SIMULATION OF BIOGAS PRODUCTION FROM THE ANAEROBIC DIGESTION PROCESS

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Abstract. *The model describing the transformation of biomass into biogas, process called Anaerobic Digestion (AD), is complex, because it involvs nonlinear and coupled ordinary differential equations. One of the advantages of this process is the transformation of waste into usable energy, reducing the amount of toxic gases released in the atmosphere. In this work, we model the chemical kinetics of the anaerobic digestion process. The system of ordinary differential equations of the model was solved numerically by the Runge-Kutta method of fourth order. Furthermore, the equations were simplified to obtain an analytical solution. The numerical results obtained agree well with the analytical solution and data found in the literature.*

Keywords: *Biomass, Biogas, Chemical kinetics, Simulation*

1 - INTRODUCTION

In the last years, with the increase of the cost of oil and with its reserves decreasing worldwide, the need for alternative sources of energy using local resources has increased rapidly. One of the resources available that has great potential for development and viability is the biomass (McKendry, 2002), (Twidell and Weir, 2006), most abundant raw material in the world, consisting of substances of organic origin (plants, animals and microorganisms). Unlike fossil fuels, such as oil and coal, biomass is renewable in a short period of time (Demirbas, 2001).

From the process of anaerobic digestion, which is the biological degradation of biomass, can be obtained a gas of great relevance for power generation, the methane, CH_4. This product is the main chemical component of the biogas (Ziemiński and Frac, 2006), biofuel that can be used for power generation, thermal and mechanical energy generation (Holm-Nielsen et al., 2009).

Biogas can be produced from almost all types of organic raw materials. The use of biogas has as its intention to replace the gases of mineral origin, such as LPG (Liquefied Petroleum Gas), used as cooking gas, NG (Natural Gas) used in household equipments, and NGV (Natural Gas Vehicle). The biogas can be used, for example, in household stoves, lamps, internal combustion engines (automobiles), refrigerators, incubators, grain dryers and heaters.

The anaerobic digestion is a complex process, consisting of several stages of metabolic interactions, in the absence of oxygen, and carried out by a well-organized community of microbial populations. This process can be divided into four phases of biodegradation: hydrolysis, acidogenisis, acetogenesis, and methanogenesis (Prokopová and Prokop, 2010). The mathematical model is obtained according to the number of chemical reactions presented in each stage of the process. This modeling provides a set of coupled and nonlinear ordinary differential equations.

In this work, we develop a chemical and mathematical model of the AD process, where the pulp is considered to be the substrate. Furthemore, we simulated this process, by solving the system of ordinary differential equations by the Runge-Kutta method of fourth order. Also, we developed an analytical solutions to the system of diferential equations of the problem and compare the analytical with numerical solution for biogas concentrarion.

2 - CHEMICAL AND MATHEMATICAL MODELING

The phases of the anaerobic digestion process are:

- **Hydrolysis**

  Is the first stage of degradation, in which complex organic molecules such as carbohydrates, proteins and fats decompose forming soluble monomers. Reactions are catalyzed by enzymes excreted from the hydrolytics and fermentative bacterias, such as *cellulase*, *protease* and *lipase*. A hydrolysis reaction where the organic waste is divided into a simple sugar (glucose) can be represented by Eq. (1).

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6. \tag{1}$$

- **Acidogenesis**

  In the step, the sugars are fermented to produce simple organic compounds, specially short-chain (volatile) acids (e.g., propionic, formic, lactic, butyric, or succinic acids), ketones (e.g., glycerol, acetone) and alcohols. In the following, an example of product obtained on acidogenesis phase and its respective ΔG value is given:

$$C_6H_{12}O_6 \rightarrow C_4H_8O_2 + 2CO_2 + 2H_2, \quad \Delta\text{G} = -264,19. \tag{2}$$

- **Acetogenesis**

  The third stage is acetogenesis, where the carbohydrate fermentation occurs and results a combination of acetate, carbon dioxide (CO_2), and hydrogen (H_2). Long chain fatty acids, formed from the hydrolysis of lipids, are oxidized to acetate or propionate and hydrogen gas is formed. An acetogenesis reaction can be represented by Eq. (3).

