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Citation: AIP Conference Proceedings **1775**, 030079 (2016); doi: 10.1063/1.4965199
View online: http://dx.doi.org/10.1063/1.4965199
View Table of Contents: http://aip.scitation.org/toc/apc/1775/1
Published by the American Institute of Physics

Analysis and Extension of Gompertz-Type and Monod-Type Equations for Estimation of Design Parameters from Batch Anaerobic Digestion Experiments

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Abstract. Gompertz equation, particularly its modified form is widely used to describe growth and product formation data for various types of dynamically biological systems. In anaerobic digestion, it becomes a fashion to use it as an empirical representation of biogas/methane/hydrogen accumulation data although its physical meaning is sometimes obscured. This work outlines the use of Gompertz-type model and its related extensions in more systematic and meaningful manners. Firstly these time-derivative rate equations were reformulated using unstructured reasoning which considered the effects of growth associated product formation and two forms of time-rate derivatives: Schnute postulate and Power law extension. The analysis revealed that this class of models predict non-zero product formation at zero time. Thus we propose their corrected forms to be used for meaningful parameter estimation. Secondly, we compiled currently available solutions for most popular Monod-type models for batch digestion. Some solutions were derived in this article and put in convenient forms for "Gompertz-Monod matching". Finally, we attempt to draw relations between time-derivative-type models (Gompertz model and its extensions) with substrate-limiting-type models (Monod, Andrews, Haldane, Contois and Grue 2-order models) and establish criteria to justify the validity of theses models in specific cases. The results in our analysis suggested that much more insightful mechanistic understanding of anaerobic digestion could be achieved by combined and systematic analysis of those experimental data using the best model from extended Gompertz models with the best one from substrate limiting type

INTRODUCTION

In determining biochemical methane potential (BMP), which is widely used to evaluate the anaerobic biodegradability of organic waste or wastewater [1, 2, 4-8], batch anaerobic digestion experiments are carried out and essential data, particularly accumulated biogas produced versus time, are collected. It is customary to use some form of kinetic or empirical models to describe the data and estimate the BMP from models' parameters. Recently, a modified form of Gompertz equation has been used very often for the task. It has the following form.

$$P = P_\infty \exp\left(-\exp\left(\left(R_m \cdot e / P_\infty\right)\left(\lambda - t\right)+1\right)\right) \tag{1}$$

Where P, P_∞ are accumulated methane at time t and its long time values respectively. R_m is maximum specific methane production rate (ml/d), λ is lag phase period (d) and e is 2.178282. This is equivalent to the original form of Gompertz equation.

$$P = P_\infty \exp\left(-\left(r_0/\alpha\right)\exp\left(-\alpha t\right)\right) \tag{2}$$

Where r_0 and α are parameters in Gompertz equation which directly related to R_m and λ in equation (1) [3].

Gompertz equations has been popular because of a few reasons. Firstly it requires only the accumulated biogas data. Secondly, it provides easily interpretable parameters, namely: the biogas yield potential P_∞, the maximum biogas production rate R_m, and the duration of lag phase λ. Thirdly, in general it can be adjusted to fit

International Conference on Mathematics, Engineering and Industrial Applications 2016 (ICoMEIA2016)
AIP Conf. Proc. 1775, 030079-1–030079-8; doi: 10.1063/1.4965199
Published by AIP Publishing. 978-0-7354-1433-4/$30.00

accumulated data so well. However the problem with Gompertz model is that it was formulated for describing the growth of tumor cells or later for the microbial growth without direct relation to biogas or other kinds of accumulated product data, thus lacking a sound derivation. However, because it seems to fit the biogas/CH_4/H_2-time data for batch anaerobic digestion very well, it is now widely used as an empirical model for estimating and comparing BMP as well as the rate of biogas production.

Monod-type models, on the other hand, were derived based on mechanistic considerations similar to Mechaelis-Menten-type models which is widely used in enzyme kinetic studies. In fact this group of model has been well accepted and established in microbial kinetics and form a core basis of the Anaerobic Digestion Model no. 1 (ADM1) which considered a standard model for anaerobic digestion. They offer more insight and suitable for process-design proposes.

However, a major drawback of Monod-type models, even in a simplest form, is that their analytical solutions are implicit in term of substrate concentration S and biomass concentration X which make them difficult to apply and complicate the parameter estimation. The non-linearity nature of the solutions also requires iterative methods to reach the minimum error sum square. The convergence is guaranty only with accurate initial estimates. [11]

Recently, Alt and Markov [12] proposed alternatives to Monod-type models using an analogy with Henri-Michaelis-Menten enzyme kinetics. The model formulation give similar result as the corresponding Monod's counterparts with less mathematical complexity. However, these models are not yet widely used and normally require numerical methods except in a simple cases where analytical solutions are available.

