MODELING AS A TOOL FOR CONTROLING

THE PRODUCTION OF BIOFUELS: ETHANOL FROM A BIOMASS

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Abstract:

In recent years, the new trend is towards bio-fuel. One of these biofuels is ethanol (ethyl alcohol), which could be produced economically by the controlled fermentation of biomasses. The results of the alcoholic fermentation of beet sugar molasses and wheat milling residues (Akalona) were fed into a computer program. The kinetic parameters for these fermentation reactions were determined. These parameters were put into a kinetic model. Next, the model was tested, and the results obtained were compared with the experimental results of both beet molasses and Akalona. The deviation of the experimental results from the results obtained from the model was determined. An acceptable deviation of 1.2% for beet sugar molasses and 3.69% for Akalona was obtained. Thus, the present model could be a tool for chemical engineers working in fermentation processes both with respect to the control of the process and the design of the fermenter.

Keywords: *Modeling, computation, biofuel, computer program, alcoholic fermentation.*

Nomenclature:

n_s	=	Substrate utilization coefficient
p	=	Product concentration (kg/m^3)
P_0	=	Initial product concentration (kg/m^3)
P_m	=	Ethanol concentration above which cells do not grow (kg/m^3)
$P`_m$	=	Ethanol concentration above which cells do not produce ethanol (kg/m^3)
Δp	=	Concentration driving force (kg/m^3)
q_p	=	Specific ethanol production rate (g product/g cell/h)
r_s	=	Reaction rate
S	=	Substrate concentration (kg/m^3)
S_0	=	Initial substrate concentration (kg/m^3)
S_m	=	Substrate concentration calculated from the model (kg/m^3)
t	=	Time (h)
V_0	=	Maximum specific rate of ethanol production rate at zero ethanol concentration (g ethanol/g substrate/h)
X	=	Biomass concentration (kg/m^3)
α	=	Growth associated constant (g ethanol/g cell)
β	=	Non-growth associated constant (g ethanol/g cell/h)
μ	=	Specific growth rate of cells (h^{-1})
μ_o, μ_1	=	Specific growth rate of cells in the presence of ethanol (h^{-1})
μ_{max}	=	Maximum specific growth rate of cells (h^{-1})
~	=	Kinetic parameter in Bovee model

Main nomenclature for the computer program:

FOPTIM	=	Subroutine that defines the objective function
SMIN	=	Subroutine that finds the minimum value for the objective function

1. Introduction:

Biofuels are a wide range of fuels which are in some way derived from biomass. The term covers solid biomass, liquid fuels and various biogases [1]. Biofuels are gaining increased public and scientific attention, driven by factors such as oil price spikes, the need for increased energy security, concern over greenhouse gas emissions from fossil fuels, and government subsidies.

Bioethanol is an alcohol made by fermenting the sugar components of plant materials and it is made mostly from sugar and starch crops. With advanced technology being developed, cellulosic biomass, such as trees and grasses, are also used as feedstock for ethanol production. Ethanol can be used as a fuel for vehicles in its pure form, but it is usually used as a gasoline additive to increase octane and improve vehicle emissions. Bioethanol is widely used in the USA and in Brazil.

Biofuels provided 1.8% of the world's transport fuel in 2008. Investment into biofuels production capacity exceeded $4 billion worldwide in 2007 and is growing [2].

In the simulation of chemical and biochemical processes, the prediction of data has a dominant importance. The success or failure of this calculation depends on the use of a favorable mathematical model and upon reliable experimental data obtained in industry. Further, the optimal

automatic bioreactor control requires a mathematical model adapted to the potency of reliable sensors.

James F. Bartes, et al [3] provided a nonlinear predictive integrating temperature model for a fermentation process. The model specifies or represents relationships between attributes or variables related to the temperature of the fermentation process, including relationships between inputs to the fermentation process and resulting outputs of the fermentation process. The nonlinear predictive integrating temperature model may be based on heat balance of the fermentation process, including a balance between available cooling and current fermentation heat generation. The model variables may also include aspects or attributes of other processes or sub-processes that have bearing on or that influence operations of the fermentation process.