$$C_4H_8O_2 + 2H_2O \rightarrow 2C_2H_4O_2 + 2H_2, \quad \Delta\text{G} = 48. \tag{3}$$

- **Methanogenesis**

  Carried out by methanogen microorganisms, is the last stage of anaerobic digestion, where are produced methane and carbon dioxide. In this step, the methanogenic archaea (bacteria that lives in strictly anaerobic media and that obtains energy through methane production) mainly converts acetic acid, hydrogen and carbon dioxide into methane. The methanogenic archaea are divided into two main groups (Schön, 2009):

  Acetoclastic methanogenesis: they produce methane from acetic acid or methanol. These are the predominant microorganisms in the anaerobic digestion, responsible for about 60 to 70% of all production of methane.

  Hydrogenotrophic methanogenesis: they produce methane from hydrogen and carbon dioxide. Virtualy every species of methanogenic bacteria are capable of producing methane from hydrogen and carbon dioxide.

  In addition to the methanogenic reactions, the interconversion between hydrogen and acetate, catalyzed by homoacetogenic bacteria, is important for the formation of methane. The homoacethogens can oxidize or synthesize acetate depending on the external concentration of hydrogen. The reactions related to the stage of methanogenesis are presented in Table 1, along with the ΔG value of each reaction.

Table 1: Reactions related to the methanogenesis phase.

Nomenclature	Reaction	ΔG (KJ/mol)
Hydrogenotrophic methanogenesis	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	-131
Aceticlastic methanogenesis	$C_2H_4O_2 \rightarrow CH_4 + CO_2$	-36

If the composition of the substrate is known, and the total conversion of the substrate to biogas occurs, the theoretical CH_4 and CO_2 yield can be estimated from the chemical reaction (Buswell and Mueller, 1952) given by

$$C_nH_pO_q + \left[n - \frac{p}{4} - \frac{q}{2}\right] H_2O = \left[\frac{n}{2} + \frac{p}{8} - \frac{q}{4}\right] CH_4 + \left[\frac{n}{2} - \frac{p}{8} + \frac{q}{4}\right] CO_2, \tag{4}$$

where $C_nH_pO_q$ is organic matter, and p, q, and n are dimensionless coefficients. For example, for $n = 6$, $p = 12$ and $q = 6$ is obtained $C_6H_{12}O_6 = 3CH_4 + 3CO_2$, which represents globaly the anaerobic decomposition of glucose as a product of cellulose.

The mathematical formulation of the anaerobic digestion process is associated with the four phases described previously: hydrolysis, acidogenesis, acetogenesis and methanogenesis. The mathematical model provides a set of ordinary differential equations, called *kinetic system of ordinary differential equations* (ODEs), that can be written as:

$$\frac{dY_j}{dt} = \sum_{i}^{N_R} \nu_{ij} r_i, \quad j = 1, \cdots, N_s, \tag{5}$$

where Y_j is the molar concentration of the species j, ν_{ij} is the stoichiometric coefficient of j-th species and N_s the number of species. The r_i are the rates of elementary reactions which can be calculated from the law of mass action (Turányi and Tomlin, 2014), by the formula

$$r_i = k_i \prod_{j}^{N_s} Y_j^{\nu_{ij}}, \tag{6}$$

where k_i is the rate coefficient, which can be calculated using the Gibss free energy (ΔG) of each reaction (Lethlean and Swarbrick, 2001) as follows

$$k_i = \exp\left(-\frac{\Delta \mathrm{G}}{\mathrm{RT}}\right), \tag{7}$$

where R=8,3144 J/Kmol is the universal gas constant and T the absolute temperature (in Kelvins).

In general, the kinetic system of ODEs is of first order and nonlinear, as it contains the first order derivatives with respect to time, which are a nonlinear function of concentrations. Each species participate in various reactions, with its corresponding production rate, forming the coupled system.

