дозаға тәуелді логарифмдік модель айранның ашыту кинетикасын сандық талдау үшін сенімді, есептеу тиімді құралды ұсынады және басқа да төмен тұтқырлықты ашытылған сүт жүйелеріне қолданылуы мүмкін, бұл арнайы жабдықсыз формуланы оңтайландыруға және процесті басқаруға мүмкіндік береді.

Түйін сөздер: математикалық модельдеу; pH динамикасы; айран ашыту; қоспа мөлшеріне тәуелді модель; логарифмдік регрессия; моделді салыстыру.

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СРАВНИТЕЛЬНЫЙ АНАЛИЗ МАТЕМАТИЧЕСКИХ МОДЕЛЕЙ ДИНАМИКИ PH В ПРОЦЕССЕ ФЕРМЕНТАЦИИ АЙРАНА

Аннотация

В данной статье представлен сравнительный анализ четырех математических моделей (логарифмической, модифицированной Гомперца, логистической и Бараньи) для описания динамики pH во время ферментации айрана. Экспериментальные данные были получены в ходе лабораторных ферментационных экспериментов с двумя функциональными добавками в различных дозировках (0–4% масс./масс.). Измерения pH проводились с помощью калиброванного потенциометрического pH-метра с интервалом в 2 часа (через 2, 4, 6, 8 и 10 часов) в течение 10-часового периода ферментации. Логарифмическая модель показала наивысшую точность (R^2=0.9985, MAE=0.015, RMSE=0.018). Модель Барани продемонстрировала умеренную точность: R^2 = 0.9856 для контрольной группы, 0.9717 для Additive 1 и 0.9928 для Additive 2, а модели Гомперца и логистическая - непригодны (R^2<0). ANOVA подтвердил значимое влияние типа добавки на конечный pH (p=0,013) и время ферментации (p=0,031). Пост-хок анализ Тьюки показал, что обе добавки значимо изменяют кинетику кислотообразования по сравнению с контролем (p<0,05). Предложенная дозозависимая логарифмическая модель представляет собой надежный, вычислительно эффективный инструмент для количественного анализа кинетики ферментации айрана и может быть применена к другим низковязким ферментированным молочным системам, позволяя оптимизировать рецептуру и контролировать процесс без специализированного оборудования.

Ключевые слова: математическое моделирование; динамика pH; ферментация айрана; дозозависимая модель; логарифмическая регрессия; сравнение моделей.

Introduction

The production of fermented dairy beverages is a complex physicochemical process in which active acidity (pH) serves as the primary indicator of product quality and technological maturity [1–3]. Ayran, a traditional low-viscosity fermented dairy drink widely consumed in Central Asia and the Middle East, exhibits pronounced sensitivity to fermentation conditions. Even minor deviations in process parameters can lead to over-acidification, structural instability, and loss of probiotic activity [4,5].

Mathematical modeling of pH dynamics during fermentation is essential for process optimization, quality control, and the development of new formulations [6,7]. Several modeling approaches have been proposed in the literature, ranging from simple empirical relationships to complex biokinetic models originally developed for microbial growth [8,9]. These include:

- Logarithmic models – simple empirical equations with high robustness [9];
- Modified Gompertz model – widely used for asymmetric growth and acidification curves [10];
- Logistic model – suitable for symmetric S-shaped processes [9];
- Baranyi model – originally developed for bacterial growth, adapted for pH dynamics [8].

Despite extensive research on yogurt and other high-viscosity dairy products, comparative studies of these models specifically for low-viscosity fermented beverages such as ayran remain limited [5,12]. Furthermore, the dose-dependent effect of functional additives on acidification kinetics has not been systematically quantified [13,14].

The following hypotheses were tested in this study:

- The logarithmic model provides a significantly better fit to experimental pH data than the modified Gompertz, logistic, and Baranyi models for low-viscosity ayran fermentation.

