# MODELING THE HYDROLYSIS PROCESS OF THE BIOETHANOL PRODUCTION

RANON DE SOUZA GOMES[1], CHARLES QUEVEDO CARPES[2], GREICE DA SILVA LORENZZETTI ANDREIS[3], ÁLVARO LUIZ DE BORTOLI[4]

**ABSTRACT**

In this work, we model the hydrolysis process of the bioethanol production from vegetable sources. The process of bioethanol production described in this work allows the simultaneous use of various vegetables sources having starch or sugars, such as the rice, the potato, the cassava, the maize, the sugarcane, the beet, etc. The model developed considers the use of an enzyme for the conversion of the starch into saccharides. Numerical results are in agreement with experimental results found in the literature.

**KEY WORDS:** Hydrolysis. Production of bioethanol. Numerical model.

## 1. INTRODUCTION

The present energy scenario has stimulated active research interest in nonpetroleum, renewable, and nonpolluting fuels [9]. The United States biofuel industry has grown dramatically in recent years, with production expanding from 1.6 billion gallons in 2000 to 9 billion gallons in 2008. This increase can be attributed to the increase of production of corn-based ethanol. The number of refineries has also increased [5]. Moreover, due to worldwide concern with sustainability, the production of biofuels is expected to grow considerably in the next years.

Biofuels are alternative energy sources and can still form the basis of sustainable development in terms of socioeconomic and environmental concerns. Biodiesel and bioethanol, derived from plant sources, appear to be promising future energy sources [9].

Ethanol can be produced from cellulose feedstocks such as corn stalks, rice straw, sugar cane, bagasse, pulpwood, switchgrass, and municipal solid waste, being called bioethanol, or from renewable sources which contain starch, sugar or cellulose, such as potatoes, corn, corn cobs and stalks, grains, sugarcane and sugar beet waste and molasses

[1] UFRGS/PPGMAp, Master in Applied Mathematics, ranon.souza@ufrgs.br.
[2] UFRGS/PPGMAp, Master in Applied Mathematics, charles.carpes@ufrgs.br.
[3] UFRGS/PPGEQ, Doctor in Chemical Engineering, greice.lorenzzetti@ufrgs.br.
[4] UFRGS/PPGMAp/PPGEQ, Doctor in Mechanical Engineering, dbortoli@mat.ufrgs.br.

[11]. Ethanol is an alcohol-based fuel produced by the fermentation of plant sugars. It can be obtained from many agricultural products and food wastes if they contain sugar, starch, or cellulose, which can then be fermented and distilled into ethanol. In Brazil, which is the largest ethanol producer, ethanol is produced from sugarcane [9]. Bioethanol is a renewable green fuel [3].

Bioethanol was introduced into the transportation fuel supply chain as early as the 1970s with the introduction of the PROÁLCOOL program by the Brazilian government in an original effort to stabilize the international price of sugarcane, which was highly sensitive to subsidies by other domestic producers [7]. Bioethanol is currently one of the most important biofuels because it can be used in full or in partial replacement of gasoline in modern internal combustion engines. The world's largest producers of bioethanol are the United States and Brazil, whose products are derived primarily from corn and sugarcane, respectively.

The demand for food and possible changes in climate may cause fluctuations in the price of fuel from these sources, hence the diversification of used raw materials becomes increasingly necessary as the world increases the consumption of fuel.

In this paper one describes the hydrolysis process for the bioethanol production.

## 2. PROCESS DESCRIPTION

The ethanol can be obtained directly from fermentation of sugars such as glucose, sucrose, maltose, etc. This fermentation can be performed by several species of yeasts, being the *Saccharomyces cerevisiae* the species most used [4], [12]. The product of the fermentation process is a mixture of several alcohols, water and solids waste, that are obtained from the steps prior to the process. With respect to the volume of alcohols contained in this mixture, there are, on average, between 90% to 95% of ethanol [2]. The mixture of alcohols and water can be distilled to obtain ethanol with any degree of purity desired.

The steps described previously are well known in the industry for the production of beverages, fuel ethanol, ethanol for cosmetic, etc. Therefore, the differences between the production of wines and beers, for example, reside only in the vegetable raw material which was used in the production of the mash (water mixture + sugars). Similarly, the difference between a drink as the whisky and the ethanol fuel is the purity degree of the ethanol, i. e., the form of distillation used in the process.

This paper focuses the attention in the initial steps of this process, i. e., in the choice of vegetable sources that are used, and in the form of transforming them into sugars for a subsequent fermentation process. As the ethanol is obtained from vegetable sources by

fermentation of sugars, those who have large amounts of sugar in its composition will produce larger amounts of fuel. Thus, vegetables such as the sugarcane and the beets are able to produce more ethanol, by direct fermentation, in opposition to other vegetables that need a preliminary hydrolysis process. However, factors such as the climatic characteristics of each region of the planet, periods of harvests, competition with the food supply, prevents that the use of a single vegetable source be economically viable. To avoid this problem it is possible to use a process of preliminary hydrolysis.

