Gompertz Equation's First and Second Derivatives for Kinetics Analysis of Batch Dark Fermentation on Bio-Hydrogen Production

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Abstract—Based on results of different works carried out under the project of hydrogen and sustainable energies of the Department of Energy and the perspective shown by Bergues et al [6], concerning the presentation and interpretation of results obtained by Aleman [21], Sandoval and Yanez [10] and Morales and Argueta [22]; it is established a rigorous method for the analysis of the results obtained using as a model the Gompertz equation, and its first and second derivatives as indicators, that focuses on dark fermentation bio-hydrogen production, from the perspective of the conversion of the product –i.e., not of reagents–, for purposes of its maximization and operation control.

Index Terms—Biohydrogen Production; Dark Fermentation; Gompertz Equation; Gompertz's Inflection Point.

I. INTRODUCTION

The amount of hydrogen obtained from the fermentative process could be quantified in terms of rate and yield. The yield is defined as the amount of hydrogen produced per amount of consumed substrate and it is expressed in H₂ mol/glucose mol. The rate of hydrogen production (RHP), is defined as the amount of H₂ (mL) produced per volume unit of the reactor (volumetric rate) or per unit of fresh biomass fed, massic base [1].

It is possible to adjust mathematically hydrogen production by dark fermentation through Gompertz equation [2], which is a model adapted to describe the cumulative progress of hydrogen production [3]. A detailed study was carried out of that model and is aimed to model the behavior of reactions for the hydrogen production using activated sludge and molasses, as a culture medium, allowing organic waste recovery [4].

Gompertz equation allows to follow the evolution of the global reaction that leads to the production of hydrogen to maximize it. In chemical reaction kinetics it is accustomed to follow the decrease of reactive species, for the case the

decay of molasses, which does not necessarily mean hydrogen production in a bioproduction system [5].

With the model, previous works made by several researchers were related to a new perspective to the interpretation of the results mentioned on references [6]–[10]. Among the parameters to study were: pH, organic load, lag time (λ_0), H₂ production rate (R_{max}); as well as H₂ production potential (H_{max}).

Once new model found, it is documented its importance on the presentation of the results using both Gompertz equation first derivative and the second derivative –through calculation methods of differentiation and respective numerical operation–, and its interpretation by chemical engineering reactor kinetics, as the experimental results were obtained in our laboratory at the Sustainable Technologies Research Group of Department of Energy.

II. MODEL DESCRIPTION

A. Gompertz equation

Previous biohydrogen researchers have used modified Gompertz equation like that on following expression (1), to describe hydrogen evolution by dark fermentation; an adapted model to describe the production rate of hydrogen production. In this approach, three model parameters –lag time, H₂ production potential, and H₂ production rate–, are adjusted to fit the Gompertz equation, as cited as back on Winsor (1932) [11], Lay (2001) [12], Wen-Hsing (2006) [13], and Bergues (2008) [6], and pH conditions, to observe their influence in the kinetics of the hydrogen production reaction.

$$H(t) = H_{max} e^{-e^{\left[\frac{R_{max} \cdot e}{H_{max}} (\lambda_0 - t) + 1\right]}} \quad (1)$$

B. Experimental Gompertz equation

While (1) represents the base of the study, it was algebraically manipulated, to get, in this work, the modified experimental Gompertz equation (2):

$$\frac{H(t)}{H_{max}} = e^{-e^{\left[R_{max} \cdot e \left(\frac{\lambda_0}{H_{max}} - \frac{t}{H_{max}}\right) + 1\right]}} \quad (2)$$

hence, a plot $\frac{H(t)}{H_{max}}$ versus $\frac{t}{H_{max}}$ will give the R_{max} and λ_0 parameters as geometrical projections like those on Fig. 1, i. e. the first term in (2), $\frac{H(t)}{H_{max}}$, basically indicates the conversion of hydrogen depending on time, and $\frac{t}{H_{max}}$,

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represents the time employed to produce a part of total hydrogen that will be theoretical produced.

It was used both terms to obtain Fig. 1, the relationship of time to the maximum production of hydrogen for abscissa axis, and the conversion of hydrogen for ordinates axis. It is important to consider for the solution of (2), the relationship $\frac{\lambda_0}{H_{max}}$ obtained from the intersection on the x-axis, at y zero level, of maximum slope line or $\frac{R_{max}}{H_{max}}$ value.

Fig. 1. Search of λ_0 and R_{max} from a geometrical projection.

The modified form of (2) may be sustained by the following reasons: it is well possible to find the parameter H_{max} by means of extended time experimentation or based on the theoretical maximum production of the dark fermentation through the stoichiometry of the reaction, as shown on (3), and/or (4) and (5), which follows.

For chemical reaction on (3), the maximum is 4 mol of H_2 , for oxidized hexose and acetic acid as a sub-product of the reaction; however, in practical experimentation, the production is lower due to biomass production and another kind of sub-products (butyrate, ethanol, propionate, and lactate).