In biochemical processes, the mathematical model is a relationship describing the kinetic behavior which relates the biological rate of substrate consumption to substrate and product concentrations. The model has several parameters that can be estimated by fitting them to the experimental data.

The decrease in growth rate and the cessation of growth due to the depletion of substrate may be described by the relationship between μ and the residual growth limiting substrate, represented in the following equation [4]:

$$\mu = \frac{\mu_{\max} S}{k_s + S} \qquad (1)$$

k_s is numerically equal to the substrate concentration when μ is one-half μ_{max} and is a measure of the affinity of the organisms. The formation of a growth-linked product may be described by the equation:

$$dp/dt = q_p x \qquad (2)$$

$y_{p/x}$ is the yield of product in terms of substrate consumed ($y_{p/x}$ = d*p*/d*x*).

Combining the above two equations:

$$q_p = y_{p/x} \mu \qquad (3)$$

The relationship between the specific ethanol production rate and the specific growth rate of cells can be represented by the following equation [5]:

$$q_p = (\alpha\mu) + \beta \qquad (4)$$

The constants α and β are 2.2-2.9 g ethanol/g cell and 0.25-0.5 g ethanol/g cell/h, respectively. The data show that the overall good ethanol production rate was mainly contributed by the high specific growth rate.

Two other kinetic models were also proposed to describe the kinetic pattern of ethanol inhibition on the specific rates of growth and ethanol fermentation [6]:

$\mu_1/\mu_o = 1-(P/P_m)^{\alpha}$ (for growth) (5)

$v_i/v_o = 1-(p/P^{-}_m)^{\beta}$ (for ethanol production). (6)

The maximum allowable ethanol concentration above which cells do not grow was predicted to be 112 g/l. The ethanol-producing capability of the cells was completely inhibited at 115 g/l ethanol. On the other hand, there was a threshold concentration of ethanol (26 g/l) below which there was no inhibition.

At a high value of α (α > 3), the inhibitory effect of ethanol was less pronounced, the ratio μ_1/μ_0 remained almost unchanged (close to unity) even though p/p_m increased from 0 to 0.3.

This kinetic model seemed to be useful for representing the kinetics of alcohol fermentation. The model parameters (α, β, p_m and p'_m) depend on the microbial species, the physiological conditions of the micro organism and the status of the culture medium.

Four types of dependence of μ_1 on the ethanol concentration *p* are as follows:

(1) ***Linear relationship***:

$$\mu_1 = \mu_0 - k_1 p = \mu_0 (1 - p/p_m) \qquad (7)$$

where k_1 is an empirical constant.

The above relationship was found to fit the kinetics of cellulose hydrolyzate to ethanol by *Saccharomyces cerevisiae.*

(2) ***Exponential relationship***:

$$\mu_1 = \mu_o \exp(-k_2 P) \qquad (8)$$

where k_2 is an empirical constant which depends on the method of cultivation (batch or continuous) (dimension l/g).

(3) Hyperbolic relationship:

$$\mu_1 = \mu_0 \frac{1}{1 + p/k_3} \qquad (9)$$

where k_3 is a constant (g/l).

(***4) Parabolic relationship:***

$$\mu_1 = \mu_0 (1-p/p_m)^{0.5} \qquad (10)$$

or

$$\mu_1 = \mu_0 - (\alpha p/b - p) \qquad (11)$$

At similar $p\ (b - p = b)$, the relationship becomes linear.

