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Analysis of the conversion of cellulose present in lignocellulosic biomass for biofuel production

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Abstract: Among the steps for the conversion of biomass into bioenergy, there is enzymatic hydrolysis. However, factors such as composition, formation of inhibitors, inhibition and enzymatic deactivation can affect the yield and productivity of this process. Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin. However, lignin is organized in a complex and non-uniform way, promotes biomass recalcitrance, which repress the enzymatic attack on cellulose to be converted into glucose, and, consequently, the production of biofuel. Thus, a challenge in enzymatic hydrolysis is to model the reaction behavior. In this context, this study aims to evaluate the performance in enzymatic hydrolysis for the conversion of cellulose present in sugarcane bagasse into glucose. Therefore, modeling and optimization will be proposed to produce high glucose concentration rates. Therefore, a previously developed study will be used, in which the authors proposed a kinetic model for the hydrolysis step. However, as a differential to what has been proposed, the calculation will be carried out evaluating the evaporation, in order to maximize the response to the glucose concentration. Thus, considering evaporation and optimized kinetic parameters, it was possible to obtain high rates of glucose concentration at 204.23 $g.L^{-1}$ in initial potential glucose concentration of 44 $g_{ppotential-glucose}.L^{-1}_{solution}$.

Key words: Biomass, bioethanol, enzymatic hydrolysis, kinetic model.

INTRODUCTION

The increasing demand for energy has encouraged researchers in the search for clean and sustainable energy, since fossil fuels have finite reserves and degrade the environment. In addition, greenhouse gas emissions (GHG), air pollution, acid rain and global warming are intensifying every day by the increase in the use of these fossil fuels (Tabatabaei & Aghbashlo 2020, Nanda & Berruti 2021). Tabatabaei & Aghbashlo (2020) affirm that the transport sector represents 30% annual of the consumption of the fossil fuel in the world.

Moreover, there is a concern with the disposal of waste from industries, agribusiness, urban solid waste, among others. From the perspective of environmental sustainability, agro-industrial waste has been gaining ground as feedstock for the generation of renewable products (Yaashikaa et al. 2022).

According to Łukasik et al. (2021) sustainability is a new criterion that integrate The RED II Directive, that sets as a goal the reduction of the GHG, until 2026, in 80%. Thus, energy production facilities with power greater than 50 MW of solid biomass must follow this standard and to combine production of electricity with the heat and/or cooling systems they have. Besides, it must offer other alternative for

the use of biomass with the purpose of producing advanced fuels with GHG emission reductions close to 100%, achieving a more complete and sustainable process for production of energy or bioenergy.

The annual production of cellulosic biomass is estimated to be 130 billion metric tons on a dry weight basis, equivalent to 65 billion metric tons of standard coal (Wang et al. 2022b). Worldwide, the use of advanced biofuels and other renewable fuels are alternative proposals until 2030 (Łukasik et al. 2021). Therefore, there are studies related to the conversion of cellulosic biomass into biofuels, including bioethanol. The bioethanol and biodiesel have been the most promising biofuels in substitution to fossil fuel (Tabatabaei & Aghbashlo 2020).

In this context, researchers like Sewsynker-Sukai & Kana (2018), e Silva et al. (2018), Malik et al. (2021), Lyu et al. (2021) and Ai et al. (2021), with the objective of producing bioethanol, used potato and corn cobs, jam, cotton stalk, cassava straw and rice straw, respectively. Therefore, biomass can be converted into bioenergy through production processes, like bioethanol. Worldwide, this type of conversion has been considered a priority to minimize carbon dioxide emissions into the atmosphere (Freita et al. 2017, Liu et al. 2022, Wang et al. 2022b).

In view of non-edible resources and biomass, according to Tabatabaei & Aghbashlo (2020) the bagasse was labeled as feedstock of the third-generation biofuels, because they are generated through different processes and they are not related with any upstream environmental burdens (GHG emissions nor carbon footprints). For example, Su et al. (2020), from cellulose present in sugar sorghum bagasse, produced bioethanol and biobutanol. In contrast, Zhang et al. (2021a) obtained bioethanol from the hemicellulose constituent in corn fiber.

Therefore, aiming to improve energetic efficiency and process productivity with the sustainable use of biomass, there is research related to the development of processes that generate multi-products, with the objective of improving the economic viability that this feedstock demands (Tabatabaei & Aghbashlo 2020).

According to Laltha et al. (2021) and Liu et al. (2022), biomass is composed of cellulose, hemicellulose, lignin, starch, oil, inorganic components and little water. In addition, Silveira et al. (2015) point out that cellulose and hemicellulose can be converted into fermentable sugars and other chemicals. Lignin can serve as binders in construction systems, biodegradable plastic additives, adhesives, phenolic and epoxy resins, among others (Silveira et al. 2015).

Those components are organized in a complex and non-uniform way in the cell wall of the biomass and the lignin promotes the recalcitrance on the cell wall of the biomass (Gu et al. 2019, Ashokkumar et al. 2022). In other words, this behavior makes it difficult for chemical and biological access to cellulose. According to Ashokkumar et al. (2022), recalcitrance is affected by cellulose crystallinity, lignin hydrophobicity and cellulose encapsulation by the lignin-hemicellulose matrix, associated by strong covalent and hydrogen bonds.

Fockink et al. (2020) highlighted that the removal of lignin is one of the essential factors for the efficiency of enzymatic hydrolysis, because lignin promotes the unproductive and/or irreversible between binding of cellulases and β-glycosidases, fact that hinders enzymatic hydrolysis. The same researchers point out that the increase in surface area allows increased accessibility of the enzyme to carbohydrates. Furthermore, the change and reduction in the crystallinity of the biomass, it can improve efficiency on enzymatic hydrolysis (Bernardo et al. 2019, Fockink et al. 2020). For example, Fockink et al. (2020) and Bernardo et al. (2019) analyzed the effectiveness of different pretreatments

and the observed performance by yield on enzymatic hydrolysis. Fockink et al. (2020) used cotton spinning residues (dirty cotton residue – DCR and cotton filter powder - CFP) as feedstock, to conversion of glucan to glucose and xylan to xylose. And Bernardo et al. (2019) wheat straw and eucalyptus, to conversion of glucan to glucose. In addition, imidazole and ionic liquid pretreatments were applied by Fockink et al. (2020) and, hydrogen-bond acidic 1-ethyl-3-methyimidazolim hydrogen sulphate ionic liquid, as also hydrogen-bond basic 1-ethyl-3-methylimidazolium acetate by Bernardo et al. (2019), allowing this last process to produce high purity cellulose, hemicellulose and lignin fractions. From the pretreatment methods proposed, Fockink et al. (2020) and Bernardo et al. (2019) observed a change in biomassa crystallinity from cellulose, fact that affects the glucose yield. Therefore, the researchers concluded that crystallinity and delignification are important to yield on the enzymatic hydrolysis.

Moreover, Fockink et al. (2020) reached 45.5% $(w.v^{-1})$ of delignification for biomass DCR, being possible to achieve 78.0 and 94.9 mol% of yield to conversion of glucan and xylan, respectively. In contrast, from CFP biomass with 16.0% $(w.v^{-1})$ of delignification, they reached 75.8 mol% of glucan and 94.9 mol% of xylan. Then, applying 13.7% $(w.w^{-1})$ substrate total solids and 20 $FPU.g^{-1}$ glucan, they obtained 40 $g.L^{-1}$ glucose.

