Photo-Biological Reactor for Organic Waste Consumption and Hydrogen Production

L. F. de Souza[1]
[1]Universidade Federal do Paraná, Curitiba, Paraná, Brazil
*Corresponding Author: Rua Cerro Azul 1498, Colombo - PR – Brasil 83410-500, leonardo@pinho.com.br

Abstract: A simple photo-fermentative biochemical model was developed using the Transport of Diluted Species, using bacterial concentration as one of the diluted elements. This preliminary approach is based on a dimensionless model seeking optimal physical parameters based on given biochemical parameters found in literature. This kind of approach enables parametric sweep of the physical factors, without altering the mesh. Other biochemical processes and limitations can be easily added to this model, but were omitted for simplicity. A daily substrate load was made constant and the model responded as expected and several combinations of physical parameters for complete degradation and optimal production were found, so eventually many reactor designs are discarded from the project development. Even with all the simplifying hypotheses made, this model becomes a breakthrough and leads the search for optimal bioreactor conditions, so other important considerations can be reviewed and ultimately enhance this initial study.

Keywords: Biohydrogen, Photofermentation, purple bacteria, dimensionless, biochemical reactor.

1. Introduction

Photosynthesis is critical for life on earth but it can also be directed toward the generation of industrially useful bio-products, including hydrogen. Even though hydrogen gas is not naturally available in our environment, it is the most abundant element on the universe and a potential energy carrier. While organic wastes are normally the major portion of anthropic residues and using the fact that it is a pollutant if disposed inadequately, a model of a biochemical reactor was created to predict organic waste consumption and hydrogen production by photosynthetic bacteria, seeking lower costs, automation and optimal reactor conditions.

The aim of this work is to model and find optimal physical parameters for a biochemical reactor where enzymatic photo-fermentative reactions govern bacterial growth, substrate consumption, and product formation. A dimensionless approach is used, and a simple model was developed for future studies, which would include many other important considerations, neglected on this preliminary approach. The proposed organic waste treatment system is shown in Figure 1, the current model will only study the photo-fermentation stage.

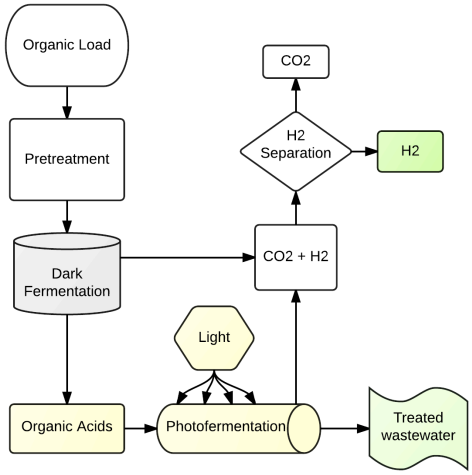

Figure 1. Proposed waste treatment.

2. Governing Equations

2.1 Stoichiometric Model

Theoretically, the complete oxidation of one mole of glucose may produce 12 moles of hydrogen [8]. Intermediate products from a dark fermentation process, the organic acids, can be consumed by purple non-sulfur (PNS) bacteria, and with low nitrogen concentration environment, they produce hydrogen gas. This reaction (Equation 2) is not thermodynamically favorable ($\Delta G'_0 = +209$kJ mol-1) but energy can be harvested from light, by a coupled process involving enzymes and photosynthetic pigments, to overcome this energy barrier. These PNS

bacteria are able to consume many types of substrates, but have a preference for organic acids. Acetic Acid is the main chemical compound produced during dark fermentation [12] (Equation 1) because it has the smallest carbon chain among other organic acids, so it will be used as substrate for this model

$$C_6H_{12}O_6 + 2H_2O \Rightarrow 2CO_2 + 2CH_3COOH + 4H_2 \quad (1)$$

$$2CH_3COOH + 4H_2O \Rightarrow 4CO_2 + 8H_2 \quad (2)$$

2.3 Biochemical Kinetic Model

Bacteria reproduction occurs by binary fission, where a symmetric division of cell material produces two daughter cells, after ordered nuclear material separation [5]. Bacterial growth is modeled following Monod enzymatic kinetics, with metabolic pathways that involve the *Nitrogenase* enzyme, producing hydrogen with complete absence of oxygen and stressful nitrogen concentrations; the latter will not be studied yet. Carbon dioxide concentration and light penetration studies are also important factors not considered for this introductory model.