A generalized non-linear equation is:

$$\mu_1 = \mu_0\ (1-p/p_m)^n \qquad (12)$$

From the literature

P_m = 68 *g/l, p'm* = 112 g/l, or P_m = 92.7 *g/l, p'm* = 114.5 *g/l*

The maximum specific growth rate (μ_{max}) could be calculated using experimental data for the exponential growth phase according to the definition:

$$\mu = 1/t\ \mathrm{In}[(X_i + l)/X_i] \qquad (h^{-1}) \qquad (13)$$

The values of μ_{max} were determined using linear regression analysis upon the experimental growth curves.

$$t_d = O.693/\mu_{max} \qquad (14)$$

$$Y_{x/s} = dX / - ds \qquad (15)$$

$Y_{x/s}$ = biomass yield coefficient from the sugar utilized.

$$Y_{p/s} = dp / -ds \qquad (g/g) \qquad (16)$$

$$y_{p/x} = Y_{p/s}\ / Y_{x/s} \qquad (17)$$

$y_{p/x}$ = ethanol yield coefficient with respect to biomass formed.

The values of $Y_{x/s}$ and $Y_{p/s}$ were calculated from experimental data using linear regression analysis. The conversion yield Y (% of theoretical) was calculated from the relationship:

$$Y = Y_{p/s} /0.538 \qquad (18)$$

where 0.538 is the theoretical ethanol yield coefficient for the sucrose or glucose consumed.

The productivity of fermentation was calculated from:

$$P_r = \frac{P_{\max} - P_0}{\text{time to obtain p}} (\mathrm{g}/\mathrm{l\ h}) \qquad (19)$$

A particular test [7] was performed to determine the alcoholic inhibition constant in the reaction kinetic model. It was deduced that the alcohol concentration had no substantially different effect on the metabolic activity of the immobilized cells as opposed to free ones. To evaluate the substrate utilization coefficient, n_s, experimental measurements of the amount of substrate consumed, ΔS, and ethanol produced, ΔP, in the reactor were carried out and substituted in the form:

$$-\Delta S = n_s\ \Delta P \qquad (20)$$

2. Selection of the kinetic model:

A relationship describing the kinetic behavior of alcoholic fermentation was investigated by Bovee [8] in the form:

$$r_s = dS/dt = k\ S^{\alpha}\ p^{\beta} \qquad (21)$$

Using the yield relation between product and substrate, it is possible to describe, in both batch and continuous cultures, the ethanol and sugar concentration versus time. This pattern has been successfully tested on several fermentations performed by yeasts, including *Saccharomyces Cerevisiae* used in the experimental part of the present work, and a bacterium.

This simple relationship is proposed as a tool for process control alcoholic fermentation. Parameters α and β were correlated to the activation or inhibition effects of the substrate and product. Parameter *k* increases with the initial sugar concentration.

The constraint of this model is:

$$p = -(S_o - S) + P_o \qquad (22)$$

A flexible digital computer program, SUGAR, was developed in the present work, to fit the model's parameters to the experimental data, by minimizing the following objective function which was proposed by Bovee [8].

$$Q = I / N^2 \sum_{i=1}^{N} [(S_{iexp} - S_m)^2 + (P_{iexp} - P_m)^2] \qquad (23)$$

where S_{iexp} and P_{iexp} are the experimental values of substrate and product, and S_m and P_m are the values calculated by the model. The parameters obtained can then be used for the calculations needed to design bioreactors.

3. Program "SUGAR" for kinetic calculations:

The program “SUGAR” is written in FORTRAN-77 code for the VAX II computer with a DEC version 4.5 operating system. “SUGAR” consists of the main program,

four subprograms and one minimization routine "SMIN". The flow diagram of SUGAR is shown in Fig. 1.

The input data consists of the experimental data of substrate and product concentrations, time and number of data sets. The parameters *k*, α and β are now calculated by minimizing the objective function. The substrate concentration is calculated by using the Runge - Kutta method. The input data to the program are the experimental results of N. A. Mostafa [9] and are given in Fig. 2 for one run. The output data of the program are the values of the computed parameters α, β and *k* and the calculated data and the deviation between experimental and calculated data. These outputs are given in Fig. 3.