Bernardo et al. (2019), on pretreatment with acetate, on conversion of glucan in glucose they achieved yield of 93.1 mol% and 82.9 mol% for wheat straw and eucalyptus, respectively. In contrast, from biomass wheat straw and eucalyptus with hydrogen sulphate ionic liquid on pretreatment, they obtained 61.6 mol% and 7.9 mol%, respectively.

Therefore, it is noted that the lignocellulosic feedstocks must be exposed to additional processing to obtain the biofuel (Silveira et al. 2015, Tabatabaei & Aghbashlo 2020). Thus, the main steps for the process in the production of bioethanol include pre-treatment, hydrolysis, fermentation and distillation. In the production of bioethanol from lignocellulosic material, it is necessary that the cellulose is accessible to enzymatic attack, and subsequent production this liquid biofuel (Gu et al. 2019).

Therefore, from that a conversion process in biofuel to make economically and efficient viable, the first prerequisite is the development of adequate and sustainable pretreatment techniques to maximize the yield of fermentable sugars (Silveira et al. 2015). In general, the main objectives of pretreatment in lignocellulosic biomass are to reduce and promote changes in the crystallinity of the biomass, increase the accessibility of cellulose and surface area, as well as the partial solubilization of lignin-carbohydrate complexes and hemicellulose (Silveira et al. 2015, Fockink et al. 2020).

In this context, to overcome these challenges, it is necessary to start using physical, physical-chemical, chemical and biological pre-treatment techniques (Silveira et al. 2015, Jugwanth et al. 2020, Saravanan et al. 2022). In addition, new technologies with the use of nonaqueous and nonderivatizing solvents, sub/supercritical fluids for biomass processing are reported by Silveira et al. (2015) in their study, classified as green solvents. There are several methods described in the literature, and the selection of the type of pre-treatment to be used in the delignification of biomass is based on the chemical composition and physical nature of the raw material, as well as the desired final product (Silveira et al. 2015, Bernardo et al. 2019). However, there is no universal pre-treatment technique for different biomasses, as these methodologies are in a development stage (Gírio et al. 2010, Silveira et al. 2015).

As pointed out, making cellulose more accessible to the enzyme is one of the goals of pre-treatment for biofuel production (Silveira et al. 2015). Therefore, various pretreatment methods remove hemicellulose fractions to reduce structural constraints in the enzymatic hydrolysis of cellulose step (Gírio et al. 2010). However, hemicellulose is also a material of interest and it can increase the biofuel yield from lignocellulosic biomass (Gírio et al. 2010, Akhtar et al. 2016).

Then, depending of pretreatment and operating conditions, this component can be converted in hexose and pentose sugars, which can be transformed into value-added products, as xylitol, ethanol, butanediol, butanol, polylactates, among others (Gírio et al. 2010, Akhtar et al. 2016). Gírio et al. (2010) point out that, to produce a selective solubilization of hemicellulose and solids enriched with cellulose for subsequent bioprocessing, the most commonly used pre-treatments are acids, water and steam. Thus, obtaining the hemicellulose present in lignocellulosic biomass in pre-treatment processes occurs at lower severity factors, preventing the degradation of the hemicellulosic sugars (Gírio et al. 2010). In order to achieve high efficiency in the enzymatic hydrolysis of cellulose, pre-treatment of the biomass must be carried out at higher severity conditions (Gírio et al. 2010).

In the production of bioethanol, the second crucial step is the hydrolysis of cellulose and hemicellulose, in which biological methods are the most conducive to breaking down cellulose and hemicellulose into simple monomers (Melendez et al. 2022). The enzymatic hydrolysis process can achieve high specificities in the hydrolysate and minimizes the formation of inhibitory compounds compared to chemical hydrolysis (de Godoy et al. 2019, Melendez et al. 2022). In addition, this process works under mild conditions of pH and temperature, and provides high glucose concentration rates without causing corrosion problems (Panahi et al. 2020, Meenakshisundaram et al. 2021).

Zhang et al. (2021b) point out that, with the use of cellulosic feedstock in enzymatic hydrolysis, the process becomes complex, since the enzymatic molecules need to adsorb and diffuse on the surface of the cellulose present in the biomass. The adsorption must be efficient in order to reach high rates of glucose concentration and production of biofuel, for example bioethanol.

The representation of chemical, physical and biological processes that occur in bench tests to large-scale processes can be analyzed using mathematical and simulation methods. In the literature, there are numerous studies related to process modeling and simulation (Coelho et al. 2020b, Singh et al. 2022, Oliveira et al. 2021, Wang et al. 2022a, Storchak et al. 2022).

Furthermore, with the aim of better process efficiency, optimization is being widely used by researchers (Whitaker 1972, de Godoy et al. 2019, Coelho et al. 2020a). From the optimization, it is possible to identify the optimal operating conditions, making it possible to maximize the yield and efficiency of a process, as well as reduce cost and operating time (Saravanan et al. 2022).

According to de Godoy et al. (2019), with the objective of obtaining high yields in hydrolysis, there are researches related to the use of high solids loads ($> 15\%\ w.w^{-1}$) in the enzymatic hydrolysis of cellulose. However, the same researchers stress that this type of strategy causes some problems, such as an increase in the viscosity of the reaction medium, limitations in mass transfer and, often, with the increase in the initial solids content, there is a decrease in the conversion of cellulose to glucose.

In addition, Angarita et al. (2015) highlights others barriers to the production of cellulosic bioethanol by biochemical route, such as the high cost of the enzymes and the slow kinetics that reflect the mechanism (low operating rate). Therefore, it is important to model the enzymatic hydrolysis stage to evaluate the reaction behavior and determine adequate feeding policies in this process, as well as

analyze and optimize the main parameters in the conversion system (de Godoy et al. 2019, Zhang et al. 2021b).

Therefore, there are numerous kinetic models to predict the properties in enzymatic hydrolysis of lignocellulosic biomass (Cavalcanti-Montaño et al. 2013, Angarita et al. 2015, Sitaraman et al. 2019, de Godoy et al. 2019, Wojtusik et al. 2020, Zhang et al. 2021c). These models are composed of mathematical equations that aim to evaluate the behavior of the physicochemical process. Thus, from experimental tests and modeling, one can have an understanding of the mechanism in hydrolysis, as performed by Cavalcanti-Montaño et al. (2013), Carvalho et al. (2013), Sitaraman et al. (2019), Coelho et al. (2020a), Wojtusik et al. (2020), Yu et al. (2021), Zhang et al. (2021c).

For example, Zhang et al. (2021c) developed a kinetic model based on the Michaelis-Menten theory and an enzymatic deactivation model to describe the yield of fermentable sugars, glucose and xylose in the enzymatic hydrolysis step. They determined empirical equations for the conversion of glucan to glucose and conversion of xylan to xylose. Therefore, fast equilibrium assumption, in which the enzyme/substrate bond in the product formation was considered the limiting step; xylan hydrolysis products cannot inhibit cellulase activity and the product of glucan hydrolysis cannot inhibit xylanase activity. Then, those researchers concluded that the combination of models allowed a high precision of fit to the experimental data, for enzymatic hydrolysis by different compositions of pre-treated bagasse, in addition to providing the analysis of the yield in the pre-treatment step.