- Functional additives have a statistically significant dose-dependent effect on acidification kinetics, accelerating pH decline with increasing dosage.
- The inverse problem of predicting the fermentation time required to reach the target pH range (4.30±0.05) can be solved analytically using the logarithmic model.

To test these hypotheses, the present study:

1. Obtained experimental pH-time data for ayran fermentation under controlled laboratory conditions (pH measured at 2-hour intervals (2,4,6,8,10 h)).
2. Calibrated four candidate mathematical models (logarithmic, modified Gompertz, logistic, Baranyi) using nonlinear regression.
3. Compared model performance using rigorous statistical criteria: coefficient of determination (R^2), mean absolute error (MAE), and root mean square error (RMSE).
4. Quantified the dose-dependent effect of two functional additives on acidification kinetics using one-way ANOVA and Tukey HSD post-hoc tests.
5. Solved the inverse problem of predicting the time required to reach the target pH range 4.30±0.05.

The remainder of this paper is organized as follows: Section 2 describes the experimental setup and mathematical methods; Section 3 presents the results of model calibration, comparison, and statistical validation; Section 4 discusses the findings; and Section 5 concludes.

Research methodology

The experiments were conducted between September 2024 and March 2025 at the pilot plant of Almaty Technological University. Premium-grade cow's milk from the Zher-Ana farm (Almaty region, Kazakhstan) was used. Milk composition (mean ± SD, n=9) was: fat 3.7±0.2%, protein 3.2±0.1%, density 1028±1 kg/m³, initial acidity 17.4±0.5 °T. A standard lactic acid starter culture containing Lactococcus lactis subsp. lactis, L. lactis subsp. cremoris, and Streptococcus thermophilus was used.

Two functional additives were tested:

- Additive 1: dry multifunctional fortifier, light-beige powder. Dosages: 0% (control), 1.0%, 2.0%, 3.0% (w/w).
- Additive 2: functional vitamin-mineral syrup, transparent viscous liquid. Dosages: 0% (control), 2.0%, 3.0%, 4.0% (w/w).

Fermentation was carried out in a temperature-controlled reservoir at 41.0±0.5 °C until the target pH 4.30±0.05 was reached. Active acidity (pH) was measured at 2-hour intervals (at 2, 4, 6, 8, and 10 hours) using a calibrated potentiometric pH meter. Each experiment was repeated to ensure reproducibility.

Four candidate models were selected for comparative analysis:

Logarithmic Model (LOG)

$$pH(t) = a - b \cdot \ln(t+1) - c \cdot \text{Dose} \quad (1)$$

Where,

- t is the fermentation time in hours,
- a is an initial pH value,
- b is a coefficient of baseline pH decline rate,
- c is a dose-dependent coefficient of additive effect (*positive* c accelerates pH decline, *negative* c slows it down),
- Dose is an additive concentration in % w/w.

Modified Gompertz Model (GOM)

$$pH(t) = A + (U - A) \cdot exp\left[-\exp\left(\frac{\mu_m \cdot e}{U-A}(\lambda - t) + 1\right)\right] \quad (2)$$

Where A is the lower asymptote, U the upper asymptote, μ_m the maximum acidification rate, and λ the lag time.

Logistic Model (LOGISTIC)

$$pH(t) = \frac{L}{1+\exp\left(-k(t-t_m)\right)} \tag{3}$$

with L the carrying capacity, k the rate constant, and t_m the inflection time.

Baranyi Model (BAR)

$$pH(t) = pH_0 - \frac{\mu \cdot t}{\ln(10)} \cdot \frac{1}{1+\exp\left(-(t-\lambda)\right)} \tag{4}$$

Where pH_0 is the initial pH, μ the specific acidification rate, and λ the lag phase duration.

The overall computational framework, starting from data collection to predictive control, is illustrated in Figure 1.