2 - SOLUTION PROCEDURE

The system of ODEs of the anaerobic digestion process considers the reactions of the phases: (I) hydrolysis, (II) acidogenesis, (III) acetogenesis, (IV) hydrogenotrophic methanogenesis, and (V) acetoclastic methanogenesis. Table 2 shows the set of chemical reactions of the stages (I), (II), (III), (IV) and (V) utilized to write the kinetic system of ODEs.

Table 2: Set of chemical reactions of the anaerobic digestion process.

Phases	Reactions	Rates
(I)	$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$	$r_0 = k_0[C_6H_{10}O_5][H_2O]$
(II)	$C_6H_{12}O_6 = C_4H_8O_2 + 2CO_2 + 2H_2$	$r_1 = k_1[C_6H_{12}O_6]$
(III)	$C_4H_8O_2 + 2H_2O = 2C_2H_4O_2 + 2H_2$	$r_2 = k_2[C_4H_8O_2][H_2O]^2$
(IV)	$CO_2 + 4H_2 = CH_4 + 2H_2O$	$r_3 = k_3[CO_2][H_2]^4$
(V)	$2C_2H_4O_2 = 2CH_4 + 2CO_2$	$r_4 = k_4[C_2H_4O_2]^2$

Table 3 shows the chemical compounds involved in the anaerobic digestion process, described previously. Each chemical compound is associated with its chemical formula and respective abbreviations.

Table 3: Chemical compounds, chemical formulas and abbreviations.

Chemical compounds	**Chemical formulas**	**Abbreviations**
Cellulose	$C_6H_{10}O_5$	Y_1
Glucose	$C_6H_{12}O_6$	Y_2
Butyric acid	$C_4H_8O_2$	Y_3
Acetic acid	$C_2H_4O_2$	Y_4
Methane	CH_4	Y_5
Carbon dioxide	CO_2	Y_6
Hidrogen	H_2	Y_7
Water	H_2O	Y_8

The concentration varations Y_j ($j = 1, \cdots, 8$) are based on Eq. (5). In this way, the kinetic system of ODEs is composed of eight ordinary differential equations, as follow:

$$1)\ \frac{dY_1}{dt} = -k_0 Y_1 Y_8$$

$$2)\ \frac{dY_2}{dt} = k_0 Y_1 Y_8 - k_1 Y_2$$

$$3)\ \frac{dY_3}{dt} = k_1 Y_2 - k_2 Y_3 Y_8^2$$

$$4)\ \frac{dY_4}{dt} = 2k_2 Y_3 Y_8^2 - 2k_4 Y_4^2$$

$$5)\ \frac{dY_5}{dt} = k_3 Y_6 Y_7^4 + 2k_4 Y_4^2$$

$$6)\ \frac{dY_6}{dt} = 2k_1 Y_2 - k_3 Y_6 Y_7^4 + 2k_4 Y_4^2$$

$$7)\ \frac{dY_7}{dt} = 2k_1 Y_2 + 2k_2 Y_3 Y_8^2 - 4k_3 Y_6 Y_7^4$$

$$8)\ \frac{dY_8}{dt} = -k_0 Y_1 Y_8 - 2k_2 Y_3 Y_8^2 + 2k_3 Y_6 Y_7^4$$

The kinetic system of ODEs and its initial values provide the following initial value problem:

$$\begin{cases} Y'(t) = \dfrac{dY(t)}{dt} = f(t, Y(t)),\ t \in [a, b] \\ Y(t_0) = Y(a) \end{cases}, \tag{8}$$

where

$$Y'(t) = \begin{bmatrix} Y_1'(t) \\ Y_2'(t) \\ \vdots \\ Y_8'(t) \end{bmatrix}, f(t, Y(t)) = \begin{bmatrix} f_1(t, Y(t)) \\ f_2(t, Y(t)) \\ \vdots \\ f_8(t, Y(t)) \end{bmatrix} \text{ and } \begin{bmatrix} Y_1(t_0) = Y_1^0 \\ Y_2(t_0) = Y_2^0 \\ \vdots \\ Y_8(t_0) = Y_8^0 \end{bmatrix}.$$

It is observed that the kinetic system obtained is nonlinear and coupled; in this way, a numerical method is necessary to solve it.