Tervasmäki et al. (2017) developed a model applicable to fed-batch hydrolysis aiming at high substrate concentration. Thus, they developed two models, one simplified and one complete model. The simplified model includes only the enzymatic adsorption and the first-order reaction of the enzyme-substrate complex. The complete model involves competitive glucose inhibition and decreasing rate factors related to substrate and enzyme behavior. Therefore, the substrate composition is structurally uniform and there is no distinction between the hydrolysability of amorphous or crystalline cellulose; the non-cellulosic part is considered inert; there is no distinction between endo/exo-enzymatic behaviors; the rate of cellobiose to glucose conversion is not a limiting factor and is not explicitly included in the model; the enzymatic adsorption follows the Langmuir-type adsorption behavior, and the reaction rate is of the first order in relation to the concentration of enzyme-substrate complexes; there is competitive inhibition of glucose. The solids concentration varied between 5 to 50 $g.L^{-1}$. In the experimental tests, they obtained glucose concentrations of up to 100 $g.L^{-1}$. On the other hand, for the complete model that presented the best fit, they found results below 40 $g.L^{-1}$, for initial concentration of solids from 30 $g.L^{-1}$.

The models differ from each other by the substrate to be analyzed and its composition, enzyme used in the hydrolysis process, operating conditions (temperature, pressure and agitation), as well as simplifications for modeling. As exposed by Zhang et al. (2021c), the calculated kinetic constants can be used to analyze the bioethanol production process, determining optimal hydrolysis conditions with low cost and high efficiency.

Presently, advances are observed in the production of biofuel from the synergy between experimental studies, modeling and simulation in the enzymatic hydrolysis stage (Zhang et al. 2021b). In view of this synergy, strategies can be applied to optimize parameters, aiming to reduce enzyme consumption and its reuse, as well as obtaining high rates of conversion of cellulose into glucose. For example, de Souza Soares et al. (2019) used non-linear regression to determine the kinetic

parameters, maximum reaction rate and Michaelis-Menten constant, present in the model that defines the enzymatic hydrolysis of sucrose. Based on experimental data, Carvalho et al. (2013) analyzed different models and determined the kinetic parameters. Cavalcanti-Montaño et al. (2013) proposed a kinetic model to determine glucose concentration with simultaneous feeding of enzyme and substrate. With this, Cavalcanti-Montaño et al. (2013) performed a manual fine-tuning to define the parameters present in the model.

Moreover, optimization was used by Cruz et al. (2020), Leite et al. (2021) and Silveira et al. (2017) to estimate parameters in different processes. Cruz et al. (2020) analyzed empirical models proposed in the literature that determine the adsorption capacity of a given adsorbent in the adsorption system, Silveira et al. (2017) worked with empirical equations to describe the diffusion coefficient in essential oil extraction and Leite et al. (2021) evaluated a kinetic model for heat-induced denaturation of milk proteins. These researchers applied different strategies, linear and non-linear models, to set up the optimization problem and to estimate the parameters present in each model. Thus, these parameters were estimated by solving an optimization problem based on the sum of squared errors between simulated and experimental values.

Therefore, with the objective of performing modeling and optimization in the enzymatic hydrolysis step to achieve high glucose levels, the dynamic model chosen for this study was developed by Cavalcanti-Montaño et al. (2013), being composed of kinetic equation. It is noteworthy that the choice of this model came from the opportunity to be able to replicate the experimental results obtained by Cavalcanti-Montaño et al. (2013) in their study, but also for presenting as a differential to the models provided in the literature, the feeding of enzyme and substrate simultaneously in the proposed system presented by the researchers. Thus, for maximizing the concentration of glucose, as a differential to the one already carried out by the researchers who proposed the model, this work will analyze the influence of evaporation on the response to the concentration of the final product in the enzymatic hydrolysis of the cellulose present in the sugarcane bagasse.

MATERIALS AND METHODS

The dynamic model analyzed in this study was developed by Cavalcanti-Montaño et al. (2013), consisting of kinetic equations and mass balances. To calculate the model and analyze the evaporation in the response to the glucose concentration in the enzymatic hydrolysis of cellulose present in sugarcane bagasse, the experimental data also obtained by Cavalcanti-Montaño et al. (2013) has been considered.

Model presentation

The model chosen to be analyzed in this study was the dynamic model developed by Cavalcanti-Montaño et al. (2013). These researchers used a pseudo-homogeneous Michaelis-Menten kinetic model, with product inhibition, proposed by Cavalcanti-Montaño et al. (2013). This model was developed for the dynamic modeling of a fed-batch reactor in order to sustain high rates of glucose production by adding enzyme and substrate simultaneously during the process.

The model is represented by mass balances for volume, substrate concentration and product concentration, equations 1, 2 and 3 respectively.

$$dV/dt = F_{feed} \tag{1}$$

$$\frac{dS}{dt} = \frac{F_{feed} \cdot S_{feed}}{V} - r - \frac{F_{feed} \cdot S}{V} \tag{2}$$

$$\frac{dP}{dt} = r - \frac{F_{feed} \cdot P}{V} \tag{3}$$

Where, F_{feed} represents the substrate flow rate fed $\left(L.\,\mathrm{min}^{-1}\right)$, S_{feed} the substrate concentration in the feed in terms of potential glucose $(g.L^{-1})$, V the reaction volume at a given instant of time (L), r denotes reaction rate by the Michaelis-Menten model with inhibition by the product (glucose) $\left(g.L^{-1}.\,\mathrm{min}^{-1}\right)$ and P represents the time glucose concentration $(g.L^{-1})$.

The reaction rate that describes the kinetic behavior of the system is represented by equation 4. It is noteworthy that, in the kinetic model (equation that determines the reaction rate), it was not explicitly considered ineffective enzyme adsorption on lignin, interference effects (overcrowding of enzymes in the substrate matrix), cellobiose inhibition and thermal inactivation of enzymes. However, these phenomena were considered in the kinetic constants present in the equation that determines the hydrolysis rate, which will be presented in the sequence of this work. Enzymes were grouped into a single pseudo-catalyst.

$$r = \frac{K \cdot e \cdot S}{K_m \cdot \left[1 + \frac{P}{K_i}\right] + S} \tag{4}$$

Where, K represents the maximum reaction speed $\left(g.L^{-1}.\,\mathrm{min}^{-1}\right)$, e is the concentration of enzyme inside the reactor (unit: $(g.L^{-1})$), S is the substrate concentration at a given instant of time $(g.L^{-1})$, K_m is the Michaelis-Menten constant $(g.L^{-1})$, P represents the time glucose concentration $(g.L^{-1})$ and K_i represents the enzyme inhibition constant by the product $\left(g.L^{-1}.\,\mathrm{min}^{-1}\right)$.

In addition, Cavalcanti-Montaño et al. (2013) developed the feed dynamics for enzyme and substrate, in a fed-batch reactor. Equations 5 and 6 represent the feed profile of additional amounts of enzyme (e_{feed}), to maintain a high reaction rate (r close to *rinitial*), while the reaction proceeds, even with the presence of the enzyme inhibitor (product P).

$$e_{feed} = e \cdot V \cdot 108 - e_{accumulated} \tag{5}$$

The enzyme concentration is calculated by:

$$e = \frac{r_{initial} \cdot K_m \cdot \left(1 + \frac{P}{K_i}\right) + S_0}{K \cdot S_0} \tag{6}$$

Where, e denotes the concentration of enzyme inside the reactor (unit: $(g.L^{-1})$), e_{feed} represents the additional amounts of enzyme to the reactor (unit: FPU – Filter paper Unit), V reactor volume (unit: L), $e_{accumulated}$ represents the amount of enzyme already introduced into the reactor, in other words, enzyme already accumulated inside the reactor (unit: FPU) and 108 FPU the concentration of the enzyme complex used in the study, with FPU representing the unit of filter paper.

