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**Acid hydrolysis of hemicellulose from *Ipomoea arborescens*: kinetics of xylose production**  
**Hidrólisis ácida de hemicelulosa de *Ipomoea arborescens*: Cinética de producción de xilosa**

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**Abstract**

In this paper the composition change of *Ipomoea arborescens* was evaluated under acid hydrolysis pretreatment, and the kinetic parameters of this reaction were determined. The goal was to evaluate the effects of particle size in the reaction rate of hemicellulose hydrolysis, and to find the concentration of sulfuric acid in which the reaction mechanism favors hemicellulose hydrolysis of *Ipomoea arborescens* particles. Once the best conditions were found, *Ipomoea arborescens* particles were hydrolyzed at different temperatures. A pseudo-homogenous model was adopted to describe hemicellulose hydrolysis. The empirical formula of hemicellulose was determined experimentally to have 21 molecules of xylose, 5 molecules of glucose and 1 molecule of galactose. The mathematical model of hemicellulose hydrolysis is successful to describe the experimental results when the temperature is between 120 and 160°C.

*Keywords:* Hemicellulose, xylose, acid hydrolysis, rate constants, activation energy.

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**Resumen**

En este escrito los cambios de composición de *Ipomoea arborescens* fueron evaluados bajo pretratamiento de hidrólisis ácida y los parámetros cinéticos de la reacción fueron determinados. El objetivo fue evaluar los efectos del tamaño de partícula en la velocidad de reacción de la hidrólisis ácida de hemicelulosa y encontrar la concentración de ácido sulfúrico en la cual el mecanismo de reacción favorece la hidrólisis de las partículas de *Ipomoea arborescens*. Las partículas de *Ipomoea arborescens* fueron hidrolizadas a diferentes temperaturas. Un modelo pseudo-homogéneo fue adoptado para describir la hidrólisis de la hemicelulosa. La fórmula empírica de la hemicelulosa determinada experimentalmente consta de 21 residuos de xilosa, 5 de glucosa y uno de galactosa. El modelo matemático de la hidrólisis de hemicelulosa es exitoso para describir los resultados experimentales obtenidos en temperaturas del rango de 120 a 160°C.

*Palabras clave:* Hemicelulosa, xilosa, hidrólisis ácida, constante de velocidad, Energía de activación.

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## 1 Introduction

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Currently, research on biofuels production tends to focus in replacing crops, mainly seeking alternative sources not intended for human consumption. Due the lignocellulosic materials are abundant can be a potential option to processed into fuels, chemicals and other materials is considered. Lignocellulosic materials are cheap and renewable; therefore, they are a real alternative to produce ethanol (Mousdale, 2008; Sunggyu Lee, 2014). The lignocellulosic materials are considerably complex to convert into fermentable sugars (Mosier, 2005; Gómora-Hernández, 2020). In spite of this, vegetal biomass stemming from trees and herbs presents a wide range of possibilities for pretreatment because of its structure and composition (Mousdale, 2008; Yan Zhao, 2014). Plant cell walls in lignocellulosic materials are composed primarily of three components: cellulose, hemicellulose and lignin. Cellulose is a homopolymer which has glucose as its structural unit, covered by a network of heteropolymers such as hemicellulose and lignin. The last components affect the accessibility of cellulose. Cellulose is the main component, followed by the hemicellulose and lignin. In hardwood, cellulose composition is about 40-50% w/w, hemicellulose is 23-40% w/w and lignin 18-25% w/w. Crops and agricultural waste materials contain a high proportion of hemicellulose (30-33% w/w) relative to cellulose (38-45% w/w) and low lignin content (10-17% w/w) (Sun, 2002).

Several materials have been investigated and tested with different kinds of physical, chemical, physicochemical and biological pretreatments (Brienzo, 2009; Pingali, 2010; Salvi, 2010; Thomas Ingram, 2011; Silva, 2011; Lam, et al., 2015). Chemical pretreatment has resulted in an effective and economic process to break down or remove interactions between lignin, hemicellulose and cellulose (Lynd, 1996; Mosier, 2005; Eggeman, 2005). Acid hydrolysis has been used with a wide variety of lignocellulose-containing materials, and it shows important aspects regarding hemicellulose removal and carbohydrate recovery (Sun, 2002; Neureiter, 2004; Tunc, 2008; Yang, 2009; Jeong, 2010; Saucedo-Luna J. C.-M.-G., 2020). Acid hydrolysis allows accessing the cellulose that is covered with hemicellulose, thus recovering xylose as the main product of hemicellulose hydrolysis (Sun, 2002; Neureiter, 2004; Saha B. C., 2005; Yang, 2009;