This work focuses on the reformulation of Gompertz model as well as its more generalized forms namely Schnute and Power law rate model in the context of biogas production. We also attempted to bridge the Gompertz-type models on one side and a Monod-type models on the other side. By combining this two approaches together we aim to extract maximum benefits and meaning from both approaches in describing biogas production data, so paving the way for the researchers in designing biogas production experiments which result in not only easily interpretive parameters but also with more mechanistic meaning offered by Monod-type models.

MODEL DEVELOPMENT AND ANALYSIS

Reformulation and Extending the Gompertz-type Models

Schnute's postulates and the unified equation for product formation in batch digestion

Schnute [9] proposed an accelerated growth model for explaining the growth of fish population by imposing the following assumptions.

1. The relative growth rate, r, of a population with density, N, was given by
$$(1/N)(dN/dt)=r \tag{3}$$
2. The the derivative of relative growth rate, dr/dt changes linearly with time in the following form,
$$(1/r)(dr/dt)=-(\alpha+\beta r) \tag{4}$$

Here, the parameter α is a fixed changing rate of r, and α/β is the scale of relative rate change. Schnute model is actually a generalized form of a class of growth model which includes exponential model $(\alpha<0,\beta=1)$, logistic model $(\alpha>0,\beta=-1)$, Gompertz model $(\alpha>0,\beta=0)$, Richards model $(\alpha>0,\beta<0)$ and others [3].

Because Gompertz/Schnute models were developed from quite different contexts, they are not easy to interpret in a meaningful manner except being treated as empirical models to represent the biogas/biomethane/H_2 datasets. Thus, in this article we propose a new reformulation which directly based on the time rate of product formation. In addition, the resulting solutions can be applied to not only for batch anaerobic digestion experiments but also for similar classes of fermentation studies.

Assuming that the biogas generation is purely growth-associated with constant biomass and product yield coefficients $Y_{X'S}=\Delta X'/\Delta S=const$ and $Y_{PS}=\Delta P/\Delta S=const$ from Schnute's postulates, we obtain
$$dP'/dt=rP', \quad dr/dt=-r(\alpha+\beta r) \tag{5}$$
Where X', P', r, α and β are biomass and product generated (partially unobservable), the specific product forming rate, and the Schnute parameters respectively. The second part of equation (5) is readily integrated to obtain the expression for r and upon substituting it into the first expression in equation (5) we have
$$r=r_0/\left[e^{\alpha t}+(\beta r_0)(e^{\alpha t}-1)/\alpha\right], \quad dP'/dt=rP'=r_0P'/\left[e^{\alpha t}+(\beta r_0)(e^{\alpha t}-1)/\alpha\right] \tag{6}$$
After integration, the following solutions result

$$P' = P'_{\infty} e^{-\alpha t/\beta}\left(e^{\alpha t} - \gamma\right)^{1/\beta} \quad \text{where} \quad P'_0 = P'_{\infty}(1-\gamma)^{-1/\beta} \quad \text{and} \quad \gamma = \beta r_0/(\alpha + \beta r_0) \tag{7}$$

Or in a modified form as derived by Zwietering et. al. [3]

$$P' = \left(R_m(1-\beta)/\alpha\right)\left[(1 - \beta\exp(1-\beta+\alpha(\lambda - t)))/(1-\beta)\right]^{1/\beta} \tag{8}$$

However P'_0 is not observed because it exists prior to the batch experiments as a result of the microbial growth and tightly associated with the initial cell concentration X_0 (assuming no microbial death) or $P'_0 = Y'_{P'X'} X_0$. Thus equation (5) must be corrected for P'_0 That is

$$P = P' - P'_0 = P'_{\infty}\left[e^{-\alpha t/\beta}\left(e^{\alpha t} - \gamma\right)^{1/\beta} - (1-\gamma)^{1/\beta}\right] \tag{9}$$

Where P is actual observed product accumulation. It should be noticed that neither P'_0 nor $P'_{\infty}(= P_{\infty} + P'_0)$ is fully observable but it can be treated as a parameter in non-linear curve-fitting.