## 3. HYDROLYSIS PROCESS

Several plants are rich in starch and generally these plants have a certain amount of sugar in its composition. Some vegetables rich in starch are, for example the corn, the potatoes, the rice and the cassava.

The hydrolysis is the breakdown of starch molecules into smaller molecules, sugars, which may then be fermented by the traditional process. The process of hydrolysis is not modern and is used in the production of fuel ethanol from corn in the United States for a long time. The FIGURE 1 shows the two main molecules that compose the cassava starch.

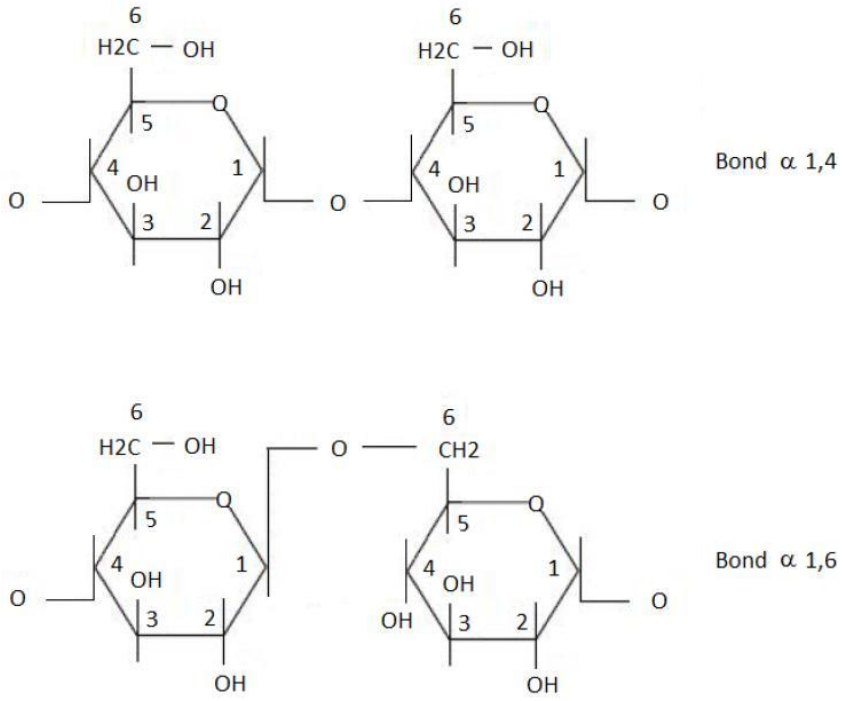


Figure 1. Main molecules that compose the cassava starch.

As is shown in the previous figure, the starch molecules are natural polymers, where each monomer is a single molecule of a monosaccharide. Therefore, to obtain sugars by

fermentation it is sufficient for the chemical bonds between each of the monomers be disrupted, releasing the saccharides. In the case of the example, the links that must be broken are the α1,4 and the α1,6 for each of the different molecules.

The molecular composition of the starch differs from one plant to another; however, the starch is always composed by saccharide in different molecular arrangements. This process of breaking the bonds between the saccharides that compose the starch is called the process of hydrolysis.

The hydrolysis process can be divided into two categories: the enzymatic hydrolysis and the acid hydrolysis. In the acid hydrolysis, one uses a strong acid such as sulfuric acid ($H_2SO_4$) or the hydrochloric acid ($HCl$), for the disruption of chemical bonds. This process is performed at relatively high temperatures, approximately 120°C and 1 *atm* pressure. The acid hydrolysis has the following disadvantages: high energy consumption, waste generation and low chemical selectivity. This low selectivity means that not only links between monomers are broken, but many sugar molecules are also destroyed in this process. This turns the acid hydrolysis unattractive commercially.

The process of enzymatic hydrolysis employ enzymes to break the chemical bonds of the starch molecules. The enzymes are chosen according to the vegetable source to be used in order to make them highly selective, i. e., acting almost exclusively on the links between the monomers that compose the starch. The most widely used commercial enzymes are the alpha-amylase of fungal origin and/or glucoamylase and/or the enzyme pupullase. The major disadvantage of this process is the high cost of the commercial enzyme, corresponding to about 50% of the total cost of the process.

Whereas the enzymatic hydrolysis is more advantageous from the viewpoint of sustainability and in order to mitigate the cost of commercial enzymes, there are papers that propose the use of an enzyme from a vegetable source, such as sweet potato (*Ipomoea batatas*). Sweet potato has several enzymes including alpha-amylase and beta-amylase [13] and can be used in total or partial replacement of the commercial enzymes of fungal or bacterial origin.