Ashutosh Mittal, 2019). In the literature, research work has focused on describing the kinetics of xylose production using homogeneous models for the hydrolysis reaction with sulfuric acid (Jacobsen, 2000; Neureiter, 2004; Yat, 2006; Canettieri E. V., 2007; Yang, 2009; Morinelly, 2009; Jeong, 2010; Sediawan, 2010; Hu, 2010; Riansa-Ngawong, 2011). Previous studies of lignocellulosic materials include grass, forest and agricultural residues, and soft and hard woods have shown a real possibility of replacing the current raw materials such as sugar cane and corn (Canettieri E. V., 2007; Mousdale, 2008; Bessou, 2011; Saucedo-Luna J. C.-M.-P.-A.-G., 2011; Sánchez, 2011; Komolwanich, 2014; Fernandes, 2021).

This paper presents *Ipomoea arborescens* as a potential raw material to produce ethanol. *Ipomoea arborescens* is a wild tree that grows in the Sonoran desert in Northwest Mexico and in the north of Sinaloa; it is also known as morning-glory tree, and for its Spanish names: palo blanco, palo santo and casahuate (Meyer, Bertelsen, & Devender, 2003-2006). During extreme dry seasons, local farmers feed their cattle with *Ipomoea arborescens*. Bovines have cellulolytic bacteria in their digestive tract that can digest it at some extent under the conditions of their body temperature and pH of their digestive tract (Anthony, 1969; Weimer, 1996). Inside their stomach, ruminants have the conditions to break down the cell wall of *Ipomoea arborescens* and release the glucose present. The latter suggests that *Ipomoea arborescens* could be easily pretreated by dilute acid hydrolysis, and the products of this process fermented to produce ethanol. The aim of this research is to study the kinetics of the sulfuric acid hydrolysis of *Ipomoea arborescens* under controlled laboratory conditions; for this purpose experimental data was collected to obtain the kinetic parameters of the hemicellulose degradation reaction and test a mathematical model that describes the evolution in the time of xylose concentration as the main reaction product. Due to lack of information on the organic composition of *Ipomoea arborescens*, this work also includes the determination of the percentage composition of cellulose, hemicellulose and lignin from the carbohydrates present in each of the cell wall components.

### 1.1 Experimental work

Stems of *Ipomoea arborescens* were manually collected at Ejido Los Hornos, Cajeme, Sonora,

México. The stems of *Ipomoea arborescens* were dried in a convection flow oven at 80°C during 24 hours to ensure to remove all moisture from the wood. Batches of 500 g of dried stems were ground in a rotating disc saw. After that, the ground and dried material was divided into four groups sorted by particle size (1.41-2.0, 1.41-0.841, 0.841-0.595 and < 0.595 mm). The sieved particles were placed and sealed in labeled bags in order to prevent contamination with moisture, and were kept at 25 °C to be used when needed. The hydrolysis reaction was done in a 2 L high pressure bench top Parr reactor model 4522, which can be operated isothermally with a variation of  $\pm 1^\circ\text{C}$ , thanks to the reactor controller model 4850 that controls the internal cooling. The reactor has an agitator that allows to mix the acid solution and wood particles in the vessel reactor. Preliminary experiments were carried out in this reactor to find the amount of solids and the acid volume allowed to carry out the experiment without obstruction problems in the pipeline for sample collection. The experiments were carried out with the solid proportion 1:20 sulfuric acid solution. In order to neglect the mass transfer and ensure perfect mixing, the stirring speed of the reactor was set at 600 rpm. The overall reaction time was established as a function of the xylose, the main product of the hydrolysis, at 60 minutes because after this time a degradation process begins (Yat, 2006).

The best conditions for the hydrolysis were assessed with four different sulfuric acid concentrations (0.25, 0.5, 0.75 and 1 wt %). At room temperature, 50 grams of sieved particles of *Ipomoea arborescens* were introduced with 1 L of sulfuric acid solution in the reactor, then hermetically closed and the stirrer was turned on with the selected speed. The heating system was operated at 100, 120, 140, 160 and 180°C and held constant for one hour of reaction time. The time versus temperature data for the heating system is shown in Figure 1. During the experiments, the system temperature  $T$ , increased linearly prior to reaching the setpoint temperature.

When the target temperature was reached, samples of 1 mL were withdrawn every 10 min during a period of one hour. The samples were cooled at room temperature (25°C), centrifuged and filtered with a 0.22  $\mu\text{m}$  Millipore filter to remove any solids. Afterwards the filtered solutions were diluted at a ratio of 1:6 and analyzed by high performance liquid chromatography (HPLC) to determine the concentration of xylose, glucose and galactose as a function of time.