Gompertz Model: a Simple Analysis

Although Gompertz model is a special case of Schnute model, deriving the solution for Gompertz model from equation (7) is awkward because of the singularity when $\beta \to 0$. So we need to start a flash formulation by setting $\beta = 0$ in equation (5), which finally the following set of solutions are obtained.

$$P' = P'_{\infty}\exp\left(-(r_0/\alpha)\exp(-\alpha t)\right) \quad \text{and} \quad r = r_0\exp(-\alpha t) \tag{10}$$

Clearly, P'_0 and P'_{∞} can be found by setting $t = 0$ and $t = \infty$ in equation (10) and we obtain.

$$P'_0 = P'_{\infty}\exp\left(-r_0/\alpha\right) \quad \text{and} \quad P'_{\infty} = P'_0\exp\left(r_0/\alpha\right) \tag{11}$$

Or in a modified form

$$P' = P'_{\infty}\exp\left[-\exp\left((R_m \cdot e/P'_{\infty})(\lambda - t) + 1\right)\right] \tag{12}$$

Where P', P'_{∞} are accumulated product at time t and its long time values respectively. R_m is maximum specific product formation rate (ml/d), λ is lag phase period and e is 2.178282. It must be emphasized that P', P'_{∞} are partly unobserved, strictly speaking it is not equivalent to the observed accumulated product formation P, P_{∞} but they are related through the relation $P = P' - P'_0$. Both forms are identical and

$$\lambda = [\ln(r_0/\alpha) - 1]/\alpha, \quad R_m = P'_{\infty}\left[\ln(r_0/\alpha) - 1\right]/(e\lambda) \tag{13}$$

Since both Schnute and Gompertz models are formulated and solved in a similar way, P'_0 and P'_{∞} are not directly observable experimentally as discussed previously. In practice the corrected forms suitable for fitting experimental product formation from biogas/biomethane/H_2 batch data are.

$$P = P' - P'_0 = P'_{\infty}\left[\exp\left(-\exp\left((R_m \cdot e)(\lambda - t)/P_{\infty} + 1\right)\right) - \exp\left(-\exp\left((R_m\lambda \cdot e)/P'_{\infty} + 1\right)\right)\right] \tag{14}$$

or based on the original form.

$$P = P' - P'_0 = P'_{\infty}\left[\exp\left(-(r_0/\alpha)\exp(-\alpha t)\right) - \exp\left(-r_0/\alpha\right)\right] \tag{15}$$

In comparison, and with strict correctness, it is recommended to do curve-fitting using equation (15) to estimate r_0 and $P_1 = 0.5P_{\infty}$ Then λ and R_m are calculated from equation (13). Until currently the normal practice is to ignore P'_0 and most researchers use Gompertz model without any correction or perhaps they were not aware of the implicit assumption of the models. The fact that both equation (10) and (12) have no explicit P'_0 in them, so it may be ignored unintentionally. However, if we are not so serious about this minor theoretical discrepancy, it is generally fine to treat Gompertz and Schnute models as empirical representation of batch data.

Power Law Extension of Gompertz Equation

One can consider Schnute model as a linear extension of Gompertz model, but it is not the only possible extension. In the following section we will explore the so-called "Power Law Extension of Gompertz Equation", which starts by the following differential equations.

$$dP'/dt = rP', \quad dr/dt = -\alpha r^{n+1} \tag{16}$$

Integrating the second equation in (16), we have

$$r = r_0\left(\alpha n_0^n t + 1\right)^{-1/n} \tag{17}$$

Substituting equation (17) into the first equation in (16), the solutions of four cases are as follow

Case 1: $n = 0$ In this case we have the Gompertz model which was discussed in previous section.

Case 2: $0 < n < 1$ We have the following solution.

$$P' = P'_0 \exp\left(\zeta\left(1-(\alpha n r_0^n t+1)^{(n-1)/n}\right)\right) \quad \text{where} \quad \zeta = r_0/[\alpha r_0^n(1-n)] \tag{18}$$

Clearly, as $t \to 0$, we have $P' \to P'_0$, and as $t \to \infty$, $P' = P'_\infty$. That is $P'_\infty = P'_0 \exp(\zeta)$

Case 3: $n=1$ we have

$$P' = P'_0 (\alpha t+1)^{1/\alpha} \tag{19}$$

In this case, $t \to 0$, we have $P' \to P'_0$, and as $t \to \infty$, $P' = \infty$. So this is not valid for batch digestion.

Case 4: $n>1$ We obtain the same solution as equation (18). However, this solution is also not valid because as $t \to \infty$, $P' = \infty$. This is not realizable because the product would increase infinitely while substrate is bounded.

Thus we can conclude the for the Power law extension of Gompertz model, the only realizable range of n for batch digestion is $0 \le n < 1$. So all subsequent development will be restricted to this range of n. Now we will turn to Monod-type model development.

Adapting Monod-type Models for Anaerobic Digestion

In this section we will derive specific solutions of some popular Monod-type models based on the recent progress of model solutions of Monod-type kinetics for batch bio-reactions as given in a few authors [12,13]. The main purpose of this section is to prepare specific solutions for Gompertz-Monod parameter matching in the subsequent sections. Only two detail developments (traditional Monod kinetics and Monod kinetics with constant microbial concentration) will be elaborated here. However, some solutions of more complicated Monod-type kinetics are derived here and summarized in Table 1 without detailed solution steps.