2.1 Numerical Solution

The initial value problem presented in Eq. (8) is solved by the Runge-Kutta44 method (Burden and Faires), a fourth order method that provides good approximation for the solution of coupled systems of equations.

Initially, it is considered an uniform partition of the interval $[a, b]$:

$$a = t_0 < t_1 < \cdots < t_n = b,\ t_{k+1} = t_k + h,\ k = 0, \cdots n-1,\ h = \frac{b-a}{n}.$$

The Runge-Kutta44 is given by

$$\begin{cases} Y_j^0 = Y_j(t_0) \\ Y_j^{k+1} = Y_j^k + h\Phi(t_k, Y^k, h) \end{cases}, \tag{9}$$

where the index j represents the chemical species, and k the iterations of the method, $\Phi(t_k, Y^k, h) = \dfrac{1}{6}\left(\kappa_1 + 2\kappa_2 + 2\kappa_3 + \kappa_4\right)$, and

$$\kappa_1 = f_j\left(t_k, Y^k\right),$$

$$\kappa_2 = f_j\left(t_k + \frac{h}{2}, Y^k + \frac{h}{2}\kappa_1\right),$$

$$\kappa_3 = f_j\left(t_k + \frac{h}{2}, Y^k + \frac{h}{2}\kappa_2\right),$$

$$\kappa_4 = f_j\left(t_k + h, Y^k + h\kappa_3\right).$$

For example, to obtain the concentration of the specie Y_1 in the interval [0, 50], the follow-

ing problem is solved:

$$\begin{cases} Y_1'(t) = f_1\left(t, Y_1(t), \cdots, Y_8(t)\right) = -k_0 Y_1(t) Y_8(t),\ t \in [0, 50] \\ Y_1(0) = Y_1^0 = 1 \\ Y_8(0) = Y_8^0 = 1 \end{cases} . \tag{10}$$

Consider $h = 0.1$ and $k_0 = 1$. So the first iteration of the method ($k = 0$) is given by

$\kappa_1 = f_1\left(t_0, Y_1^0, \cdots, Y_8^0\right) = f_1\left(0, 1, 1\right) = -1,$

$$\kappa_2 = f_1\left(t_0 + \frac{h}{2}, Y_1^0 + \frac{h}{2}\kappa_1, \cdots, Y_8^0 + \frac{h}{2}\kappa_1\right) = f_1\left(0.05, 0.95, 0.95\right) = -0.9025,$$

$$\kappa_3 = f_1\left(t_0 + \frac{h}{2}, Y_1^0 + \frac{h}{2}\kappa_2, \cdots, Y_8^0 + \frac{h}{2}\kappa_2\right) = f_1\left(0.05, 0.9549, 0.9549\right) = -0.9118,$$

$\kappa_4 = f_1\left(t_0 + h, Y_1^0 + h\kappa_3, \cdots, Y_8^0 + h\kappa_3\right) = f_1\left(0.1, 0.9088, 0.9088\right) = -0.8259$, and

$$\Phi(t_0, Y^0, h) = \frac{1}{6}\left(\kappa_1 + 2\kappa_2 + 2\kappa_3 + \kappa_4\right) = -0.9091.$$

The approximation obtained for Y_1, in the first iteration of the Runge-Kutta44 method, is given by

$$Y_1^1 = Y_1^0 + h\Phi(t_0, Y^0, h) = 0.9091. \tag{11}$$

In this work, the computational program was developed in *Fortran90*.

2.2 Analytical Solution

In order to obtain the analytical solution, the set of equations (8) was decoupled, assuming constant values for concentrations of some species, as follow:

$Y_4 = a = 0.01$, $Y_7 = b = 0.1$, $Y_8 = c = 0.1$.