A simplified model was developed as a first approach, so a perfectly mixed anoxic environment, at constant temperature, pH and light intensities are some of the basic hypothesis used inside the constant volume reactor. Growth of microbial culture, consuming substrate for energy purposes, for incorporation to its own cellular material, or for the synthesis of a product, gives rises to the concept of stoichiometric conversion efficiency (e_{H2}) and yield coefficient (y), the latter being defined by mass of bacterial growth or product formation per mass of substrate consumed. Yield coefficient depend and vary with different reactor conditions, but will be held constant. Taking μ_{max} as the specific bacterial growth rate and k_s the Monod half saturation constant, variations due to biochemical processes for bacteria (b), substrate (s) and hydrogen (h2) concentrations, are modeled as follows:

$$\frac{\partial b}{\partial t} = \mu_{max}\left(\frac{s}{k_s + s}\right) b \quad (3)$$

$$\frac{\partial s}{\partial t} = -\frac{1}{y_B}\frac{\partial b}{\partial t} \quad (4)$$

$$\frac{\partial h2}{\partial t} = (1 - y_B) e_{H2}\frac{\partial b}{\partial t} \quad (5)$$

2.3 Transport Model

The first hypothesis used for the transport model is the mass conservation, so by the Reynolds theorem, the time and space variations of a solute concentration must be equal to the summation of sources and sinks, which can be divided between those that occur inside the control volume and the ones crossing the surfaces through non-advective methods.

In this case, sources and sinks are biochemical reactions occurring inside the control volume. The solvent used is water, so bacterial concentration is modeled as a diluted chemical compound, which controls the reactions of every other element. Another set of hypothesis used is considering constant density and diffusion coefficient, no diffusion flux on the surface, and that only biochemical reactions occur inside the control volume. The conservation of mass becomes:

$$\frac{\partial}{\partial t} C + (\boldsymbol{u} \cdot \boldsymbol{\nabla}) C - D_i \boldsymbol{\nabla}^2 C = \mu C \quad (6)$$

Three-dimensional problem solving using space and time dependence are extremely complex, so usually dimensional reductions and steady-state approaches are applied to simplify the problem solving. This model considers tubular reactor, a two-dimensional axis symmetrical component, with a one-dimensional inflow of diluted species that will control the search for the physical parameters, based on the biochemical enzymatic reactions. The inflow of any chemical species is defined by its mass flux divided by the mass flow of the solvent.

$$c_{0,i} = \frac{\dot{m}_i}{\dot{m}_w} \quad (7)$$

3. Use of COMSOL Multiphysics® software

3.1 Transport of Diluted Species

The physics interface being used is the Transport of Diluted Species, which uses molar concentrations. Bacterial molar mass is extremely variable, so mass is usually considered as the governing dimension. Also, a dimensionless approach was a crucial strategy for the parametric sweep of physical reactor parameters.

3.2 Dimensionless Model

A dimensionless model was formulated seeking optimal physical parameters. This model considers a parametric study based on values from zero to one, even though the real parameters differ in many orders of magnitude. Taking L as the total length, r_{max} as the total radius, and s_0 as the initial substrate concentration, dimensionless quantities are defined as:

$$Z = \frac{z}{L} \qquad P_e = \frac{u_0 L}{D} \qquad S = \frac{s}{s_0}$$
$$R = \frac{r}{r_{max}} \qquad L_k = \frac{\mu_m L}{u_0} \qquad B = \frac{b}{b_{max}} \qquad (8)$$
$$T = \frac{u_0\, t}{L} \qquad K_s = \frac{k_s}{s_0} \qquad H2 = \frac{h2}{h2_{max}}$$

where P_e and L_k are Peclet and Damkohler numbers, which describe ratios between advection (u) over dispersion (D) and reaction over advection, respectively. Maximum quantities are found integrating the biochemical reaction models. Dimensionless equations become:

$$\frac{\partial B}{\partial T} = \frac{1}{Pe}\frac{\partial^2 B}{\partial Z^2} - \frac{\partial B}{\partial Z} + L_k\left(\frac{S}{K_S + S}\right)B$$

$$\frac{\partial S}{\partial T} = \frac{1}{Pe}\frac{\partial^2 S}{\partial Z^2} - \frac{\partial S}{\partial Z} - \frac{1}{Y_B}\frac{\partial B}{\partial T} \qquad (9)$$

$$\frac{\partial H2}{\partial T} = \frac{1}{Pe}\frac{\partial^2 H2}{\partial Z^2} - \frac{\partial H2}{\partial Z} + (1 - Y_B)e_{H2}\frac{\partial B}{\partial T}$$

Yield and efficiency were used as a percentage factor, meaning that substrate could be used in other forms not being considered on this model, such as carbon dioxide production or energy released as heat. Real biochemical modeling needs in-depth studies and prototype analyses seeking parameters that best fit to actual applications.