The substrate feed rate is represented by equation 7, which relates reaction speed (substrate consumption rate) (r), multiplied by the reactor volume (V). These two variables are divided by the difference between the substrate concentration fed (S_{feed}) and potential glucose concentration (S_0). This substrate flow aims to $\frac{dS}{dt} = 0$, in other words, the substrate is added to the reactor as it is consumed.

$$F_{feed} = \frac{r \cdot V}{S_{feed} - S_0} \tag{7}$$

Thus, the dynamic model proposed by Cavalcanti-Montaño et al. (2013) is represented by equations 1 to 7, as previously presented. This model was used in the present work to determine the glucose concentration in the enzymatic hydrolysis step.

System analyzed for the determination of glucose concentration

The system analyzed in this work is represented in Figure 1, in which substrate (sugar cane bagasse) and enzyme are added to produce glucose. Additional details about the system and experimental data can be found in Cavalcanti-Montaño et al. (2013).

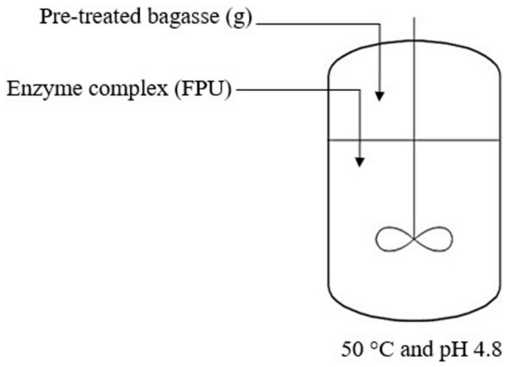

Figure 1. Scheme of the system to be studied.

Therefore, in order to make the model calculation possible, the kinetic parameters of the dynamic model were determined. This parameter estimation was performed from the experimental results presented by Cavalcanti-Montaño et al. (2013), for a single-batch reactor. With the kinetic parameters defined, the calculation of the dynamic model was performed, based on the experimental results also obtained by the same researchers and evaluating the influence of evaporation in the system, but for a reactor operating in fed-batch.

The substrate used by Cavalcanti-Montaño et al. (2013) and analyzed in this work is bagasse pre-treated and delignified with 4% NaOH, according to the chemical composition described in Table I.

The enzyme used in the experimental tests by Cavalcanti-Montaño et al. (2013) was the commercial complex of Accellerase cellulases® 1500 of Trichoderma reesei. Cavalcanti-Montaño et al. (2013) point out that the complex has better stability between 50 and 65 °C, at a pH range of 4.0 to 5.0. Thus, the researchers worked at a temperature of 50 °C, since at higher temperatures the efficiency time of this complex is compromised, due to the inactivation of the enzyme. Furthermore, it was considered that 1 g of enzyme complex is equivalent to 108 FPU.

Table I. Chemical composition of pre-treated bagasse for enzymatic hydrolysis (Cavalcanti-Montaño et al. 2013).

Chemical composition of bagasse	Pre-treated bagasse
Cellulose	70.12%
Hemicellulose	3.79%
Lignin	19.32%
Ashes	4.25%

Furthermore, Cavalcanti-Montaño et al. (2013) used the Total Reducing Sugars method, being determined that the concentration of the enzymatic activity used in the process was 842.4 $FPU.L^{-1}$. Therefore, Table II presents the operating conditions for the system to be analyzed.

Table II. Operating conditions of the system to be studied (Cavalcanti-Montaño et al. 2013).

Operating conditions	Reference values
Humidity (%)	82
% Cellulose	0.7
Reactor volume (L)	0.2
Temperature (°C)	50
Initial reaction volume in the reactor (L)	0.05
Initial substrate concentration ($g.L^{-1}$)	44.44
Initial enzyme concentration ($FPU.L^{-1}$)*	842.4

* The initial enzyme concentration corresponds to the concentration of the enzyme activity used in the process (FPU: filter paper units).

In order to estimate the kinetic parameters, the experimental data was used from Cavalcanti-Montaño et al. (2013). Thus, Cavalcanti-Montaño et al. (2013) used a reactor operating in single-batch, in which enzyme was added only once to the bench reactor, the initial concentration of enzyme was 7.8 $g.L^{-1}$ which corresponding to 842.4 $FPU.L^{-1}$. In addition, the initial concentration of potential glucose present in sugarcane bagasse was 44 $g.L^{-1}$, at a constant volume of approximately 0.05 L.

The experimental procedure for a fed batch reactor applied by Cavalcanti-Montaño et al. (2013) is: a 200 mL reactor operating in fed batch, with mechanical agitation (Rushton impeller), was initially fed with 0.39 g (equivalent to 42.5 FPU) from the enzyme extract Accellerase® 1500, along with 37.3 mL of 50 mM sodium citrate buffer. This amount of mass is equivalent to the initial enzyme concentration of 7.8 $g.L^{-1}$, which corresponds to 842.4 $FPU.L^{-1}_{solution}$ (107.95 $FPU.g^{-1}$). The experiment started with the addition of pre-treated wet bagasse, containing 70% cellulose, corresponding to a potential glucose concentration of 44 $g_{potential_glucose}.L^{-1}_{solution}$. Substrate feeding occurred approximately every 1 hour. This substrate feeding occurred until approximately 87h.

The enzyme feeding performed by Cavalcanti-Montaño et al. (2013), occurred in three pulses throughout the process, being added before the first 30h. An amount of enzyme of 35.6 FPU was added at 3.3h of the experiment, followed by 78.8 FPU at 9.7h, and in the last pulse 239.1 FPU at 24h. It is noteworthy that, in the initial time, the simulation has already started with an initial value of 42.5 FPU, totaling 396 FPU at the end of the process. Therefore, for this work, the analysis for the enzyme feed followed the same methodology applied by Cavalcanti-Montaño et al. (2013) in their experiments.

The supernatant was collected by Cavalcanti-Montaño et al. (2013) and analyzed in order to determine the glucose concentration throughout the process, in fed batch. Thus, the glucose concentration and the reactor volume obtained by Cavalcanti-Montaño et al. (2013), were also analyzed in the simulation. It should be noted that these values were collected from the study carried out by Cavalcanti-Montaño et al. (2013).

Methodology

Two different algorithms were developed. The first computational routine aimed to estimate the kinetic parameters of the dynamic model analyzed in this study, namely: maximum reaction rate (K), Michaelis-Menten constant (K_m) and inhibition constant by the product (K_i). The second routine had the purpose of determining the glucose concentration, using the kinetic parameters optimized in the first algorithm and considering the evaporation that occurred in the enzymatic hydrolysis process.

Therefore, for the first computational routine, it was considered that the volume for the determination of the kinetic parameters is constant and equal to 0.05 L. The variables of this first routine were the substrate concentration and glucose concentration. Furthermore, it was considered that the enzyme feeding occurs only once with the concentration of 842.4 $FPU.L^{-1}$ (107.95 $FPU.g^{-1}$).