In this work we model the enzymatic reaction to approximately describe some of the steps of these chemical reactions. The model allows the analysis and optimization of this process without the need of making repeatedly experiments that, in general, are expensive.

## 4. MODEL AND NUMERICAL RESULTS

The simplest case of an enzyme-catalyzed reaction, based in the work from Michaelis and Menten [6], is the conversion of a single substrate into a product, as occurs in the

isomerization and disruption reactions. This model involves an enzyme $E$ and a substrate $S$ reacting to form a complex $ES$. After the complex disruption, occurs the enzyme liberation and the formation of product $P$. This may be represented schematically [1] as

$$S + E \underset{k_{-1}}{\overset{k_1}{\rightarrow}} SE \tag{1}$$

$$SE \overset{k_2}{\rightarrow} E + P \tag{2}$$

where $S$ represents the starch and $P$ the saccharides. The constants $k_1$, $k_{-1}$ and $k_2$ are the reaction rates (or rate constants) and the double arrow corresponds to reversible reactions, while the single arrow indicates that the reaction proceeds in one direction. The differential equations that describe the variation of the species concentration in time for the reactions (1) and (2) are given by

$$\frac{d[s(t)]}{dt} = -k_1 s(t)e(t) + k_{-1}c(t) \tag{3}$$

$$\frac{d[e(t)]}{dt} = -k_1 s(t)e(t) + (k_{-1} + k_2)c(t) \tag{4}$$

$$\frac{d[c(t)]}{dt} = k_1 s(t)e(t) - (k_{-1} + k_2)c(t) \tag{5}$$

$$\frac{d[p(t)]}{dt} = k_2 c(t) \tag{6}$$

where $s$, $e$, $c$ and $p$ correspond to the concentrations of starch (substrate), enzyme, complex and saccharides (product), respectively. The complexity of the biochemical/biological processes implies, in most cases, the use of a simplified model. Note that in some cases, the simplest model is still sufficiently complex to hinder the mathematical treatment. The idea is to reduce the complexity of the model, allowing to obtain an approximate solution that contains an acceptable description of the main phenomena.

Adding the Equations (4) and (5) one obtains

$$\frac{d}{dt}[c(t) + e(t)] = 0 \tag{7}$$

After integration and evaluation of the initial conditions it results

$$c(t) + e(t) = e_0 \tag{8}$$

Thus, after replacing (8) in to Equations (3), (4) and (5), the system may be reduced to three equations

$$\frac{d[s(t)]}{dt} = -k_1 s(t) e_0 + [k_1 s(t) + k_{-1}] c(t) \tag{9}$$

$$\frac{d[c(t)]}{dt} = -k_1 s(t) e_0 + [k_1 s(t) + k_{-1} + k_2] c(t) \tag{10}$$

$$\frac{d[p(t)]}{dt} = k_2 c(t) \tag{11}$$

whose numerical solution corresponds to the curves presented in the FIGURE 2.

The numerical integration of the system (9) is performed using the four-step Runge-Kutta scheme. The substrate ($s$) presents a decreasing behavior, whereas the product ($p$) has a increasing behavior. This occurs because in the model, the substrate is transformed in the product of the reaction. The complex ($c$) also depends on the amount of substrate that still can be converted into product. Thus, when no more substrate to react, there will be no complex formation and, therefore, it is observed that the complex increases to a certain point and then decreases to zero. Finally, the enzyme ($e$) acts only as a catalyst, accelerating (or decelerating) the reaction and, at the end of this process, it will not show loss. The enzyme suffers a small decay and then returns to its original shape. This decay occurs at the moment it joins the substrate, forming the complex.

The FIGURE 3 compares the starch concentration with the experimental data given from Özbek and Yüceer [8]. In this case, it applies the model given by the system 9, where the substrate is the starch, the enzyme is the alpha-amylase and the product is the saccharide [8]. The behavior of the starch concentration on time agrees with the experimental data. The constants $k_1 = 9.4$, $k_{-1} = 8.1$ and $k_2 = 5$ were adjusted numerically from the constants presented by Schnell and Maini [10], with T = 60°C and pH = 6:5.

There is an optimum temperature range for this process to occur. At temperatures above this optimum range, there is the breaking of the molecules of the enzyme, which implies in a decrease of the process efficiency. For temperature values below the optimum range, the process also loses efficiency due to the endothermic characteristic of the reaction.

The influence of temperature on the process can be observed in the work from Özbek and Yüceer [8].

