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SELECTION OF KINETIC MODELS APPLIED TO ALCOHOLIC FERMENTATION USING AMAZONIAN FRUITS

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ABSTRACT

This study evaluated two mathematical models to simulate ethanol production by microbial fermentation, aiming to produce liqueurs derived from Amazonian fruits (açaí and cupuaçu). The processes in both cases were carried out in a batch reactor, where the effect of substrate inhibition on ethanol production was evaluated. The method used for estimating the kinetic parameters of the process was Markov chain Monte Carlo with the Metropolis-Hastings algorithm. Metrics for comparing experimental measurements with estimated ones included the Bayesian information criterion (BIC), Akaike information criterion (AIC), and relative root mean square error (rRMSE). The results indicated that the model that included the maximum concentration of ethanol and substrate in the inhibition of the process, presented rRMSE values below 10%, demonstrating an excellent fit. These results indicate greater precision estimating the essential kinetic parameters to optimize ethanol production and ensures more accurate predictions of the process performance.

Keywords: Markov chain Monte Carlo method. Microbial Fermentation. Modeling and Simulation. Ethanol Production.

1 INTRODUCTION

Ethanol production in Brazil is predominantly driven by sugarcane; however, there is a growing interest in exploring alternative biomass sources, such as lignocellulosic industrial residues and renewable raw materials. This diversification not only broadens the base for ethanol production but also contributes to the energy matrix diversification, reducing the exclusive dependence on sugarcane. Moreover, the utilization of lignocellulosic industrial residues fosters the circular economy and enables a more sustainable and efficient production process.[1, 2]

The production of liqueurs derived from Amazonian fruit pulps represents a convergence of fermentation technology and the valorization of natural resources. This approach promotes the circular economy by utilizing fruit by-products and contributes to scientific advancement by providing insights into fermentation kinetics and sensory aspects. Furthermore, it enhances regional sustainability by integrating Amazonian biodiversity into the beverage industry both efficiently and scientifically.[3, 4]

The literature[5] has already investigated the kinetics of alcoholic beverages made with two Amazonian fruits: açaí (*Euterpe precatoria*) and cupuaçu (*Theobroma grandiflorum*). In the fermentation of cupuaçu liqueur, complex sugars favored ethanol production, delaying the inhibitory process. For açaí liqueur, obstacles such as rancidity due to high anthocyanin concentration were identified. In this context, the objective of this work was to evaluate two kinetic models for ethanol production by microbial fermentation from Amazonian fruits. For this purpose, the Markov chain Monte Carlo (MCMC) method with the Metropolis-Hastings algorithm was used to estimate the kinetic parameters of each model. The results of the estimates were compared with experimental measurements in the literature[5], followed by calculations of the Bayesian information criterion (BIC), Akaike information criterion (AIC), and relative root mean square error (rRMSE) for the analysis and comparison of the studied models.

2 MATERIAL & METHODS

Table 1 presents the two models used in this work for alcoholic fermentation using Amazonian fruits (açaí and cupuaçu). Model A describes the kinetic modeling of the process based on the Monod kinetic model[5], considering the behavior and reaction rates of sugars, biomass, and ethanol, as well as product inhibition by the microorganism, including the substrate inhibition constant. Model B describes the kinetic modeling of the ethanol production, process considering the inhibitory effect of the substrate[6]; additionally, it also includes cell growth based on Monod kinetics.[6] The difference between the equations is that Model B considers a maximum concentration of ethanol at which the process is inhibited. For model A, the terms $Y_{X/S}$ and $Y_{E/S}$ are represented by Eqs. (1) and (2), respectively.[5]

$$Y_{X/S} = m_{X/S}S_a + b_{X/S} \quad (1)$$

$$Y_{E/X} = m_{E/X}S_a + b_{E/X} \quad (2)$$

Table 1 Kinetic models for the alcoholic fermentation process.