Traditional Monod kinetics with and without microbial death

A classical and most widely used approach in describing growth and product kinetics is due to Monod [10,11] and its various modified forms. The basic formulation, taking into account microbial death, is as follows.

$$dX'/dt = \mu X = \mu_m S X/(K_S+S) \tag{20}$$

$$dX/dt = (\mu - k_d) X = \left[\mu_m S/(K_S+S) - k_d\right] X = \left[\mu_m (S_0 Y_{PS} - P)/[(K_S+S_0) Y_{PS} - P] - k_d\right] X \tag{21}$$

Here prime notation in X' denotes the total accumulated microbial growth assuming no death. μ_m, μ are maximum and general specific growth rate, k_d is specific death rate and K_S is the saturation constant. If we assume that all yield coefficients are constant. Using the definitions $Y_{PS} = \Delta P/\Delta S$, $Y_{X'S} = \Delta X'/\Delta S$, $Y_{PX'} = \Delta P/\Delta X = Y_{PS}/Y_{X'S}$, and noting that $P'_0/Y_{PS} = X'_0/Y_{X'S}$, the rate changes of substrate and product can be written as follows

$$dS/dt = -(1/Y_{X'S})(dX'/dt) = -(\mu/Y_{X'S}) X = -(1/Y_{X'S}) \mu_m S X/(K_S+S) \tag{22}$$

and

$$\frac{dP}{dt} = -Y_{PS}\frac{dS}{dt} = Y_{PX'}\mu X = Y_{PX'}\frac{\mu_m S}{K_S+S} X = \frac{Y_{PS}}{Y_{X'S}}\frac{\mu_m (P_\infty - P)}{K_S Y_{PS} + P_\infty - P} X \tag{23}$$

In general $X' \neq X$ and X must be found as a function of S by the following integral.

$$dX/dS = Y_{X'S}\left(k_d/\mu - 1\right) \;\rightarrow\; \int_{X_0}^{X} dX = \int_{S_0}^{S} Y_{X'S}\left[(k_d/\mu_m)(K_S+S)/S - 1\right] dS \tag{24}$$

Or sometimes it is more convenient to find the X as a function of P

$$\frac{dP}{dS} = \frac{Y_{X'S}}{Y_{PS}}\left(1 - \frac{k_d}{\mu}\right) \;\rightarrow\; \int_{X_0}^{X} dX = \int_0^P \frac{Y_{X'S}}{Y_{PS}}\left(1 - \frac{k_d}{\mu_m}\frac{K_S Y_{PS} + P_\infty - P}{P_\infty - P}\right) dP \tag{25}$$

The result is the cell biomass X as a function of a limiting substrate concentration S or product P

$$X(S) = X_0 + (Y_{X'S}/\mu_m)\left[k_d K_S \ln(S/S_0) - (\mu_m - k_d)(S - S_0)\right] \tag{26}$$

or

$$X(P) = X_0 + (Y_{X'S}/\mu_m)\left[k_d K_s \ln[(P_\infty - P)/P_\infty] + (\mu_m - k_d)(P/Y_{PS})\right] \tag{27}$$

Until now there is no explicit solution for S and X in term of time t given as a solution of equation (21), (22) and (23). However in simple cases, closed-formed implicit solution (or explicit in term of t) can be found by the following integration after substituting $X(S)$ and $X(P)$ from equation (26) and (27) into (28) to obtain

$$t = \int_{S_0}^{S} \frac{Y_{X'S}}{\mu_m}\left(\frac{K_S}{S}+1\right)\frac{1}{X(S)} dS = \int_0^P \frac{Y_{X'S}}{Y_{PS}\mu_m}\left(\frac{K_S Y_{PS}}{P_\infty - P}+1\right)\frac{1}{X(P)} dP \tag{28}$$

In general this requires numerical integration except some simple cases of which a few of them are presented in Table 1. Solutions of Andrew and Heldane kinetics in terms of S were obtained from Alt and Morkov [12] whereas the rests are derived or extended here.

Andrew and Heldane equations are two forms of Monod-type kinetics which take substrate inhibition into consideration. Other more complicated forms or those with death term are not considered here and numerical methods are generally more appropriate for those cases.