The following simplified system is obtained:

$$Y_1' = -k_0 c Y_1$$
$$Y_2' = k_0 c Y_1 - k_1 Y_2$$
$$Y_3' = k_1 Y_2 - k_2 c^2 Y_3$$
$$Y_4' = 0$$
$$Y_5' = k_3 Y_6 b^4 + 2k_4 a^2$$
$$Y_6' = 2k_1 Y_2 - k_3 b^4 Y_6 + 2k_4 a^2$$
$$Y_7' = 0$$
$$Y_8' = 0$$

From the theory of differential equations (Rubinstein, 1969), the solution of linear systems

of ODEs is given by

$$Y(t) = c_1 e^{\lambda_1 t}\mathbf{v}_1 + c_2 e^{\lambda_2 t}\mathbf{v}_2 + c_3 e^{\lambda_3 t}\mathbf{v}_3 + c_5 e^{\lambda_5 t}\mathbf{v}_5 + c_6 e^{\lambda_6 t}\mathbf{v}_6, \tag{12}$$

where c_i are constants obtained from initial conditions, λ_i and $\mathbf{v}_i$ are the real eigenvalues and eigenvectors of the system matrix, respectively.

The following values are obtained for the eigenvalues and eigenvectors, respectively:

$\lambda_1 = 0$, $\lambda_2 = -0.00011$, $\lambda_3 = -0.0098$, $\lambda_5 = -1.1$, and $\lambda_6 = -0.1$.

$$\underbrace{\begin{bmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 0 \end{bmatrix}}_{\mathbf{v}_1}, \underbrace{\begin{bmatrix} 0 \\ 0 \\ 0 \\ -0.70711 \\ 0.70711 \end{bmatrix}}_{\mathbf{v}_2}, \underbrace{\begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \end{bmatrix}}_{\mathbf{v}_3}, \underbrace{\begin{bmatrix} 0 \\ 0.40454 \\ -0.41189 \\ 0.00008 \\ -0.81651 \end{bmatrix}}_{\mathbf{v}_5}, \underbrace{\begin{bmatrix} 0.36605 \\ 0.0366 \\ -0.45046 \\ 0.00086 \\ -0.81348 \end{bmatrix}}_{\mathbf{v}_6}.$$

The eigenvalues λ_i and eigenvectors $\mathbf{v_i}$ were calculated by the *GNU OCTAVE* software (version 4.0).

It was assumed the following initial conditions:

$Y_1(t_0) = 1$, $Y_2(t_0) = 0$, $Y_3(t_0) = 0$, $Y_5(t_0) = 0$, $Y_6(t_0) = 0$.

After making some algebraic work and apply simplifications (numbers of the order of 10^{-4} or smaller are considered to be zero), the following analytical solution for biogas yield $Y_B(t)$ was obtained.

$$Y_B(t) = 6.00 + 0.594e^{-1.11t} - 6.59e^{-0.1t}. \tag{13}$$

3 - RESULTS AND DISCUSSION

We simulate the process of anaerobic digestion using the set of chemical reactions presented in Table 2, considering cellulose as substrate.

To obtain the constants k_1, k_2, k_3 and k_4 we used the values of ΔG, given in Equations (2), (3) and Table 1, using Eq. (7), for $T = 298,15K$. The values of the paramenters utilized in the simulation are presented in Table 4.

Figure 1 shows the comparison of the analytical solution with the numerical solution for the production of biogas. Is observed that the production of biogas increases rapidly in the first few days of the process. After that, the solution tends slowly to the value six. This shows that the methanogenic phase occurs in about 50 days. The analytical solution given by Eq. (13) (represented by solid line in Figure 1) is in agreement with the numerical solution.

Globally, the numerical solution is in accordance with the analytical values. However, the discrepancy between the analytical and numerical values are larger at the beginning of the process. The differences observed are due to the great simplifications adopted in the analytical model.

Table 4: Data for simulations of the process of biogas production.