3.3 Boundary Conditions

The model will be governed by the inflow of diluted species in water. Wall boundary condition and axis symmetric conditions are easily applied with the Transport of Diluted Species physics interface. Using c_i for any species concentration:

$$D\frac{\partial c_i}{\partial z} - u\, c_{i,0} + u\, c_{i,in} = 0 \qquad \text{at z = 0} \quad (10)$$

$$\frac{\partial c_i}{\partial z} = 0 \qquad \text{at z = L} \quad (11)$$

In dimensionless quantities:

$$\frac{1}{P_e}\frac{\partial C_i}{\partial Z} - C_{i,o} + C_{i,in} = 0 \qquad \text{at Z = 0} \quad (12)$$

$$\frac{\partial C_i}{\partial Z} = 0 \qquad \text{at Z = 1} \quad (13)$$

This kind of modeling approach considers unitary velocity, the diffusion coefficient as one over the Peclet number and the reaction rate as the Damkohler number, because all three parameters are built in on the dimensionless numbers.

3.4 Geometry

The geometry used is an axisymmetric rectangle, where axial symmetry is applied on one of the walls, denoting the center of the tubular reactor. The dimensionless reactor is actually a unitary square, where a parametric length is a factor of the real length compared to the total length wanted. Figure 2 displays the two-dimensional revolution of the unitary square that used a default physics-controlled mesh.

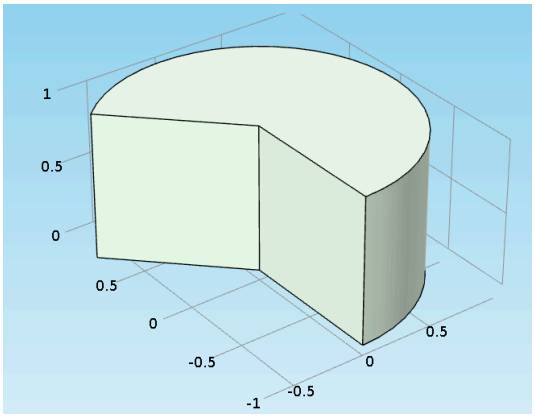

Figure 2 – Two-dimensional axis symmetric component revolution**.**

4. Results

4.1 Reactor Conditions

Taking an arbitrary load of 5.0kg of acetic acid per day, hypothetically coming from a dark fermentation reactor, diluting until the maximum concentration suggested 2.56 $kg.m^{-3}$, a total volume of 2,083.0 $L.day^{-1}$ should be continually fed at 22.6 $mL.s^{-1}$, for total continuous substrate degradation, with uninterrupted illumination. Parameters used are summarized on Table 1 at the Appendix.

4.2 Results

A parametric sweep of physical parameters is possible. From Figure 3, a selected length of 650m with a 0.20m radius shows complete substrate degradation. For a length of 1000m with 0.16m radius, the same result is achieved meaning different combinations demonstrate same results, so the next decision factor could be the total retention time (t), 1,3h and 3,9h, respectively. Because the load is fixed, varying the tube's radius reflects on the inlet velocity, meaning the retention time would vary and it would alter the total degradation capability. Note that for the larger lengths and radiuses, means substrate could potentially be consumed before the end of the tube, wasting money with material for manufacturing.

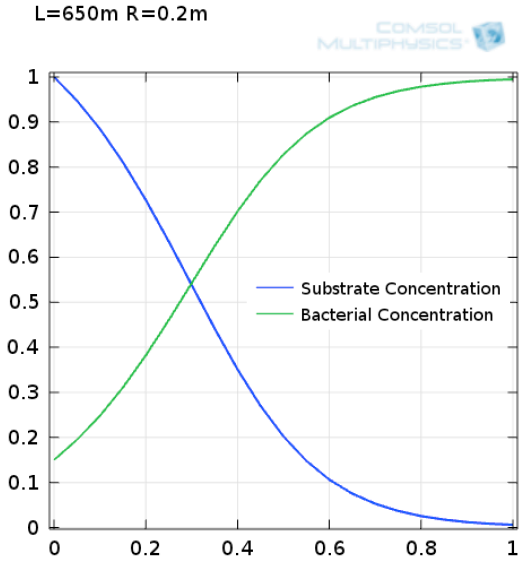

Figure 3 –Substrate and Biomass Concentration.