Monod-type kinetics with constant cell density

In the determination of BMP, if the cell density is high enough such that occurs in the upflow anaerobic sludge blanket reactor (UASB), the cell biomass may appear approximately constant during the anaerobic process $(dX/dt=0,\ X=X_0)$. Assuming constant biomass yield coefficient and product yield coefficients, we have

$$\frac{dS}{dt}=-\frac{1}{Y_{XS}}\mu X_0=-\frac{\mu_m X_0}{Y_{XS}}\frac{S}{K_S+S}=-K_1\frac{S}{K_S+S}\quad\text{where}\quad K_1=\frac{\mu_m X_0}{Y_{XS}}=\frac{\mu_m P'_0}{Y_{PS}} \tag{29}$$

Integrating equation (28), after substituting $S=S_0-P/Y_{PS}$, $P_\infty=S_0Y_{PS}$, $X_0/Y_{XS}=P'_0/Y_{PS}$ we obtain

$$t=(1/K_1)\left[K_S\ln(S_0/S)+S_0-S\right]=(1/K_1)\left[K_S\ln(P_\infty/(P_\infty-P))+P/Y_{PS}\right] \tag{30}$$

Or in explicit forms for S and P

$$S=K_S W\left((S_0/K_S)\exp\left((1/K_S)(-K_1t+S_0)\right)\right) \tag{31}$$

and

$$P=P_\infty-K_SY_{PS}W\left[\left[P_\infty/(K_SY_{PS})\right]\exp\left(-(1/K_S)(K_1t-P_\infty/Y_{PS})\right)\right] \tag{32}$$

Here W(t) is Lambert W function. Notice that if biomass changes with time we can not find explicit solution for S and P as a function of t. Even the biomass is constant with time, only simple cases that explicit solution can be found. For convenient, all solutions in Table 1 were formed in such a way that either S or P is used as independent variable for each solution.

TABLE 1 (Cont). solutions of popular Monod-type models with no microbial death expressed in terms of S and P.

Kinetic functions	Solutions
Any model with constant yield coefficients and no microbial death	$X=X_0+Y_{X'S}(S_0-S)=X_0+(Y_{X'S}/Y_{PS})P,\ S=S_0-\frac{P}{Y_{PS}},S_0=\frac{P_\infty}{Y_{PS}},\ Y_{X'S}=Y_{XS}$ (33) $P=Y_{PS}(S_0-S),\ C=\frac{X_0}{Y_{X'S}}+S_0=\frac{X_0}{Y_{X'S}}+\frac{P_\infty}{Y_{PS}}=\frac{P'_0+P_\infty}{Y_{PS}}=\frac{P'_\infty}{Y_{PS}}\quad\frac{X_0}{Y_{XS}}=\frac{P'_0}{Y_{PS}}$ (34)
Monod kinetics $\mu=\mu_m\frac{S}{K_s+S}$	$t=\frac{1}{\mu_m}\left[\frac{K_S}{C}\ln\left(\frac{S_0(C-S)}{S(C-S_0)}\right)+\ln\left(\frac{C-S}{C-S_0}\right)\right]=\frac{1}{\mu_m}\left[\frac{K_sY_{PS}}{P'_\infty}\ln\left(\frac{P_\infty}{P_\infty-P}\frac{P'_0+P}{P'_0}\right)+\ln\left(\frac{P'_0+P}{P'_0}\right)\right]$ (35) *Constant biomass* $t=\frac{Y_{XS}}{\mu_mX_0}\left[K_S\ln\left(\frac{S_0}{S}\right)+S_0-S\right]=\frac{Y_{PS}}{\mu_mP'_0}\left[K_S\ln\left(\frac{P_\infty}{P_\infty-P}\right)+\frac{P}{Y_{PS}}\right]$ W is Lambert W function (36) $S=K_SW\left(\frac{S_0}{K_S}\exp\left(\frac{1}{K_S}(-K_1t+S_0)\right)\right),\ P=P_\infty-K_SY_{PS}W\left(\frac{P_\infty}{K_SY_{PS}}\exp\left(-\frac{1}{K_S}(K_1t-\frac{P_\infty}{Y_{PS}})\right)\right)$ (37)
Andrew kinetics $\mu=\mu_m\frac{S}{K_S+S+S^2/K_I}$	$t=\frac{1}{\mu_m}\left[\frac{K_S}{C}\ln\left(\frac{S_0(C-S)}{S(C-S_0)}\right)+\left(1+\frac{C}{K_I}\right)\ln\left(\frac{C-S}{C-S_0}\right)+\frac{1}{K_I}(S-S_0)\right]$ (38) $t=\frac{1}{\mu_m}\left[\frac{K_sY_{PS}}{P'_\infty}\ln\left(\frac{P_\infty}{P_\infty-P}\frac{P'_0+P}{P'_0}\right)+\left(1+\frac{P'_\infty}{K_IY_{PS}}\right)\ln\left(\frac{P'_0+P}{P'_0}\right)-\frac{P}{K_IY_{PS}}\right]$ (39) *Constant biomass* $t=\frac{Y_{XS}}{\mu_mX_0}\left[K_S\ln\left(\frac{S_0}{S}\right)+\frac{(S_0^2-S^2)}{2K_I}+S_0-S\right]=\frac{Y_{PS}}{\mu_mP'_0}\left[K_S\ln\left(\frac{P_\infty}{P_\infty-P}\right)-\frac{P^2-P_\infty P}{2K_IY_{PS}^2}+\frac{P}{Y_{PS}}\right]$ (40)
Heldane kinetics $\mu=\frac{\mu_mS}{(K_S+S)(1+S/K_I)}$	$t=\frac{1}{\mu_m}\left[\frac{K_S}{C}\ln\left(\frac{S_0(C-S)}{S(C-S_0)}\right)+\left(1+\frac{C+K_S}{K_I}\right)\ln\left(\frac{C-S}{C-S_0}\right)+\frac{1}{K_I}(S-S_0)\right]$, (41) $t=\frac{1}{\mu_m}\left[\frac{K_sY_{PS}}{P'_\infty}\ln\left(\frac{P_\infty}{P_\infty+P}\frac{P'_0+P}{P'_0}\right)+\left(1+\frac{P'_\infty}{K_IY_{PS}}+\frac{K_S}{K_I}\right)\ln\left(\frac{P'_0+P}{P'_0}\right)-\frac{P}{K_IY_{PS}}\right]$ (42)