Concentrations	Model A	Model B
Substrate	$\frac{dS}{dt} = -\frac{\mu}{Y_{X/S}} Xe^{-\frac{K_L S_a}{t}}$	$\frac{dS}{dt} = -\frac{dX/dt}{Y_{X/S}} - m_X X$
Cells	$\frac{dX}{dt} = X\mu e^{-\frac{K_L S_a}{t}}$	$\frac{dX}{dt} = \mu_{max} \frac{S}{S + K_S + \left(S^2/K_i\right)} \left(1 - \frac{P}{P_{max}}\right)^n X$
Ethanol	$\frac{dE}{dt} = \left(Y_{E/S}\mu X + \gamma X\right) e^{-\frac{K_L S_a}{t}}$	$\frac{dE}{dt} = \alpha \frac{dX}{dt} + \beta X$
Cell Growth	$\mu = \frac{\mu_{max} S}{S + K_S + K_i S^2}$	$\mu = \mu_{max} + \frac{\mu_{max}}{K_S} S$

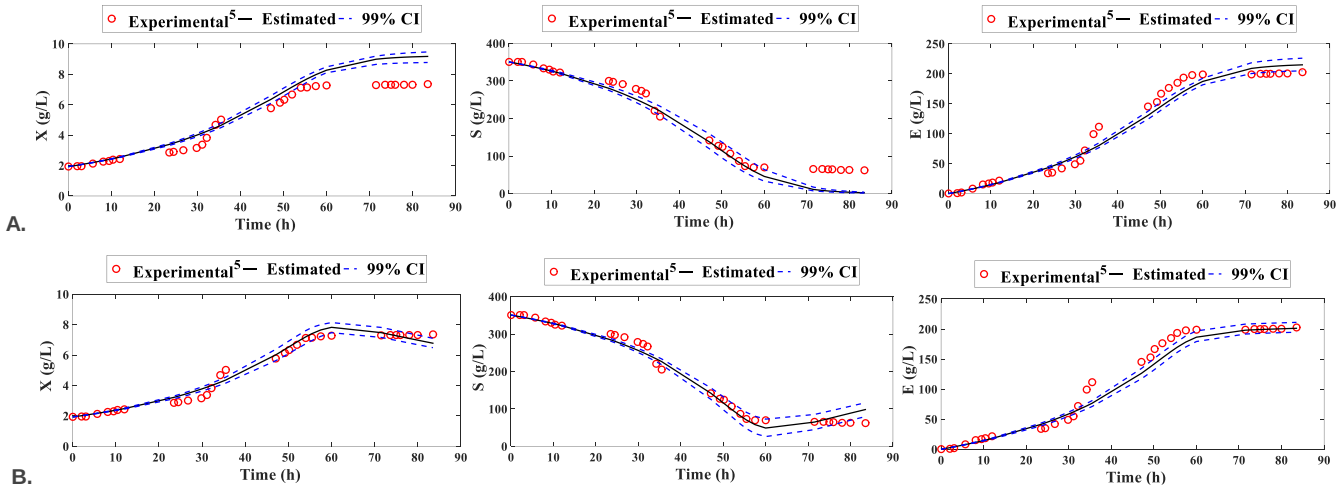
Description: From models A and B, the following parameters were estimated: μ_{max}(h^{-1}), which represents the maximum specific cell growth rate; K_i (g/L), the inhibition constant; K_S (g/L), the saturation constant; K_L (Lh/g), the lag phase constant; μ (h^{-1}), the specific growth rate; $Y_{X/S}$ (dimensionless), the interaction between biomass and substrate; $Y_{E/S}$ (dimensionless), the interaction between ethanol and substrate; P_{max} (g/L), the maximum product concentration at which cell growth begins to be inhibited; S (g/L), the substrate concentration; X (g/L), the biomass concentration; E (g/L), the ethanol concentration; γ (h^{-1}), the kinetic constant of ethanol production; S_a (g/L), the sum of added sugars; n, a parameter related to product inhibition and t (h), time. For substrate consumption, m_X represent the cell maintenance coefficient. In ethanol formation, α and β denote the product formation constants of the Luedeking-Piret equation associated and not associated with cell growth, respectively.

