Mechanistic Modelling of pH Influence on Product Spectrum from Sugarcane Vinasse

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Sugarcane vinasse, a major by-product of the bioethanol industry, represents an important biomass source for bioenergy and bio-based products generation through acidogenic fermentation. Under controlled anaerobic conditions, vinasse can be converted into hydrogen and volatile fatty acids (VFAs), such as lactic, acetic, butyric and propionic acids, but the distribution of these products depends strongly on operational parameters—particularly pH. Mathematical modeling plays a key role in understanding and optimizing these systems. The Anaerobic Digestion Model No. 1 (ADM1) is widely used to describe anaerobic processes, and its adaptations have been applied to represent incomplete fermentation. In such frameworks, stoichiometric yields are often treated as fixed parameters, despite evidence that pH profoundly influences metabolic pathways, product formation, and the associated thermodynamic landscape.

This study investigates how different initial pH conditions change the stoichiometric yields associated with vinasse acidogenesis. Thermodynamic analysis based on Gibbs free energy is integrated into the modeling approach to identify which metabolic routes are energetically favored under each condition. Batch experiments were performed at five pH levels (5.0, 6.0, 7.0, 8.8, and 10.0) using 250 mL anaerobic reactors operated at 40 °C with sugarcane vinasse (10 g $COD \cdot L^{-1}$) and inoculum derived from natural vinasse fermentation. Throughout 12 days of incubation, pH, chemical oxygen demand, carbohydrates, VFAs, and solvent concentrations were monitored to characterize system performance.

An ADM1-based model adapted for sugarcane vinasse fermentation was calibrated to estimate the pH-dependent stoichiometric yields while maintaining all kinetic parameters constant. Parameter estimation was performed using a Markov Chain Monte Carlo approach. The simulations successfully reproduced the pH-driven shifts observed experimentally: low pH favored hydrogen production, while higher pH promoted butyric acid and acetic acid formation. These trends aligned with Gibbs free energy calculations, which indicated more negative values for the pathways leading to these metabolites.

Overall, combining thermodynamic analysis with ADM1-based modeling provides a mechanistic explanation for pH-dependent metabolic shifts and offers a robust framework for optimizing biohydrogen and VFA production from sugarcane vinasse.