TABLE 1 (Cont). solutions of popular Monod-type models with no microbial death expressed in terms of S and P.

Kinetic functions	Solutions
	Constant biomass $t=\frac{Y_{XS}}{\mu_m X_0}\left[K_S\ln\left(\frac{S_0}{S}\right)+\frac{(S_0^2-S^2)}{2K_I}+\left(1+\frac{K_S}{K_I}\right)(S_0-S)\right]=\frac{Y_{PS}}{\mu_m P'_0}\left[K_S\ln\left(\frac{P_\infty}{P_\infty-P}\right)-\frac{P^2-P_\infty P}{2K_I Y_{PS}^2}+\left(1+\frac{K_S}{K_I}\right)\frac{P}{Y_{PS}}\right]$ (43)
Contois kinetics $\mu=\mu_m\frac{S}{KX+S}$	$t=\frac{Y_{XS}}{\mu_m}\left[K_C\ln\left(\frac{S_0}{S}\right)+\ln\left(\frac{C-S}{C-S_0}\right)\right]=\frac{Y_{XS}}{\mu_m}\left[K_C\ln\left(\frac{P_\infty}{P_\infty-P}\right)+\ln\left(\frac{P'_0+P}{P'_0}\right)\right]$ (44) *Constant biomass* $t=\frac{Y_{XS}}{\mu_m X_0}\left(K_C X_0\ln\left(\frac{S_0}{S}\right)+S_0-S\right)=\frac{Y_{PS}}{\mu_m P'_0}\left(K_C X_0\ln\left(\frac{P_\infty}{P_\infty-P}\right)+\frac{P}{Y_{PS}}\right)$ (45) $S=S_0-\frac{P}{Y_{PS}}=K_C X_0\ W\left(\frac{S_0}{K_C X_0}\exp\left(\frac{S_0 Y_{XS}-X_0\mu_m t}{K_C X_0 Y_{XS}}\right)\right)$ W is Lambert W function (46)
Grau 2-order model $-\frac{dS}{dt}=k_S X\left(\frac{S}{S_0}\right)^n$	$t=\frac{S_0^2}{K_S C}\left(\frac{1}{S}-\frac{1}{S_0}+\frac{1}{C}\ln\left(\frac{S(C-S)}{S_0(C-S_0)}\right)\right)=\left(\frac{P_\infty}{Y_{PS}}\right)^2\frac{1}{K_S C}\left(\frac{Y_{PS}}{P_\infty-P}-\frac{Y_{PS}}{P_\infty}\right)+\frac{1}{C}\left(\frac{P_\infty}{P_\infty-P}\right)$ (47) *Constant biomass* $t=\frac{S_0}{K_s X_0}\left(\frac{S_0}{S}-1\right),\quad S=\frac{S_0^2}{K_s X_0 t+S_0}$ (48)

Gompertz-Monod Matching

There are many ways to convert Gompertz parameters into Monod-type parameters. One obvious choice is to equate dP/dt from Gompertz equation to Monod equation as follows.