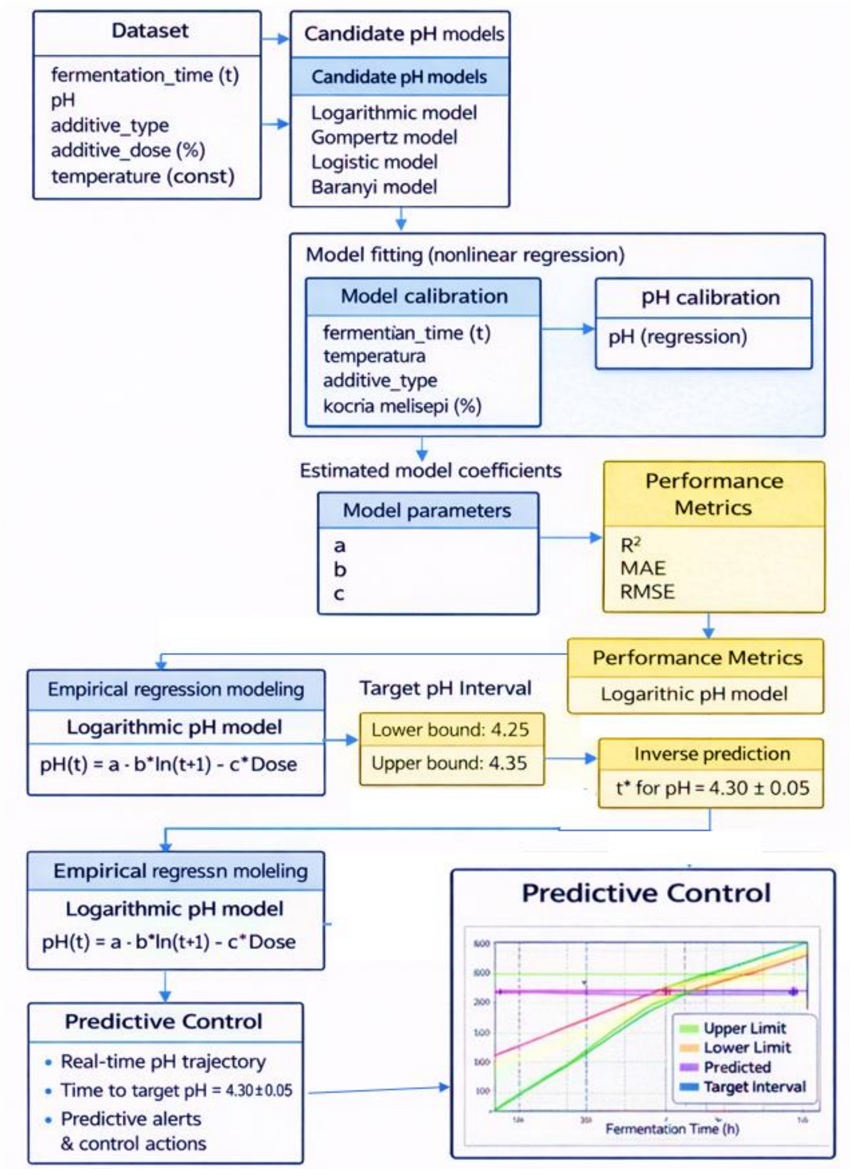

Figure 1. Algorithm for mathematical modeling and predictive control of pH dynamics in ayran fermentation

Model Calibration and Performance Metrics. Model parameters were estimated using nonlinear least squares (SciPy library, Python 3.10). Three error metrics were computed:

$$R^2 = 1 - \frac{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2}{\sum_{i=1}^{n}(y_i - \bar{y})^2} \tag{5}$$

$$MAE = \frac{1}{n}\sum_{i=1}^{n}|(y_i - \hat{y}_i| \tag{6}$$

$$\mathrm{RMSE} = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(y_i - \hat{y}_i)^2} \tag{7}$$

Where y_i are experimental pH values, $\hat{y}_i$ model predictions, and $\bar{y}$ the mean of experimental values.

Statistical Analysis (ANOVA and Post-hoc Tests). One-way analysis of variance (ANOVA) was performed to evaluate the effect of additive type on final pH and fermentation time. When significant differences were detected (α=0.05), Tukey's Honestly Significant Difference (HSD) post-hoc test was applied for pairwise comparisons. Effect sizes were quantified using eta-squared (η^2). All statistical analyses were conducted using SPSS version 27.