Parameter	Value
k_0	1.0000
k_1	1.1125
k_2	0.9808
k_3	1.054
k_4	1.015

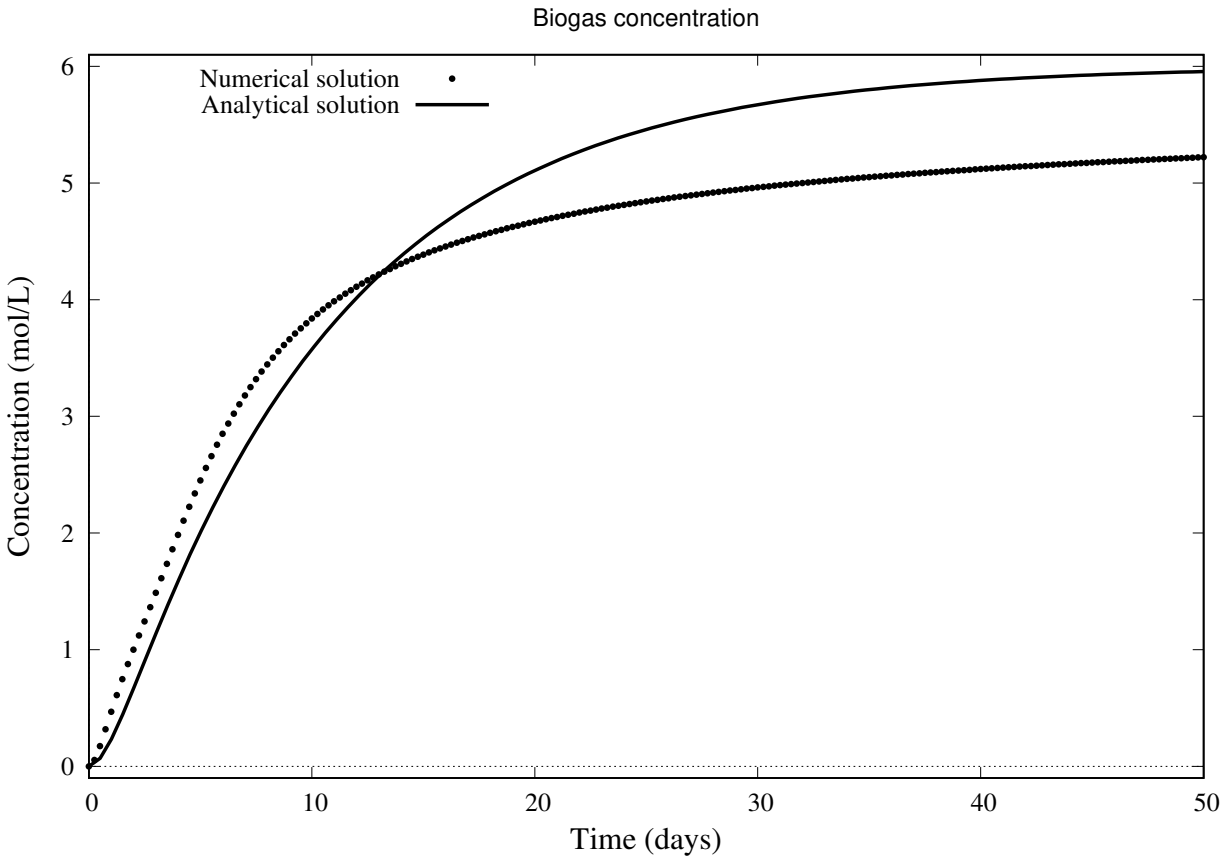

Figure 1: Numerical and Analytical solution of the biogas concentration.

Figure 2 shows the consumption of cellulose (substrate) and intermediate species of anaerobic digestion process.