So, in the first algorithm, the objective function was defined. This objective function aimed to minimize the sum of squared errors in relation to simulated and experimental data for glucose concentration, manipulating the kinetic parameters. In other words, it was used a nonlinear least-squares regression model to estimate parameters. The equation 8 represents this model, in which it uses optimization algorithm to estimate parameters that minimize the sum of squared residuals from a given model, starting from an initial guess (Leite et al. 2021).

$$SSe = \sum_{i=1}^{no} (y_i - \hat{y}_i)^2 \tag{8}$$

Where, *SSe* is the sum squared errors, *i* is the index for each estimation, *no* is the number of experimental points, y_i is the experimental observation of index *i*, $\hat{y}_i$ is the *y* value calculated by the model for the observation of index *i*, using estimated parameters.

Figure 2 presents a schematic representation of the first computational routine developed for the optimization of kinetic parameters.

With the kinetic parameters optimized, the second computational routine was developed. This second routine had volume, substrate concentration and glucose concentration as variables, (equations 1 to 3, respectively).

However, they were not provided by Cavalcanti-Montaño et al. (2013) experimental data for dry substrate concentration and volumetric feed flow. These data are important for the calculation of the dynamic model, according to the variables already reported in the previous paragraph. Therefore, it

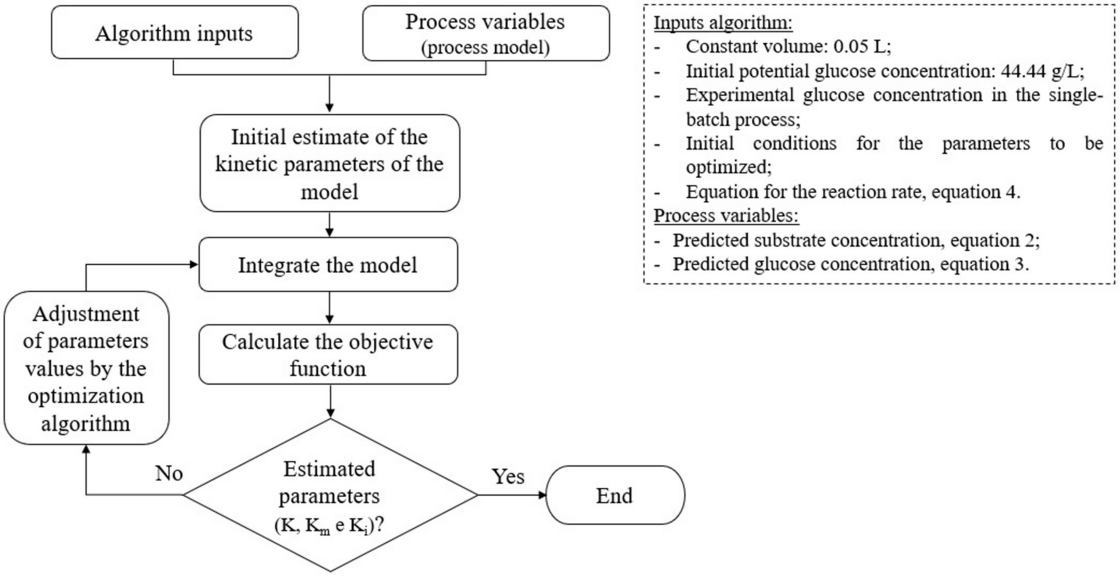

Figure 2. Scheme of the methodology used to determine the optimized kinetic parameters.

was necessary to determine the rate of dry substrate and volumetric flow of experimental feed. Thus, the experimental data for bagasse fed and reaction volume were used for the calculation.

In addition, in the second computational routine, it was necessary to define the substrate concentration in the feed, or also known as the potential glucose concentration in the feed, (S_{feed}). The equation that determines the predicted substrate concentration in the feed was based on dos Santos-Rocha et al. (2018).

As previously mentioned, this work presents as a differential the dynamic model already calculated by Cavalcanti-Montaño et al. (2013) the determination of the evaporation rate for the enzymatic hydrolysis process, as well as the analysis of the influence of this rate in the calculation of the glucose concentration. Therefore, the evaporation rate was determined at the moment when the substrate feeding was finished, according to experimental data obtained by Cavalcanti-Montaño et al. (2013). For this calculation it was assumed that the evaporation is linear (constant between the time intervals).

In addition, it was incremented other relevant information for the model calculation, obtained experimentally by Cavalcanti-Montaño et al. (2013). They are: the enzyme pulses, initial volume in the reactor of 0.05 L, initial concentration of potential glucose of 44 $g_{potential_{glucose}} \cdot L^{-1}_{solution}$, Table II, percentage of cellulose present in the bagasse of 0.7, Table I, and the optimized kinetic parameters obtained in the first computational routine carried out in this study. Thus, integration was performed to predicted glucose concentration. Figure 3 presents a scheme for the second computational routine developed to calculate the glucose concentration, evaluating the influence of evaporation on the response and using the kinetic parameters determined in the first algorithm developed in this work.

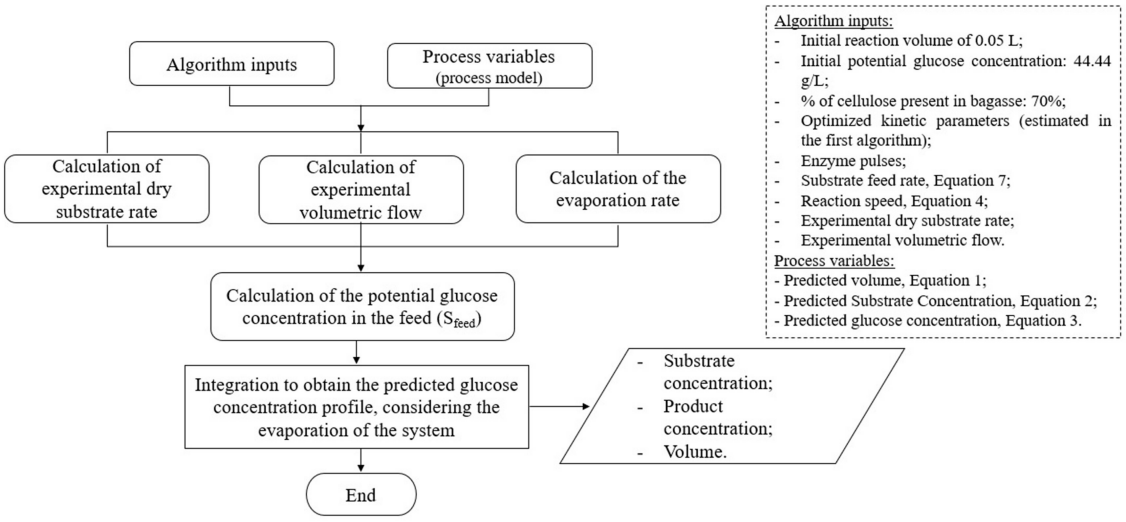

Figure 3. Scheme of the methodology used to determine the glucose concentration, evaluating the influence of evaporation.

RESULTS AND DISCUSSIONS

In the optimization, a direct search method was applied for the optimization of the parameters. According to Edgar et al. (2001), this method was developed by Nelder & Mead in 1965, being a more efficient and more complex version of the Simplex Search Method. Therefore, in the first computational routine of this work, the Matlab fminsearch optimization routine was used to estimate the kinetic parameters.