This dimensionless model simplifies the view of the tubular reactor with a length that is many orders of magnitude larger than the radius. Figure 4 displays a user-friendly view of the reactor.

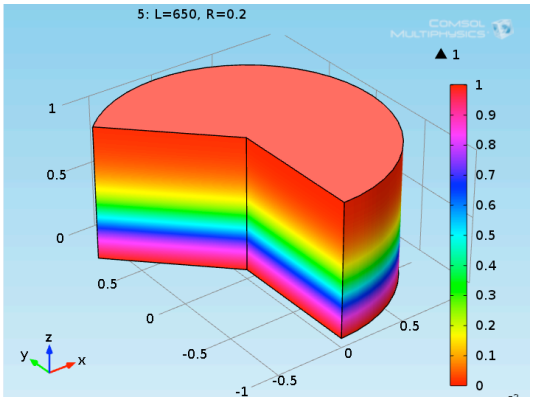

Figure 4 – Substrate Degradation (Revolution)**.**

In respect of hydrogen production, the same analysis is made, where total production capability is based on the same physical parameters, as shown in Figure 5. This means the model is responding adequately to what was proposed, and the dimensionless approach was effective on parameter estimation.

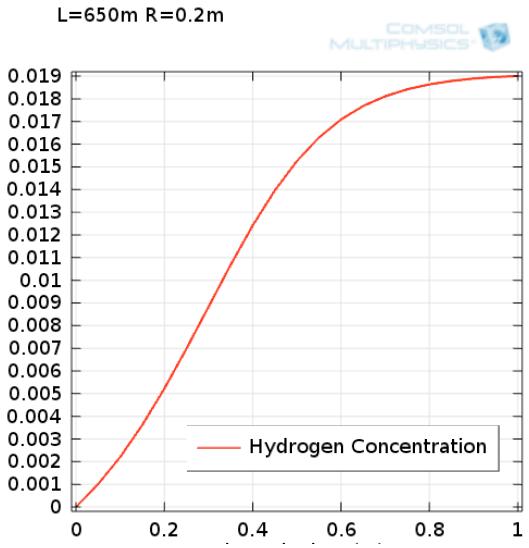

Figure 5 – Hydrogen Concentration.

5. Conclusions

This is a simple preliminary approach based on selected biochemical parameters, seeking best physical parameters based on a given substrate load and bacterial inflow. This model was created to show how we could model a biochemical photo-fermentative reactor using the Transport of Diluted Species, naming bacterial concentration as a diluted chemical compound.

The dimensionless analysis enabled the parametric sweep of physical parameters without modifying the mesh, and combinations of lengths and radiuses were found. This means reduction in project development and leads the decision taking elements to other reasons. Adaptations to this model can be easily added for an even more realistic reactor model.

Further considerations will include: heat transfer and pH variations by the biochemical reactions and how they affect the kinetic parameters, daily sunlight cycle, biofilms that immobilize bacterial cells creating porous media, integrated simulation using dark fermentation and even hydrogen flux through selective membrane or its use in fuel cells. COMSOL Multiphysics software becomes a powerful tool to study in depth these, and many other important studies that relate and could be integrated to this problem.

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7. Acknowledgements

I am thankful to the professors: Prof. Dr. Marcelo Lenzi, Prof. Dra. Agnes Scheer, Prof. Dr. Luis Fernando from PPGEQ – Programa de Pós-Graduação em Engenharia Química and PPGEA – Progama de Pós-Graduação em Engenharia de Alimentos, for their time and laboratory space to run the models. Also, Prof. Dr. Marcelo Errera from DEA – Departamento de Engenharia Ambiental, for his time and extremely helpful orientation.

11. Appendix

Table 1: Parameters used

Ac	5.0 kg day-1	Acetic acid daily load
Di	40 mmol/L	Maximum Dilution [13]
V_{in}	24.1 mL s^{-1}	Volumetric Feed
b0	0.15 kg m^{-3}	Bacterial Concentration [3]
ka	10 kg m^{-3}	Half Saturation Constant [12]
μ_{max}	0.025 h^{-1}	Specific Growth rate [3] [9]
y_{H2}	0.02 kg kg^{-1}	Hydrogen Yield [12]