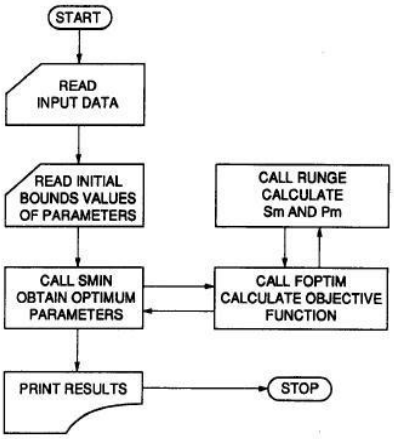

Fig. 1: Flow diagram of "SUGAR" program

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9        129.166    000.350    0.2187

003.0    125.000    001.530
024.0    100.000    007.040
048.5    046.450    019.350
096.0    012.220    022,880
120.0    010.500    026.300
123.0    007.600    023.900
144.0    004.270    022.500
147.0    004.650    025.000
168.0    004.090    022.800
```

Fig. 2: Input data to the program

4. Results and discussion:

The model so far reached is satisfactory enough when compared to other models [8]. The obtained results from the model, as shown from Figs. 4 and 5, can be evaluated as follows:

(1) For beet sugar molasses:

The model satisfies the experimental results of beet sugar molasses with a value for the standard deviation (objective function) of 1.2. This value is to be compared with the value of the Bovee model [8] which showed the range of 0-1. This difference between the two values of the deviation ranges may be due to:

(a) Bovee's work was based on pure glucose, an ideal substance for the kinetic study, whereas molasses, on which the present work is based, is a non-pure residue and is expected not to give as ideal results as given by pure glucose.

(b) In Bovee's model, the effect of the yeast produced is not taken into consideration because it is assumed to be low. On the contrary, this is the condition of the present work where the experimental results indicated that the used *S. Cerevisiae* grows rapidly, giving a high cell density compared to other yeasts. Thus, it affects the results.

(2) For Akalona hydrolyzate:

Applying the model on the results of Akalona hydrolyzate gave a deviation value of 3.69 compared to 1.2 for beet sugar molasses. This may be explained as follows:

(a) Molasses fermentation gives rise to mainly one sugar (sucrose) but Akalona hydrolyzate contains many sugars, as indicated by the analysis of Akalona hydrolyzate and by the literature [9]. This may be a reason for the deviation of the error range for Akalona hydrolyzate from its value for molasses.

(b) Akalona hydrolyzate contains strange substances due to acid hydrolysis of the cellulosic content [10,11], which have an inhibitory effect on the yeast strain (*S. Cerevisiae*). The degree of substrate inhibition was found to be higher for bagasse hydrolyzate reported for ethanol fermentation of pure sugar. This, in turn, affects the value of the kinetic parameters, thus leading to a higher value for deviation.

(c) As mentioned for beet sugar molasses, the relatively large amount of yeast produced affects the value of the standard error.

ALFA = 0.000500000024 BETA = 0.004067549016 KAPPA = 1.5000000

I	T	SE	S	DELS	PE	P	DELP