A tolerance is prescribed so that the routine is interrupted and the optimal point is determined, that is, the values of the minimum of the function are determined (Edgar et al. 2001).This tolerance was 10^{-7}.

In order to evaluate the results found in the simulation of this work, the curve of glucose concentration as a function of time was reproduced for the single-batch process obtained by Cavalcanti-Montaño et al. (2013). The kinetic parameters found by Cavalcanti-Montaño et al. (2013) by manual adjustment were: K = 0.112 $g.L^{-1}$. min^{-1}, K_m = 15.0 $g.L^{-1}$ e K_i = 4.5 $g.L^{-1}$. The sum of squared errors was determined by this simulation in order to quantify the deviation between the experimental and simulated curves, obtaining 5.60. Figure 4 shows a comparison between the experimental data and simulations obtained by Cavalcanti-Montaño et al. (2013).

Table III presents the variables considered for the optimization obtained by Cavalcanti-Montaño et al. (2013) and the parameters estimated by solving the optimization problem to minimize the *SSe*. Also, Figure 4 shows the result obtained with this simulation.

After optimization, the sum of squared errors was of 2.12. It can be seen from Figure 4 that for times less than 3.5h, a solution made by the parameters used in this work is described in a more adequate way to the experimental data. However, in the interval between 7h and 24h, a solution performed using the parameters of Cavalcanti-Montaño et al. (2013) were more appropriate. As for the time interval between 100h and 120h, a solution found through the parameters estimated in this study and by

Table III. Variables considered for the optimization and result obtained after the optimization of the kinetic parameters.

Kinetic parameters	Variables considered for the optimization, obtained by Cavalcanti-Montaño et al. (2013)	Optimized parameters in this work
K	0.112 $g.L^{-1}.\,min^{-1}$	0.214 $g.L^{-1}.\,min^{-1}$
K_m	15.0 $g.L^{-1}$	40.8 $g.L^{-1}$
K_i	4.5 $g.L^{-1}$	3.1 $g.L^{-1}$

Cavalcanti-Montaño et al. (2013) were similar. In addition, the mean relative error in the simulation was lower when compared to the value found before the parameters, 6.89% and 16.88%, respectively.

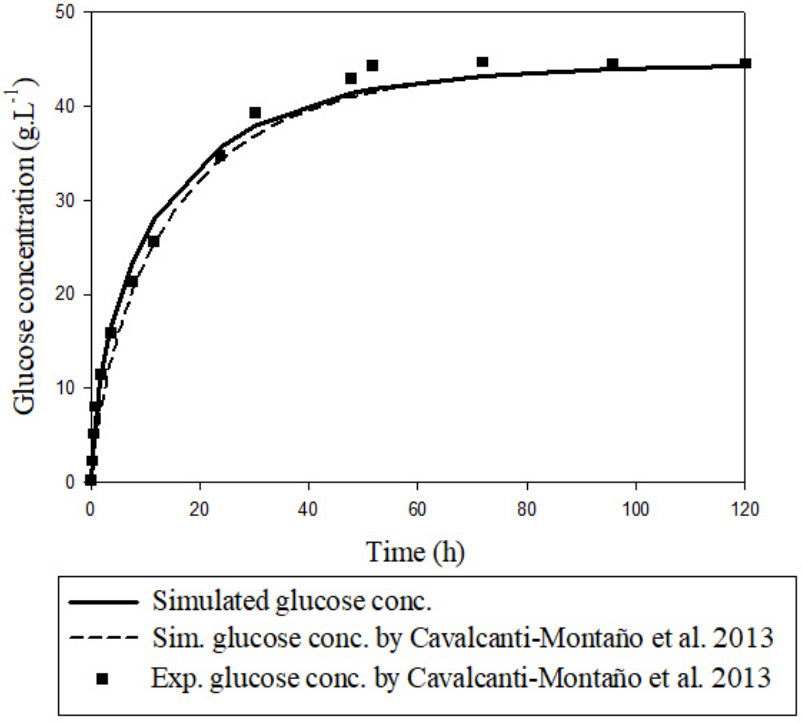

Figure 4. Experimental data by Cavalcanti-Montaño et al. (2013), simulated results by Cavalcanti-Montaño et al. (2013) and simulated results in this study.

In addition, according to research related to the subject, the results obtained for the kinetic parameters, after optimization, were similar to those already proposed in the literature (Carvalho et al. 2013, Bezerra et al. 2016, de Godoy et al. 2019, Yun & Han 2020, Zhang et al. 2021c). Haldar et al. (2018) and Saha et al. (2019) studied the hydrolysis process, also using sugarcane bagasse as lignocellulosic material, and obtained as kinetic parameters the maximum rate of reaction between 0.00433 $g.L^{-1}.\,min^{-1}$ to 0.4046 $g.L^{-1}.\,min^{-1}$ and Michaelis-Menten constant between 11.53 $g.L^{-1}$ a 45.66 $g.L^{-1}$.

The *ode*23 function from Matlab was implemented as an integrator to solve the dynamic model and, thus, the predicted values for glucose concentration, substrate concentration and volume were obtained, being evaluated the influence of evaporation on the response to glucose concentration.

Figure 5 presents a comparison of volume for the experimental and simulated data by Cavalcanti-Montaño et al. (2013) and the result obtained in this work. It can be seen that considering the evaporation that occurred in the enzymatic hydrolysis process, the behavior of the profile for the predicted volume in this work is similar to the experimental volume obtained by Cavalcanti-Montaño et al. (2013), Figure 5.

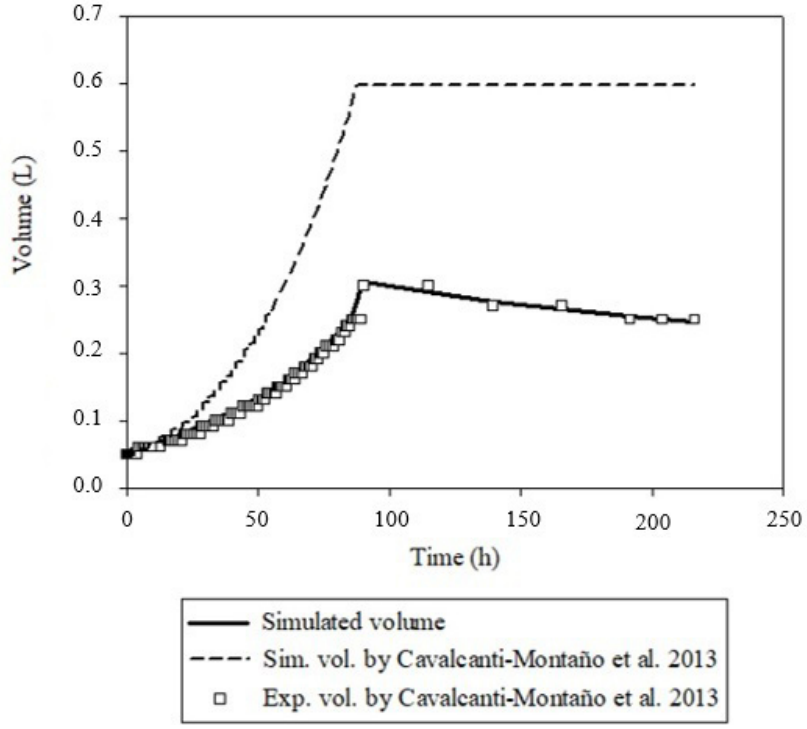

Figure 5. Experimental data by Cavalcanti-Montaño et al. (2013), simulated results by Cavalcanti-Montaño et al. (2013) and simulated results in this study.