For Gompertz model:

$$dP'/dt=d(P+P'_0)/dt=dP/dt=r_0 e^{-\alpha t}P'=r_0 e^{-\alpha t}(P+P'_0) \tag{49}$$

For Monod model without microbial death:

Using basic relations: $X(P)=X_0+P/Y_{PX}$ and $P'_0=X_0 Y_{PX}$

$$\frac{dP}{dt}=Y_{PX}\frac{\mu_m S}{K_S+S}X=\frac{\mu_m(S_0 Y_{PS}-P)}{K_s Y_{PS}+S_0 Y_{PS}-P}(X_0 Y_{PX}+P)=\frac{\mu_m(P_\infty-P)}{K_s Y_{PS}+P_\infty-P}(P'_0+P) \tag{50}$$

Equating equation (49) to (50) we have

$$r_0 e^{-\alpha t}=[\mu_m(P_\infty-P)]/[K_s Y_{PS}+P_\infty-P] \tag{51}$$

Normally, from the analysis of batch digestion data using Gompertz equation, r_0, α, S_0, Y_{PS} and P_∞ are obtained. So in equation (51) only μ_m and K_S are to be estimated. Apparently this can be done easily by using to initial condition $(t=0)$ and long-term limiting condition $(t\to\infty)$. For initial condition $t=0$, we have

$$r_0=\mu_m P_\infty/(K_s Y_{PS}+P_\infty)\quad\text{or}\quad \mu_m=(r_0/P_\infty)(K_S Y_{PS}+P_\infty) \tag{52}$$

However when applying the long-term limiting condition $(t\to\infty)$, it simply reveals that $0=0$ and no new information to be used in solving equation (51) for μ_m and K_S. To tackle this problem let us specify the time at which the product formation is that of 95% of ultimate value P_∞. That is $P=0.95P_\infty$. Then we have

$$e^{-\alpha t_{0.95}}=[0.05\mu_m P_\infty]/[K_s Y_{PS}+0.05P_\infty] \tag{53}$$

Substituting equation (52) for μ_m into (53) and solving for K_S, the following solution is obtained.

$$K_S=P_\infty(1-\exp(\alpha t_{0.95}))/(Y_{PS}(\exp(\alpha t_{0.95})-20)) \tag{54}$$

where $t_{0.95}=-(1/\alpha)\ln[(\alpha/r_0)\ln(P_\infty/P)]$ $t_{0.95}=-(1/\alpha)\ln[(\alpha/r_0)\ln(P_\infty\exp(r_0/\alpha)/(P\exp(r_0/\alpha)+P_\infty))]$ for original and modified Gompertz models and for corrected Gompertz model respectively.

Alternatively, we can write for the relation $t=-(1/\alpha)\ln[(\alpha/r_0)\ln(P_\infty/P)]$ and equation (36), that is

$$t=-(1/\alpha)\ln\left|(\alpha/r_0)\ln(P_\infty/P)\right|=(1/K_1)[K_s\ln(P_\infty/(P_\infty-P))+P/Y_{PS}] \tag{55}$$

If α, r_0, P'_0, μ_m and Y_{PS} are known and we choose to specify two matching points, say P_1 and P_2 lying between 0 and P_∞, we can solve two linear equations and obtain the K_s and K_1 from the following relations

$$K_S=\frac{t_2(P_1/Y_{PS})-t_1(P_2/Y_{PS})}{t_2\ln((P_\infty-P_1)/P_\infty)-t_1\ln((P_\infty-P_2)/P_\infty)},\qquad K_1=(1/t_1)\left[\frac{P_1}{Y_{PS}}-K_S\ln\left(\frac{P_\infty-P_1}{P_\infty}\right)\right] \tag{56}$$

In the following illustration of this matching technique (Table 2), we chose $P_1=0.5P_\infty$ and $P_2=0.99P_\infty$. This choice seems arbitrary, but it came up from the authors' experiences and it fitted satisfactory with our current data, albeit was not well optimized.

APPLICATIONS OF REFORMULATED GOMPERTZ-TYPE MODELS, MONOD-TYPE MODEL AND GOMPERTZ-MONOD MATCHING

We illustrate the application of the theoretical development in this article by using two sets of data obtained from two batches of anaerobic digestion of palm-oil-mill effluent (POME) carried out in our laboratory [14].
The batch digestion experiments used granules obtained of an industrial-scaled biogas plant. In the first experiment, the initial COD was 100,000 mg/l (14,946 mg digestible COD/l) whereas in the second one, the initial COD was 25,000 mg/l (20,825 mg digestible COD/l). This will illustrate not only show how to apply the theories for Gompertz and Monod models but also to observe the effect of substrate inhibition at high initial COD. More results, particularly the goodness of fit (by non-linear optimization technique provided in QtiPlot) for Gompertz-type models, can be found in the work published by Jijai et.al. [14]. In most case of their results, biomass concentration was approximately constant due to high cell density attached inside the granules