On another hand, the U. S. Department of Energy (USDOE), recommends that economic viable hydrogen production should be 12 mole H_2 per 1 mole of glucose [14], for this reason, at present, one stage more after dark fermentation, is necessary to convert the fermentation end-subproducts in more hydrogen or in another source of energy, such as methane. Thus, in mixing cultures, there are two main paths of fermentation for hydrogen production: butyrate-acetic (4) and ethanol-acetic (5):

In both, hydrogen production paths are the same, but butyrate-acetic's is instable [15]. Conversely, ethanol-acetate fermentation appears to be more stable than that of butyrate with respect to pH control. In spite, ethanol fermentation path to hydrogen production has many

advantages but work reported is not enough due that research on this fermentation have focused on the production of ethanol as a fuel [16].

Nevertheless, it would be possible to reach 12 mole H_2 per one glucose mole by profiting of combined conditions: dark, luminous, and recirculating operations. On the research of biological reaction mechanism authors as N. Rena [17] and P. Sinha [18], show the complexity on following reagents for optimization of hydrogen production process as Fig. 2 shows.

Fig. 2. Hydrogen production process mechanism by dark fermentation (Nanqi Rena, [17]).

This difficulty in reaction control for hydrogen production enables that modified experimental Gompertz equation here proposed as a method of data searching (2), gives the aim to optimize hydrogen production process by focusing the analysis directly on the main product i.e. H_2 , and not on reactants consumption.

III. RESULTS AND DISCUSSION

Fig. 3 shows experimental data of the hydrogen production on the conditions established by Sandoval and Yanez [19], for all the set pH values, where experimental points are shown as well as the Gompertz equation path simulation, with parameters H_{max} , R_{max} and λ_0 , obtained according to QUASI NEWTON (STATISTICAL soft), numerical method (Table I).

Fig. 3 Experimental $H(t)/H_{max}$ vs $Time/H_{max}$ performance curves depending on the pH.

This figure represents a comparison between five experimental series of the different curves from batch dark anaerobic fermentation with sludge inoculum without heat-treatment for the pH 4.0 to pH 6.5, which were adjusted through modified Experimental Gompertz equation (2). With main parameters values, shown in Table I, calculated

as explained in the previous paragraph.

TABLE I. VALUES OF THE PARAMETERS OF THE GOMPERTZ EQUATION FOR ALL PH'S.

Value of pH of the curve	Parameters of the Gompertz equation		
	Value of $H_{\max}$ (mL)	Value of $R_{\max}$ (mL/h)	Value of λ_0 (h)
4.0	142.6	13.83	7.28
4.5	172.5	15.69	7.40
5.0	264.5	13.56	12.02
5.5	232.9	12.46	15.13
6.5	235.7	29.89	15.16

As pointed above in table, as a function of pH, the maximum of hydrogen production H, was reached at pH 5.0, but the value of R was maximum at 6.5 and lag time λ_0 was minimum for pH 4.0. So, it is clear that reaction rate appears to be worth to analyze, particularly, because $R_{\max}$ is the series highest, followed by pH 4.5 and, then, similar slopes for the others.

From here, it is focused that Gompertz equation first derivatives mean hydrogen production chemical kinetics and the second one means, when changing slope from +/-, the inflection point for exponential / logarithmic behavior, that is equal to say, maximum rate reactor performance (math citations inspired by Dartmouth College, US, 2017) [20].

A. Gompertz Equation First Derivative

The first derivative (Fig. 4), performed incrementally by (6), shows the equilibrium points for pH<5.0 and pH> 5.0. Being a representation of rate hydrogen production (RHP), by biological path for different pHs.

$$\frac{\Delta H}{\Delta t} = \frac{H_{n+1} - H_n}{t_{n+1} - t_n} \quad (6)$$

Positive slope tells that, as time increases $\frac{\Delta H}{\Delta t}$ also increases, whereas, negative slope tells that, as time increases $\frac{\Delta H}{\Delta t}$ decreases. Zero slope shows here that there is a local maximum at that point. Eq. (6) defines so experimental kinetics on RHP or $+r_{H_2}$.

Fig. 4. Experimental RHP depending on the total time of reaction.

Here, it is defined two zones pH<5.0 and pH>5.0 with a maximum in pH=6.5.

pH	$\frac{\Delta H}{\Delta t}_{\max}$ (mL/h)	At Time (h)
4.0	13.83	9-12
4.5	15.69	9-12
5.0	13.56	~21
5.5	12.46	21-24
6.5	29.89	18-21

From the analysis of Fig. 4 and Table II, maximum experimental RHP is at pH 6.5, with a maximum of 29.89 mL/hour, followed by pH of 4.5, 4.0, 5.0 y 5.5, with 15.69, 13.83, 13.56 and 12.46 mL/hour values, respectively.

The use of the first derivative of the model equation allows to obtain the maximum speed of production of the bio-hydrogen for each one of the pH explored. As opposed to the geometric or numerical calculation also carried out, this method is derived from the direct experimentation and therefore allows to verify, in real time, the behavior of the production whatever the actual conditions in the respective bioreactor. This feature allows immediate correction to the best possible conditions and provides the basis for efficient process control.