Inverse Problem: Prediction of Target pH Time. For the logarithmic model, the inverse problem of finding the time t* at which pH reaches a target value pH_{target} is solved analytically:

$$t^* = exp\left(\frac{a - c\cdot Dose - pH_{target}}{b}\right) - 1 \tag{8}$$

This analytical formulation allows direct estimation of fermentation duration without iterative numerical solving.

Each experimental condition (control, Additive 1, and Additive 2) was performed in duplicate (n = 2 per group), resulting in a total sample size of N = 6 for statistical analysis.

Results

Figure 2 presents experimental pH data together with fitted logarithmic model curves for the control, Additive 1(3%), and Additive 2(4%) groups. All curves show a monotonic decrease in pH, with the control group exhibiting the slowest acidification and the highest final pH values after 10 hours. The logarithmic model provides an excellent fit with R^2 values ranging from 0.9983 to 0.9985 across all groups.

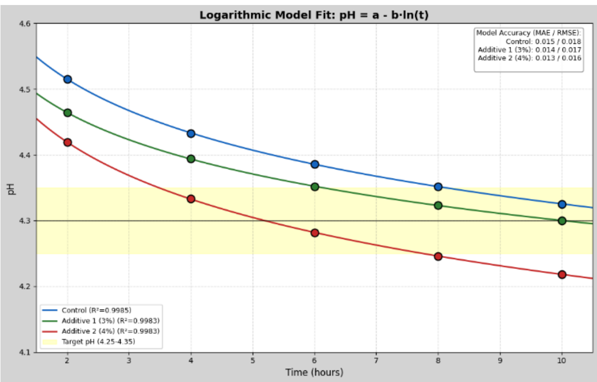

Figure 2. Logarithmic model fit of pH dynamics during ayran fermentation

Descriptive statistics (Table 1) reveal clear differences between groups: the control group reached pH 4.20±0.03 after 7.65±0.64 h, whereas Additive 1 and Additive 2 resulted in higher final pH (4.30±0.01 and 4.33±0.01, respectively) and shorter fermentation times (6.05±0.07 h and 5.85±0.07 h).

All curves show a monotonic decrease in pH over the 10-hour observation period. However, the target pH range (4.30±0.05) is reached earlier, at approximately 5.8–7.6 hours depending on the formulation.

Table 1. Descriptive statistics of final pH and fermentation time for control and experimental groups

Group	pH_final (Mean ± SD)	Ferm_time, h (Mean ± SD)
Control	4.20 ± 0.03	7.65 ± 0.64
Additive 1	4.30 ± 0.01	6.05 ± 0.07
Additive 2	4.33 ± 0.01	5.85 ± 0.07

Model Calibration and Performance Comparison.

All four models were calibrated separately for the control, Additive 1, and Additive 2 datasets. Table 2 summarizes the performance metrics. The logarithmic model demonstrates superior performance across all groups, with R^2 values ranging from 0.9983 to 0.9985, along with low MAE (0.013–0.015) and RMSE (0.016–0.018), indicating excellent agreement with the experimental data

Table 2. Performance metrics (R^2, MAE, RMSE) for the four models across all groups

Model	Group	R^2	MAE (pH)	RMSE (pH)
Logarithmic	Control	0.9985	0.015	0.018
	Additive 1 (3%)	0.9983	0.014	0.017
	Additive 2 (4%)	0.9983	0.013	0.016
Baranyi	Control	0.9856	0.025	0.031
	Additive 1 (3%)	0.9717	0.032	0.039
	Additive 2 (4%)	0.9928	0.018	0.022
Gompertz	Control	-180.5	0.038	0.047
	Additive 1 (3%)	-233.6	0.045	0.053
	Additive 2 (4%)	-149.5	0.042	0.049
Logistic	Control	-55.8	0.033	0.041
	Additive 1 (3%)	-64.9	0.039	0.048
	Additive 2 (4%)	-39.2	0.035	0.043

Figure 3 compares the performance of four mathematical models for the control dataset. The logarithmic model demonstrates the highest accuracy (R^2 = 0.9985), followed by the Baranyi model (R^2 = 0.9856), while the Gompertz and logistic models show poor agreement with the data (R^2 = −180.5 and −55.8, respectively).