TABLE 2 Gompertz and Monod variables and parameters of two datasets from batch anaerobic digestion of POME

Models	Parameters	100% POME	25% POME +water
General parameters	Initial COD (gl^{-1})	100.0	25.0
	S_0 ($mg\ l^{-1}$)	14,946	20,825
	P_∞ (ml)	365.0	621.3
	Y_{PS} ($ml/(mg\ l^{-1})$)	0.0243	0.0298
Gompertz equation	r_0 (d^{-1})	1.3851	0.4120
	α (d^{-1})	0.5225	0.1280
$P=P'_\infty\exp(-(r_0/\alpha)\exp(-\alpha t))$ or	λ (d)	-0.0482	1.317
$P=P'_\infty\exp[-\exp((R_m\cdot e/P'_\infty)(\lambda-t)+1)]$	R_m ($ml\ d^{-1}$)	70.089	29.27
	$\mathbf{R^2}$	**0.9877**	**0.9906**
Corrected Gompertz equation	r_0 (d^{-1})	1.0313	0.2439
	α (d^{-1})	0.5032	0.1065
$P=P'_\infty[(-(r_0/\alpha)\exp(-\alpha t))-\exp(-r_0/\alpha)]$	P'_0 (ml)	53.90	73.31
	P'_∞ (ml)	418.5	724.8
	$\mathbf{R^2}$	**0.9937**	**0.992**
Monod kinetics	K_1 ($mg\ l^{-1}\ d^{-1}$)	5640	962
$t=\frac{Y_{PS}}{\mu_m P'_0}\left[K_S\ln\left(\frac{P_\infty}{P_\infty-P}\right)+\frac{P}{Y_{PS}}\right]$	K_S ($mg\ l^{-1}$)	9454	5570
	μ_m (d^{-1})	2.543	0.40
	$\mathbf{R^2}$	**0.9864**	**0.9924**
Monod kinetics: estimated from Gompertz-Monod matching	K_1 ($mg\ l^{-1}\ d^{-1}$)	5470	1408
	K_S ($mg\ l^{-1}$)	9452	9249
	μ_m (d^{-1})	2.466	0.58

It is not surprised that all Gompertz-type models can fit most datasets comparatively well (not shown here, please refer to Jijai et.al. [14]). It was noticed that for Gompertz and Schnute models, non-linear fitting converged much easier than that of the Power law extension although the later is more flexible because one more parameter (n) is available. However, the Power-law model required good initial guess for its parameters otherwise it did not converge and gave incorrect results. In Table 2 we show only the parameters and goodness-of-fit for Gompertz model because they will be used for our illustration. It is recommended that the corrected forms of Gompertz-type equations should be used because it has less ambiguity in the interpretation of results as well as give a reasonable estimate for P'_0.

Besides the best estimates (by non-linear regression) of Gompertz and Monod parameters for two datasets, Table 2 also presents the results of Gompertz-Monod matching technique which is quite close to the corresponding best estimates $(K_S \text{ and } \mu_m)$. This shows the potential of this new approach although more comprehensive and analytical work should be carried out before any definite conclusion can be made.

CONCLUSIONS

So far we have achieved five development tasks. Firstly, we have successfully reformulated the Schnute and Gompertz models in terms of product formation. Secondly, we have obtained the corrected solution of Schnute and Gompertz equations which take the initial states of batch digestion into consideration. Thirdly, the solution of new Power law extension of Gompertz equation is obtained with a valid range of n, $0 \le n < 1$. Fourthly, we provides implicit (and sometimes explicit) solutions of most popular Monod-type equations in terms of not only substrate concentration (S) but also in terms of product-accumulation (P). The later form of solutions provides more convenient way for parameter estimation and converting them into Monod parameters. And lastly, we showed the fundamental relationship between Gompertz and Monod kinetics which revealed a possibility of parameter-matching. That is, from experimental data encapsulated in terms of Gompertz parameters, we can convert them into Monod parameters which has more interpretive power and more useful for the purpose of design and operation of biogas plants.

In conclusion, Gompertz-type and Monod-type models can be used together to facilitate parameter estimation and obtain better mechanistic insight from batch anaerobic process. Now, there is a new approach called "***Gompertz-Monod matching***" to convert large amount of anaerobic digestion datasets into design parameters. However, it is too early to establish the best practice for this new approach and needs further investigation.

ACKNOWLEGDEMENT

The authors would like to thanks Walailak University and Ministry of Science and Technology of Thailand grant for financial support.

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