In addition, considering the evaporation that occurred in the system under analysis, the profile for the predicted glucose concentration was obtained, as shown in Figure 6. The kinetic models developed are composed of factors that can affect this stage, as well as simplifications are performed from these phenomena to minimize the complexity in the model calculation.

In general, the most relevant factors for the model are the substrate characteristics (degree of polymerization, crystallinity, accessible surface area, lignin content) and enzyme characteristics (adsorption, inhibition, synergism and activity) (Angarita et al. 2015, Wojtusik et al. 2020). As a differential, Wojtusik et al. (2020) included in their modeling the analysis of the reactivity and intensity of the pretreatment, in order to observe the nature of the material used in the process and the severity of the pretreatment process adopted by the researchers. So, Wojtusik et al. (2020) concluded that glucose yield is affected by these factors. But Sitaraman et al. (2019) in their model, considered the fluid dynamics and the transport of solids and dissolved species.

Therefore, the Table IV shows some works related to models proposed in the literature to analyze the conversion of cellulose to glucose. Those models are represented by mathematical equations and composed by parameters with the objective of evaluate the behavior of the mechanism in the enzymatic hydrolysis step and to reach high glucose concentration.

Table IV. Mapping of kinetic models proposed in the literature for the enzymatic hydrolysis process.

Objective	Model Description	Feedstock	Results	Reference
Describe the yield of fermentable sugars, glucose and xylose in the enzymatic hydrolysis step.	They developed a kinetic model based on the Michaelis-Menten theory and an enzymatic deactivation model. Then, they determined empirical equations for the conversion of glucan to glucose and conversion of xylan to xylose.	Bagasse pre-treated with hot water, hydrochloric acid (HCl) and sodium hydroxide (NaOH).	They concluded that the combination of models allowed a high precision of fit to the experimental data, for enzymatic hydrolysis by different compositions of pre-treated bagasse, in addition to providing the analysis of the yield in the pre-treatment step.	Zhang et al. (2021c)
Describe the enzymatic hydrolysis rate, analyzing the nature and intensity of two pretreatments.	They proposed a kinetic model to analyze the nature and intensity of two pretreatments. Thus, they defined the equation for reaction rate and apparent kinetic constant. Those equation were composed by factors of intensity of pretreatment, the accessibility of the enzyme to the substrate and reactivity.	Wheat straw, corn husk and thistle stalks. These biomasses were pretreated with dilute sulfuric acid and ethanol-water.	They concluded that the kinetic model describes the experimental results obtained in the enzymatic hydrolysis for the three raw materials used in the study, in different operating conditions. In addition, wheat straw was the most reactive and thistle stalk the most recalcitrance.	Wojtusik et al. (2020)

Table IV. Mapping of kinetic models proposed in the literature for the enzymatic hydrolysis process (cont.).

Objective	Model Description	Feedstock	Results	Reference
They developed a kinetic model for the enzymatic hydrolysis reaction in a reactor, considering the fluid dynamics and the transport of solids and dissolved species.	Implementation of equations for fluid transport (substrate and enzyme), equation to determine the substrate concentration; enzyme concentration, taking into account the adsorption of the enzyme to cellulose.	Cellulose substrate.	They concluded that the proposed model perfectly predicted the conversion mechanisms that occur in enzymatic hydrolysis. In addition, the model provided fidelity to capture the substrate gradients within the reactor.	Sitaraman et al. (2019)
Describe the process of fed-batch hydrolysis for a wide range of solids content. In addition, optimization to determine the operating conditions in the fed-batch enzymatic hydrolysis step.	They proposed a kinetic model composed by empirical equations to determine the modified inhibition constant, reaction rate (involves Michaelis-Menten model with product inhibition) and developed mass balances for the concentration of cellulose and glucose.	Hydrothermally pre-treated bagasse (HB) and bagasse pre-treated with diluted and delignified acid (ADB).	They observed that the kinetic model fits the experimental data, mainly for the loading of solids 5, 15 and 20% $w.v^{-1}$. Furthermore, it was possible to achieve high sugar levels for both substrates, at 131.24 $g.L^{-1}$ for HB and 131.46 $g.L^{-1}$ ADB. They also noticed that the reaction yield for the HB substrate decreased from 67.56% to 65-63%, due to the inhibition of the product. As for the ADB substrate, the yield reduced from 66.16% to 55-52 %.	de Godoy et al. (2019)

Table IV. Mapping of kinetic models proposed in the literature for the enzymatic hydrolysis process (cont.).

Objective	Model Description	Feedstock	Results	Reference
Analyzing the saccharification of cellulose to glucose concentration in a novel fed-batch horizontal bioreactor.	They used the kinetic model proposed by Zhang et al. (2010), to describe glucose production. Thus, they considered in the model cellulase deactivation as first and second order reaction.	Hydrothermally pre-treated agave bagasse.	The model presented a good fit to the experimental data, for a horizontal bioreactor operating in fed-batch. For the experimental test and simulation, the best glucose concentration obtained was the solids load at 25% having 195.60 $g.L^{-1}$ of glucose. Working in fed batch, 30% solids load for a horizontal bioreactor, glucose concentrations of approximately 120 $g.L^{-1}$ can be reached.	Pino et al. (2019)
Show a model applicable for fed-batch hydrolysis, aiming at high substrate concentration.	It was developed two models, one simplified and one complete model. The simplified model includes only the enzymatic adsorption and the first-order reaction of the enzyme-substrate complex. The complete model involves competitive glucose inhibition and decreasing rate factors related to substrate and enzyme behavior.	Filter paper.	The solids concentration ranged from 5 to 50 $g.L^{-1}$. In experimental tests, they obtained glucose concentrations up to 100 $g.L^{-1}$. On the other hand, for the complete model that presented the best fit, they found results below 40 $g.L^{-1}$, for an initial solids concentration of 30 $g.L^{-1}$.	Tervasmäki et al. (2017)

Table IV. Mapping of kinetic models proposed in the literature for the enzymatic hydrolysis process (cont.).

Objective	Model Description	Feedstock	Results	Reference
Describe the enzymatic hydrolysis in high solid concentration.	They used kinetic model by Kadam et al. (2004). The proposed model is based on the biochemistry of enzymatic hydrolysis and includes enzymatic adsorption, product inhibition, substrate reactivity and conversion of hemicellulose to xylose. However, it neglects thermal and mechanical enzymatic inactivation.	Sugarcane straw pre-treated with hot water.	The model presented a reasonable fit to the experimental data with solids load of 10-20%, enzyme feed between (5-60 $FPU.g^{-1}$), being possible to obtain glucose concentrations up to approximately 110 $g.L^{-1}$.	Angarita et al. (2015)
They developed a dynamic model for the simultaneous feeding of substrate and enzyme, with the purpose of reaching high concentrations of glucose, in the process of enzymatic hydrolysis in a reactor operating in fed batch.	They determined the mass balances for volume, substrate and product. In addition, they considered the equation for the reaction rate, from the Michaelis-Menten equation with inhibition by the product (glucose). They proposed an equation for substrate and enzyme feeding.	Bagasse pre-treated by steam explosion and delignified with 4% NaOH.	From the simulation, it was noticed that it was necessary to feed in three pulses of enzyme for the analyzed system. Furthermore, it was possible to reach glucose concentrations of 160 $g.L^{-1}$ and, in the experimental tests for model validation, product concentration of 200 $g.L^{-1}$.	Cavalcanti-Montaño et al. (2013)

As reported by Zhang et al. (2021b) and as can be seen in Table IV, it is complex to establish a kinetic model that accurately describes the hydrolysis profiles, as there are several factors that affect this step. Thus, regardless of the proposed model, it is difficult to avoid errors in the simulations for enzymatic hydrolysis. However, to minimize errors that reflect in the process mechanism, one should work with as many parameters as possible (Zhang et al. 2021b).