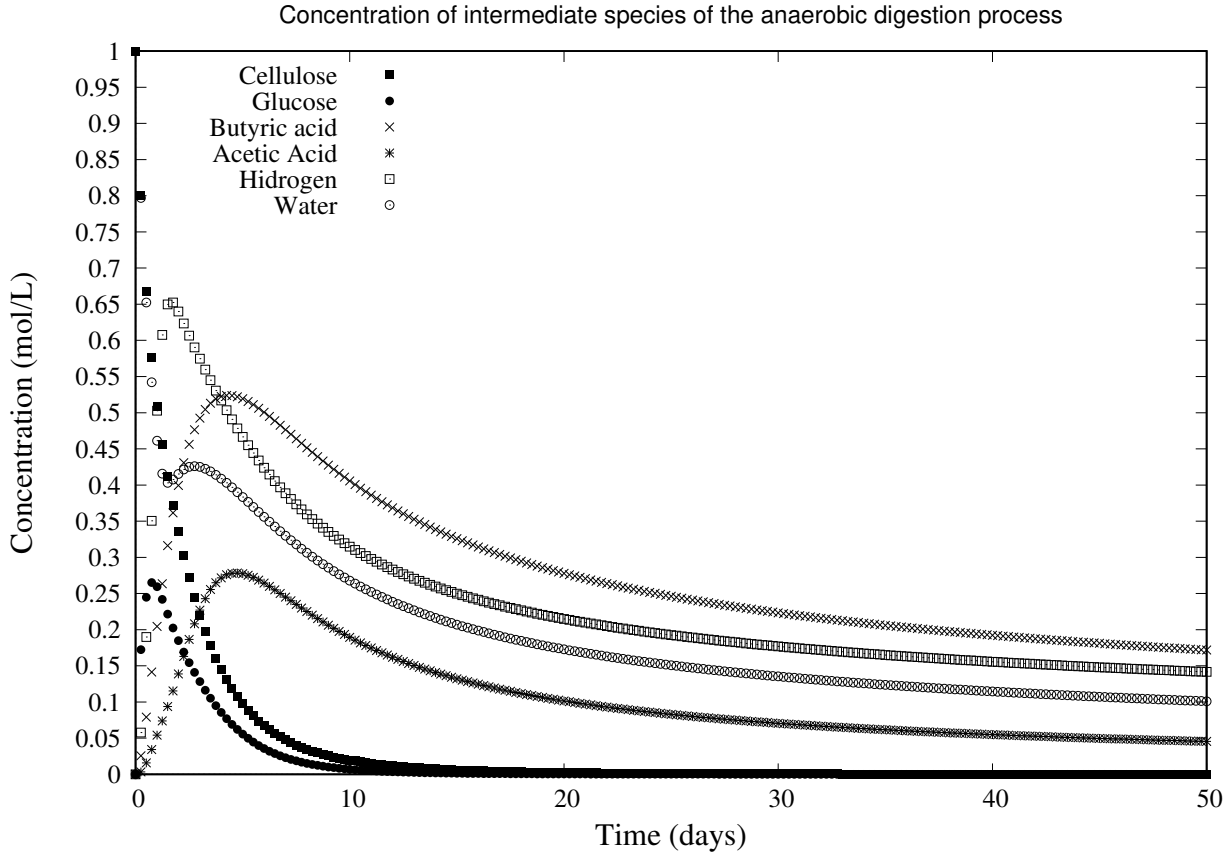

Figure 2: Numerical solution of concentration of intermediate species of the anaerobic digestion process.

It is observed that the concentration of cellulose and all intermediate species decays over time. Concentrations of cellulose and glucose tend to zero, showing the consumption of the whole substrate. The phases of hydrolysis and acidogenic are almost completed in minus than 20 days. The butyric acid-degrading, acetic acid-degrading, hidrogen-degrading and water-degrading occur in abount 50 days.

3 - CONCLUSIONS

In this work, we developed a model for the biogas production process, considering cellulose as substrate. Thus, with the value of Gibbs free energy, the production rate of each reaction is estimeted.

The anaerobic decomposition of glucose as a product of cellulose at 100% substrate possibly is given globaly by $C_6H_{12}O_6 = 3CH_4 + 3CO_2$. This shows that with 1 kmol of glucose, 6 kmol of biogas can be obtained, which is consitent with the results obtained. In addition, the development of an analytical solution, used for comparison with the numerical result, is a major contribution of the present study.

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