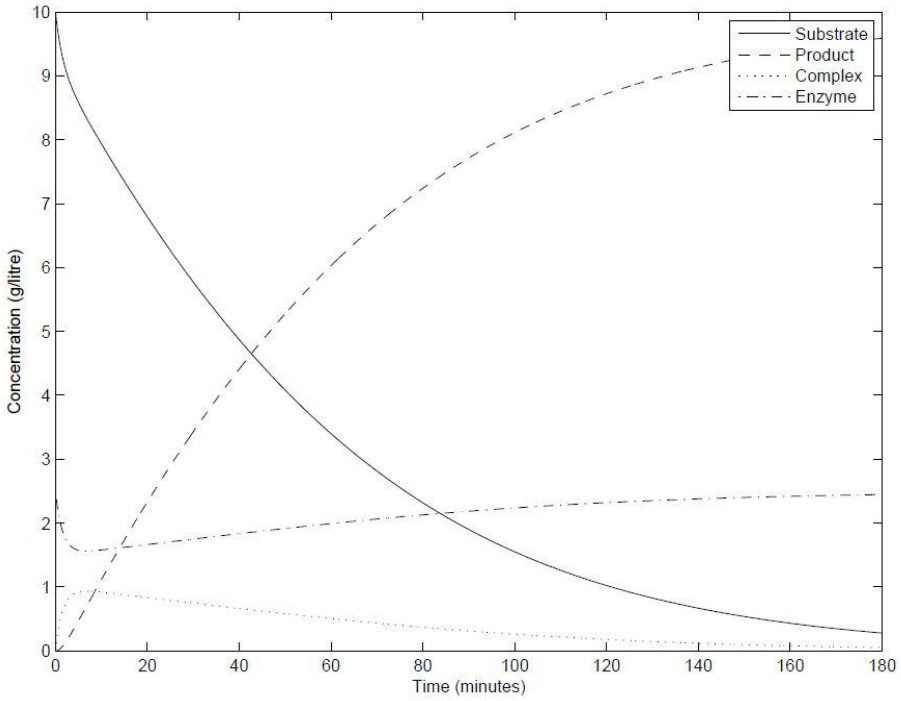


Figure 2. Concentration of the substrate, the product, the complex and the enzyme with initial condition $s(0)=10$, $e(0)=2.5$, $c(0)=0$ and $p(0)=0$.

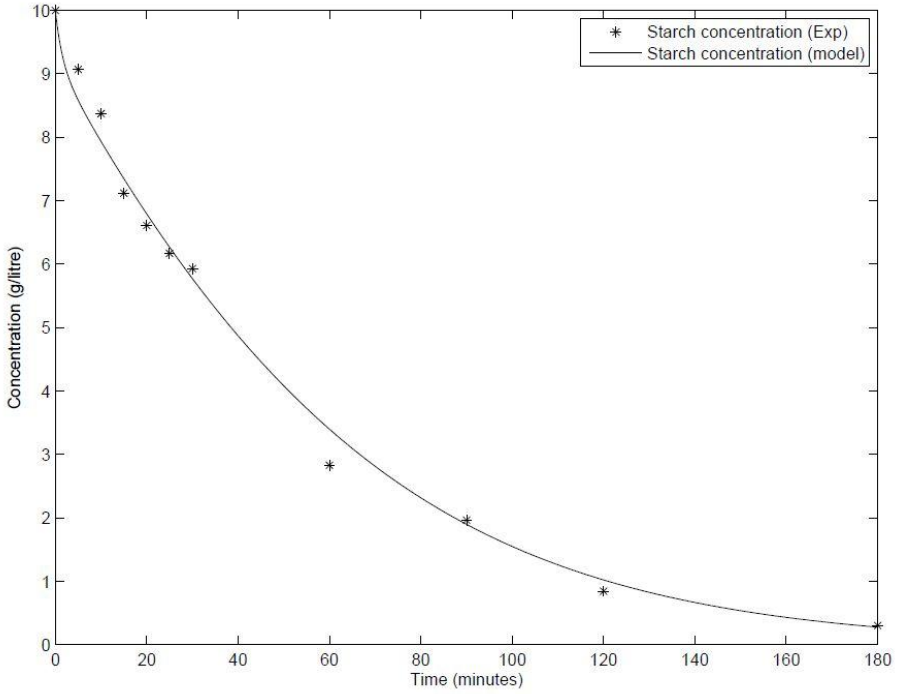

Figure 3. Starch concentration over time for $s(0)=10$ and $e(0)=2.5$ with $k_1=9.4$, $k_{-1}=8.1$ and $k_2=5$.

## 5. CONCLUSIONS

Due to the economic advantages of the enzymatic process and the large number of vegetables containing starch in its composition, the control and optimization of the hydrolysis process increases the possibility of ethanol production in various regions. The main contribution here is the development of a model for the hydrolysis process of starch. Obtained results show that this model may be employed to simulate the hydrolysis process.

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