In the present study, the phenomenon of evaporation in the enzymatic hydrolysis process for cellulose was considered. This factor is not considered by Cavalcanti-Montaño et al. (2013), however highlighted by the researchers as a point of attention. Then, in Figure 6, a discontinuity in the first derivative of the curve is observed. This fact can be explained by the end of the process in a fed batch, with the dilution of bagasse in the feed and the beginning of the operation in a single batch. Thus, the increase in glucose concentration may have occurred due to the phenomenon of evaporation.

Also, the sum of squared errors divided by the number of experiments was determined by simulation realized by Cavalcanti-Montaño et al. (2013) and in this work. In this study, the sum of squared errors was 120.95 with the mean relative error of 8.04%. In contrast, for simulation realized by Cavalcanti-Montaño et al. (2013), the sum of squared errors and the mean relative error was 163.43 and 22.20%, respectively.

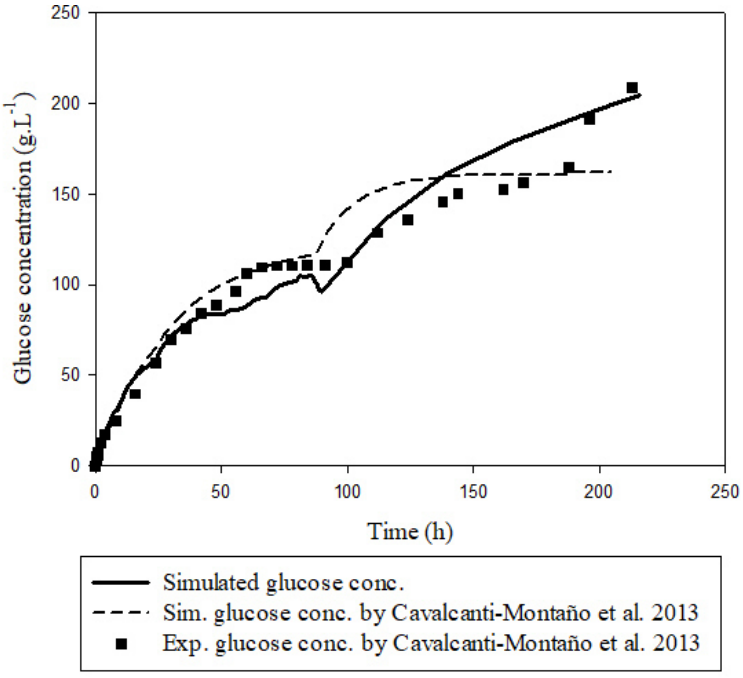

Figure 6. Experimental data by Cavalcanti-Montaño et al. (2013), simulated results by Cavalcanti-Montaño et al. (2013) and simulated results in this study.

Still in Figure 6, it can be seen that when analyzing the phenomenon of evaporation and taking into account the optimized kinetic parameters to determine the concentration of the simulated product, it is possible to obtain glucose concentrations of approximately 204.23 $g.L^{-1}$ in initial potential glucose concentration of 44 $g_{potential-glucose}.L^{-1}_{solution}$.This value found is close to that determined experimentally by Cavalcanti-Montaño et al. (2013). According to Cavalcanti-Montaño et al. (2013) highlighted the consideration of evaporation, this study confirms the importance of the phenomenon. In other words, if this phenomenon is not considered, it can be seen from the result simulated by Cavalcanti-Montaño et al. (2013), glucose concentrations up to 162 $g.L^{-1}$.

Compared to the studies briefly presented in Table IV, it is noted that it was possible to obtain a high concentration of glucose considering evaporation as a relevant factor, as well as the proposal to apply non-linear regression methods to determine the kinetic parameters present in the dynamic model. de Godoy et al. (2019) point out that, there is an acceptable limit for the production of glucose in the enzymatic hydrolysis step, in 8% $w.w^{-1}$ of glucose content. A relevant fact, since the production of bioethanol is economically viable, in the distillation process the concentration of ethanol must be $\geq$ 4% (Modenbach & Nokes 2013). In addition, for the production yield of bioethanol to be at least 90%, it is necessary to obtain a yield of more than 85% in the enzymatic hydrolysis step (Łukasik et al. 2021).

Angarita et al. (2015), Tervasmäki et al. (2017) and de Godoy et al. (2019), also evaluated the glucose concentration by applying the same optimization methodology to determine its kinetic parameters and obtained good fits of the models developed to the experimental data. However, they reached glucose concentrations of 110 $g.L^{-1}$, 40 $g.L^{-1}$ and 131.46 $g.L^{-1}$, respectively. This difference in the concentration of the final product in the enzymatic hydrolysis step can be affected by the chemical composition and physical characteristics of the lignocellulosic biomass, as well as the pre-treatment used, concentration of solids in the feed and the complexity of the enzyme used in each study. Therefore, the present study may be relevant as a proposal to improve the modeling and simulation to enzymatic hydrolysis of cellulose, proposing other factor with objective of to reach high glucose concentration.

CONCLUSIONS

The enzymatic hydrolysis step for the production of biofuel demands special attention, since it is not a trivial process. The performance of this step depends on the composition of the pre-treated biomass, the pre-treatment performed, presence of inhibitors, hydrolysate yield, enzyme concentration, among others. Therefore, the modeling and optimization at this stage can affect the best performance and yield of glucose and, consequently, improve the production of bioethanol.

Thus, with the application of a nonlinear least-squares regression model to estimate parameters was possible to obtain the sum of squared errors and the mean relative error lower than with the results shown by Cavalcanti-Montaño et al. (2013). Besides, with the analysis of evaporation in the system, the kinetic model was calculated for a reactor operating in fed batch, with substrate and enzyme feed.

The reduction in volume by approximately 50 mL, during the final batch phase, is justified by the phenomenon of evaporation. It is concluded that, for the result obtained by the model to be similar to the experimental one, the evaporation that occurred in the system must be considered. Furthermore, analyzing this phenomenon and considering the optimized kinetic parameters, high rates of glucose concentration can be found in the enzymatic hydrolysis stage of sugarcane bagasse. So, it was possible to obtain glucose concentrations of approximately 204.23 $g.L^{-1}$.

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Jaqueline Alves Roberto was responsible for data collection and organization, discussion and writing of the manuscript. Andréa Oliveira Souza da Costa reviewed the manuscript and was responsible for supervising the work. Esly Ferreira da Costa Júnior helped implemented the analyzed model and worked on the discussion of the results.