1	3.0	125.00000	125.79620	-0.79620	1.53000	1.08898	0.44302
2	24.0	100.00000	98.56013	1.43987	7.04000	7.31240	-0.27240
3	48.5	46.45000	46.79315	-0.34315	19.35000	18.67634	0.67366
4	96.0	12.22000	17.97811	-5.75811	22.88000	25.57680	-2.69680
5	120.0	10.50000	12.22000	-1.72000	26.30000	22.88000	3.42000
6	123.0	7.60000	10.50000	-2.90000	23.90000	26.30000	-2.40000
7	144.0	4.27000	7.60000	-3.33000	22.50000	23.90000	-1.40000
8	147.0	4.65000	4.27000	0.38000	25.00000	22.50000	2.50000
9	165.0	4.09000	4.65000	-0.56000	22.80000	25.00000	-2.20000

Fig. 3: Output data of the program

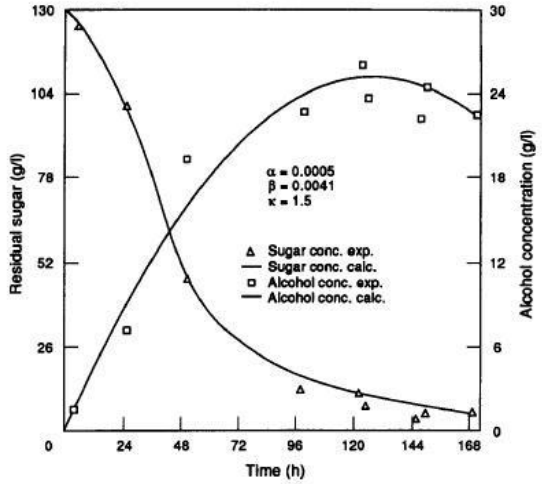

Fig. 4: Experimental and calculated results, from the model for fermentation of sugar beet molasses

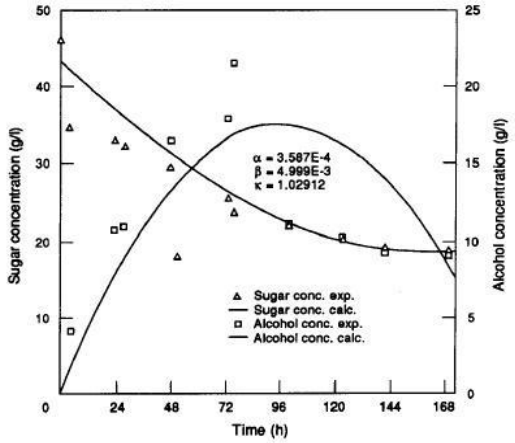

Fig. 5: Experimental and calculated results for fermentation of Akalona hydrolyzate

Conclusions:

The values of the kinetic parameters of the Bovee model [8] were determined from the experimental results [9] of alcoholic fermentation of beet sugar molasses and Akalona. The computer simulation of the model showed a value of 1.2 as standard deviation for beet sugar molasses and 3.69 for Akalona. Thus, this model with its optimized values of α, β and *k* can be used as a tool for process control alcoholic fermentation of beet sugar molasses and Akalona.

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References:

[1] Demirbas, A. (2009), "Political, economic and environmental impacts of biofuels: A review". *Applied Energy* **86**: S108–S117. doi: 10.1016/j. apenergy. 2009.04.036. edit

[2] "Towards Sustainable Production and Use of Resources: Assessing Biofuels". United Nations Environment Programme. 2009-10-16. Retrieved 2009-10-24.

[3] "Model predictive control of fermentation temperature in biofuel production", Patent 7831318 Issued on November 9, 2010. http://www.patentstorm.us/patents/7831318/description.html. **Inventors:** James F. Bartee, Maina A. Macharia, Patrick D. Noll, Michael E. Tay.

[4] P. F. Stanbury and A. Whitaker, *Principles of Fermentation Technology*, pp. 11-14, Pergamon Press, Oxford (1984).

[5] B. S. Fang; H. Y. Fang; C. S. Wu and C. T. Pan, *Biotechnol. Bioengng Syrup.*, 13, 464 (1983).

[6] J. H. Luong, *Biotechnol. Bioengng*, 27, 280 (1985).

[7] A. Gianetto; V. Speochia and G. Genon, *Chem. Engng Commun.*, *23*, 215 (1983).

[8] J. P. Bovee; P. Strehaiano; G. Goma and Y. Sevely, *Bioetechnol. Bioengng*, *26*, 328 (1984).

[9] N. A. Mostafa, "Studies on the kinetics of biochemical reactions", Ph. D. Thesis, Faculty of Engineering, Minia Univ., Minia, Egypt (1990).

[10] H. E. Grethlein, *J. Appl. Chem. Biotechnol*, *28,* 296 (1978).

[11] T. K. Ghose and R. D. Tyagi, *Biotechnol. Bioengng*, 21, 1401 (1979).