B. Gompertz Equation First Derivative Gompertz Equation Second Derivative or Inflection point

The numerical second derivative is get by (7), it allows to get the total time, point of inflection ($\lambda_0 + \Delta t_{\pm}$), to maximum RHP. It is recalled here that the graph of a function $f(x)$ has an inflection point at time x if the graph of the function goes from concave up to concave down at that point, as shown in Fig. 5.

$$\frac{d^2x}{dt^2} \approx \frac{x_{(t+1)} - 2x_{(t)} + x_{(t-1)}}{\Delta t^2} \quad (7)$$

Fig. 5. Inflection for the kinetic of the reaction +/-, 2nd derivative of experimental values. Two zones are defined: pH<5.0 and pH>5.0.

Fig. 5 shows the inflection points for different pH's, all the samples have a change of sign from plus to minus (+ to -), in the ordinate axis y level 0; the curve of pH 6.5 shows the highest amplitude of the crest and the valley. Table III describes these results:

TABLE III. INFLECTION POINTS AT Y-AXIS, 0 LEVEL, FOR MAXIMA RHP / pH

pH	$\frac{\Delta^2 H}{\Delta t^2} = \pm 0$ at time (h, a +/-)
4.0	11.34
4.5	11.64
5.0	22.46
5.5	25.27
6.5	21.53

TABLE II. MAXIMUM RATE OF HYDROGEN PRODUCTION FOR PH SERIES

The inflection point by the second derivative of Gompertz equation exemplifies the end of the concavity and the beginning of the convexity of the curve and, also, displays the medium point of the exponential growth, the exponential zone. At this point the reaction rate is maximum as well as the average of hydrogen production, therefore, it should be important to keep this points in target operation as a pH function and time optimization.

Thus, the second derivative of the Gompertz equation allows to assure the exact moment of the convergence of results, certainly it defines at the same time the maximum speed of production of hydrogen as the exact moment of arrival to the change of the curve, from exponential to logarithmic or concavity / convexity inflection point; this allows to modify the bioreactor operation mood, from batch to continuous, at maximal response conditions.

C. Gompertz classical equation analysis

Finally, if it is analyzed the point of inflection, for all experimental Gompertz equation curves, it is noticed (Fig. 6), that the point of the end of concavity and the beginning of the convexity converges at same y-axis place for all curves, so it could be permitted, for the reasons of better operation and control to begin with a starting pH and, then, changing to a faster one as the hydrogen production process carries on –i. e. starting at pH 4 – 4.5 and changing to pH 6.5 at inflection point.

Fig. 6. $H/H_{\max} = +r_{H_2}$ versus time of the reaction minus total time p/inflection $(\lambda_0 + \Delta t +/-) / H_{\max}$.

This figure has sorted out from data on Fig. 3, taking into consideration the point where the concavity ends and the convexity of each one of the pH curve paths start; so we obtain this set of curves (Fig. 6), which is a classical graph of Gompertz equation for all results.

The following Table IV, takes all values from Gompertz's first and second derivatives analysis just like for doing the final point.

TABLE IV. GOMPERTZ'S FIRST AND SECOND DERIVATIVES COMPARISON

pH	First derivative Rate (mL/h)	Second derivative Time (h)
4.0	13.83	11.34
4.5	15.69	11.64
5.0	13.56	22.46
5.5	12.46	25.27
6.5	29.89	21.53

In Table IV (as Fig. 6, suggests), it can be observed that if the starting of the reaction is favored by an acid pH, as in

the case of the bio-production of hydrogen from the dark fermentation of the molasses, the best line operation of the bioreactor will be that which reaches the point of inflection as soon as possible (time to reach maximum rate 11.34 and 11.64 h, for pH 4.0 and 4.5), and then modify the pH to the next best, pH 6.5 (to maximize RHP of 29.89 mL/h rate), for the handled situation in this study.

IV. CONCLUSIONS

The study of mathematical model that could give scientific sustenance to the biotechnology process for the hydrogen production is equivalent to the research for the optimal combination of the process variables that could maximize its production; normally, the products of chemical and biotechnological reactions are evaluated from the disappearance of the reagents, which in the case of complex reactions-as in the case of the bio-production of hydrogen, are not easy for optimization.

Therefore, it was modeled through a modified experimental Gompertz equation the behavior of the hydrogen production from composite inoculate of activated sludge and glucose, from molasses, connecting different studies previously made by Bergues [6], Aleman [21]; Sandoval [10], and others situations like that of Morales [22], on continuous application. Thus, we employed the experimentally modified Gompertz equation to notice the influence of the pH on the behavior of biological hydrogen production; it was made a study more exhaustive of the parameters ($H_{\max}$, λ_0 , $R_{\max}$), that characterized it.

Through the application of numerical calculation to the experimental results, it was recorded the importance of both; first derivative, which describes the hydrogen production kinetics and second derivative that allows noticing inflection points between concavity and convexity regions with maximal kinetics rate hydrogen production, with the aim of enhancing and optimize the operation and consequently, the bio-hydrogen production process control operation and vessel design. The final analysis of Gompertz model equation bring opportunity for designing critical path for bioreactor operation and safe control.

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