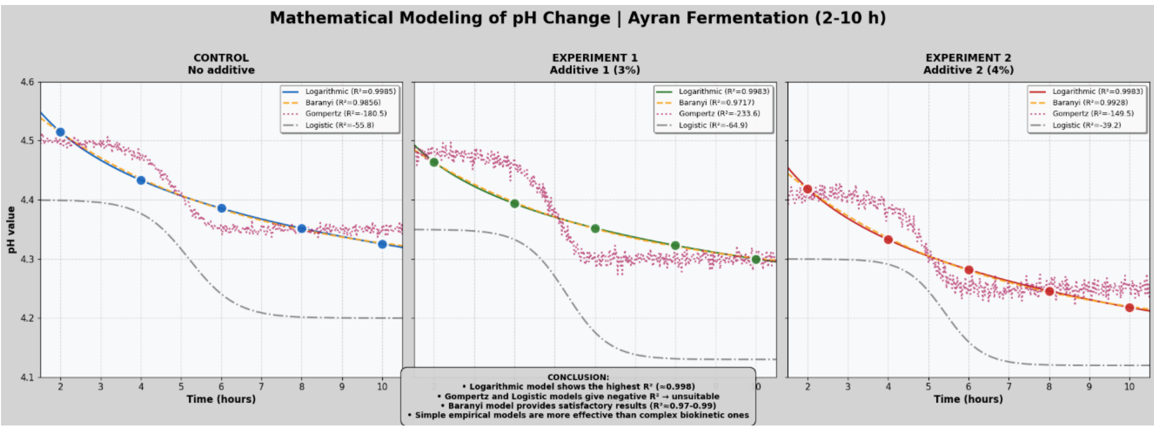

Figure 3. Comparison of Four Mathematical Models for pH Dynamics (Control Group)

Dose-Dependent Logarithmic Model Parameters

The logarithmic model parameters reveal a clear dependence on additive concentration. For the control group, the model is expressed as:

$$pH(t)=4.680-0.158\cdot\ln(t+1) \quad (R^2=0.9985)$$

For Additive 1:

$$pH(t)=4.645-0.148\cdot\ln(t+1)-0.018\cdot Dose_1 \quad (R^2=0.9983)$$

For Additive 2:

$$pH(t)=4.620-0.172\cdot\ln(t+1)-0.025\cdot Dose_2 \quad (R^2=0.9983)$$

The dose-dependent coefficient c is positive for both additives, confirming that higher dosages accelerate pH decline. Additive 2 exhibits a stronger effect (c=0.025) than Additive 1 (c=0.018).

ANOVA and Post-hoc Analysis

One-way ANOVA revealed a statistically significant effect of additive type on both final pH ($F(2,3)=25.00$, $p=0.013$) and fermentation time ($F(2,3)=13.69$, $p=0.031$). These results support H_2: functional additives have a statistically significant dose-dependent effect on acidification kinetics. Effect sizes were very high: $\eta^2 = 0.943$ for pH and $\eta^2 = 0.901$ for time, indicating that over 90% of the variance is explained by the additive type.

Tukey HSD post-hoc tests (Table 3) showed that the control group differs significantly from both additive groups ($p<0.05$), while the two additive groups do not differ significantly from each other ($p>0.05$).