The MCMC method was used to estimate the optimal process parameters. This statistical technique, based on Bayes Theorem[7,10], is characterized by its effectiveness in obtaining significant sample estimates.[7] The comparison between estimated and experimental measurements was carried out using objective metrics such as the Akaike Information Criterion and the Bayesian Information Criterion, which determine the most appropriate model considering both fit and complexity.[8] Additionally, rRMSE was used to provide a direct evaluation of the model's fit quality to experimental data, regardless of the number of model parameters, complementing AIC and BIC-based analyses.[9]

3 RESULTS & DISCUSSION

Figure 1 shows the simulation results for biomass and ethanol production, as well as substrate consumption in terms of mean and 99% credible interval (CI), compared to experimental measurements in the literature.[5]

Figure 1 Comparison of estimated concentrations and experimental measurements by Mendoza (A)[5] and Farias (B)[6].



In Figure 1, it is possible to observe that there was a good fit between the estimated concentrations and the experimental measurements. The stationary phase of microbial growth was reached at approximately 55 hours and the maximum substrate concentration is around 70 hours. In these cases, only model B presented a good fit to represent the stationary phase and substrate consumption, which is evident from the fit of the graph to the experimental data. Table 2 presents the estimated parameter values for each model. It is possible to observe that model A, with μ of 0.6 h^{-1} and Ki of 0.006 g/L, indicates rapid cell growth but low substrate sensitivity, which may limit performance at high substrate concentrations.[11] Model B, with μ_{max} of 0.232 h^{-1}, Ki of 24.4 g/L, and P_{max} of 56 g/L, is more tolerant to the substrate, proving to be robust and efficient for ethanol production even at high sugar concentrations.[12]

Table 2 Estimated parameters of models A and B.

Model A	Value	Unit	Model B	Value	Unit
μ_{max}	0.6	h^{-1}	μ_{max}	0.232	h^{-1}
$m_{X/S}$	1.81	-	K_S	1.67	g/L
$b_{X/S}$	0.04	-	K_i	24.4	g/L
$m_{E/X}$	0.13	-	P_{max}	56	g/L
$b_{E/X}$	18.58	-	m_x	0.027	-
γ	0.006	h^{-1}	Y_x	0.104	-
K_S	2.58	g/L	α	5.71	-
K_i	0.006	g/L	β	0.16	-
K_L	8.41	g/L	n	4.5	-
S_a*	1.07	g/L			

Table 2 compares models A and B based on the analysis of cell, substrate, and product concentrations. Model B showed lower rRMSE, AIC, and BIC values for all state variables, indicating superior performance in predicting biomass production, product, and substrate consumption values. Although the metrics for model B presented smaller errors, model A also simulated the process satisfactorily and can be improved with future adjustments.

Table 3 Comparison of AIC, BIC, and rRMSE values for models A and B.

Model	rRMSE (%)			AIC			BIC		
	Cell	Substate	Product	Cell	Substate	Product	Cell	Substate	Product
A	11.78	22.93	26.13	52.32	39.61	33.98	96.78	84.06	78.43
B	5.20	7.89	5.55	10.49	-2.34	-0.79	23.39	10.56	12.11

4 CONCLUSION

In this study, two mathematical models were evaluated to represent the kinetics of alcoholic fermentation using Amazonian fruits. The results of the MCMC simulations and the selection metrics indicated that the model that considered inhibition by both the substrate and the product presented a superior fit, with an rRMSE of less than 10%, compared to the model that considered only substrate inhibition, demonstrating its ability to predict the essential parameters to optimize ethanol production. This precision is important to ensure efficiency and promote better predictions of process behavior.

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