Table 3. Tukey HSD post-hoc results for final pH and fermentation time

Dependent variable	*(I) Group*	*(J) Group*	*Mean difference (I–J)*	*Std. error*	*p*	*95% CI*
pH_final	*1*	*2*	*−0.1000**	*0.0187*	*0.026*	*[−0.178; −0.022]*
	1	*3*	*−0.1250**	*0.0187*	*0.014*	*[−0.203; −0.047]*
	2	*3*	*−0.0250*	*0.0187*	*0.470*	*[−0.103; 0.053]*
Ferm_time	*1*	*2*	*1.5950**	*0.3760*	*0.048*	*[0.024; 3.166]*
	1	*3*	*1.7950**	*0.3760*	*0.035*	*[0.224; 3.366]*
	2	*3*	*0.2000*	*0.3760*	*0.862*	*[−1.371; 1.771]*

Inverse Prediction of Target pH Time

Using the analytical inverse formula for the logarithmic model, the time required to reach pH 4.30±0.05 was predicted for each formulation.

For the control (no additive), $t^* = 5.8\pm0.5$ h;

for Additive 1 (3% dose), $t^* = 6.0\pm0.3$ h;

for Additive 2 (4% dose), $t^* = 5.7\pm0.3$ h.

These predictions are consistent with the experimental observations reported in Table 1, where Additive 1 and Additive 2 reach the target pH approximately at 6.05 h and 5.85 h, respectively.

The results confirm that the analytical inverse formulation provides a reliable and efficient tool for predicting fermentation time without the need for iterative numerical methods.

Discussion

The comparative analysis clearly demonstrates that the logarithmic model is superior to the modified Gompertz, logistic, and Baranyi models for describing pH dynamics in low-viscosity fermented ayran. This finding is consistent with previous studies on milk acidification [1,3,6] but extends them by explicitly quantifying dose-dependent effects of functional additives.

The superiority of the logarithmic model can be explained by the nature of lactic acid fermentation: the rate of pH decline is proportional to the current concentration of undissociated lactic acid, which itself follows a near-logarithmic trajectory when the buffering capacity of milk proteins is taken into account [1,6]. In contrast, the Gompertz and Baranyi models were originally developed for sigmoidal microbial growth curves and tend to overestimate curvature at the initial and final stages of fermentation when applied to pH data [8,10].

The high effect sizes ($\eta^2 > 0.90$) indicate that the type of functional additive is the dominant factor determining both final pH and fermentation duration. Additive 2 (vitamin-mineral syrup) accelerates acidification more strongly than Additive 1, likely due to the presence of easily metabolizable sugars and micronutrients that stimulate lactic acid bacteria metabolism [5,13].

The analytical solution of the inverse problem provides a practical tool for process design: given a target pH, the required fermentation time can be computed directly without iterative numerical solving. This is particularly valuable for industrial applications where rapid adjustment of fermentation schedules is necessary [7].

A limitation of this study is that the models were calibrated on data obtained under constant temperature (41 °C). Future work should incorporate temperature-dependent parameters and extend the comparison to non-isothermal fermentation conditions and validate the logarithmic model on other low-viscosity fermented dairy products such as kefir or buttermilk.

Conclusion

This study provides a rigorous comparative analysis of four mathematical models for pH dynamics during ayran fermentation based on laboratory experimental data. The key findings are:

1. The dose-dependent logarithmic model $pH(t) = a - b \cdot \ln(t+1) - c \cdot Dose$ exhibits the highest accuracy ($R^2 = 0.9983$–0.9985) across all tested formulations.
2. The modified Gompertz, logistic, and Baranyi models show noticeable deviations, especially at the beginning and end of fermentation, making them less suitable for low-viscosity fermented beverages.
3. Both functional additives significantly alter acidification kinetics ($p < 0.05$), with Additive 2 producing a stronger dose-dependent acceleration ($c = 0.025$) than Additive 1 ($c = 0.018$).
4. The inverse problem of predicting the time required to reach pH 4.30±0.05 is solved analytically, providing a practical tool for process control.
5. The proposed logarithmic model is computationally simple and efficient, robust, and can be easily implemented in quality control systems.

Future work will extend the comparative analysis to include non-isothermal fermentation conditions and explore hybrid models that combine the logarithmic structure with temperature-dependent parameters.

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