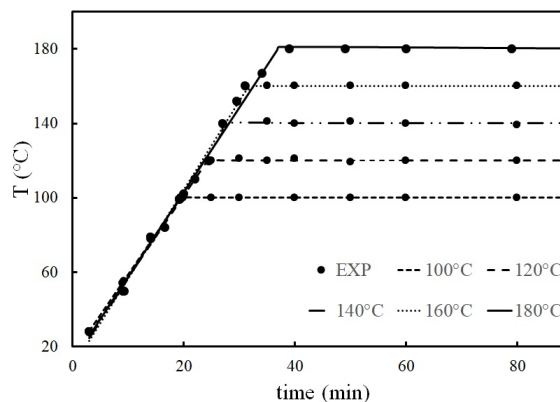


Figure 1. The ramp system heating during experiments of acid hydrolysis of *Ipomoea arborescens* particles for five setpoints (100, 120, 140, 160 and 180°C). Temperature data recorded indicated by the symbols through the elapsed time of the experiments. The continuous lines represent the linear fit of the experimental data indicate by symbols.

The kinetic study was done at four different temperatures (120, 140, 160 and 180°C). Before the HPLC analysis, the collected and filtered samples were placed into a plastic tube and centrifuged at 14000 rpm for 10 min in a Beckman ETM centrifuge unit. The liquid phase of the sample was analyzed by HPLC to determine how the concentration of monosaccharides present, as reaction products, changed over time. The HPLC Varian ProStar unit was used with a column Biorad Aminex HPX-87P size 300 x 7.8 mm, and was a packed with a polymer-based matrix 8% cross-linked resin lead ionic form, range 5-9 pH. The column was operated at 65°C; to reach this temperature it was introduced into an Eppendorf column oven model CH-30. The mobile phase was water at a flow rate of 0.45 mL/min. The refractive index detector Varian 9020 was operated at 30 °C with a range of  $2.54 \times 10^{-4}$  units of refraction index. The analysis time for the samples was 25 min, under these conditions the retention times of the main products: xylose, glucose and galactose were 15.3, 21.7 and 27.6 minutes, respectively.

The experimental conditions in this study were established based on the review of published work related to acid hydrolysis of lignocellulosic materials (Brennan, 2004; Yat, 2006; Canettieri E. V., 2007; Morinelly, 2009). Results from literature agree on the fact that the degradation of products increases at higher temperature and acid concentrations; given the experimental conditions of this work, these effects are going to be presented. Therefore, avoiding

degradation and obtaining the highest production of monosaccharides is the main objective of the diluted acid hydrolysis for the next process step. It was decided that the best method for this investigation consisted on finding the concentration of acid at which the highest concentration of monosaccharides was obtained. Upon completion of the reaction, the acid concentration was found and the temperature that favors the hydrolysis process of the hemicellulose was determined. A select number of reacted samples were observed under a JEOL 5410V scanning electron microscope (SEM) to determine the acid and temperature effect in the morphology of the *Ipomoea arborescens* particles.

### 1.2 Determination of the *Ipomoea arborescens* composition

In order to know the initial concentration of hemicellulose and its composition, a process of sequential extraction of the components of the cell wall of *Ipomoea arborescens* was performed. To find carbohydrates composition, the samples of *Ipomoea arborescens*, previously ground and sieved, were again ground and sieved in particles smaller than 0.250 mm. A particle size smaller than 0.250 mm easily allows the break down and release of the carbohydrates present, avoiding problems in mass transfer with the procedure described below. The *Ipomoea arborescens* particles were ground in a Willis blade mill. The ground samples of *Ipomoea arborescens* were slowly added in a solution with 250 mL of boiling ethanol for a period of 30 to 40 minutes, and then the solution was filtered and the insoluble material was collected. The insoluble material was washed in a Buchner funnel using filter paper (P5, medium porosity, slow flow), a Kitasato flask and a vacuum pump. The insoluble material was washed sequentially with 500 mL of boiling ethanol, 500 mL of chloroform-methanol (1:1, v/v) and 500 mL of acetone. The washed insoluble material was dried in an oven at 30 °C and stored in a desiccator. Chemical sequential extraction with 250 mL of water and thimerosal 0.1%, CDTA 50mM, Na<sub>2</sub>CO<sub>3</sub> 50mM, KOH 4% and 24 wt % was done as described by Rose et al. (Rose, 1998). The initial weight of the *Ipomoea arborescens* sample for the sequential extractions was 3 grams. The insoluble sample was dried and weighed after each extraction step; the mass obtained after each extraction is shown in Table 1.

The aliquots and soluble samples obtained after each extraction represent a fraction of *Ipomoea arborescens* cell wall (cellulose, hemicellulose, pectin and lignin). The aliquots from extractions were collected and freeze-dried in a 50 mL falcon tubes and lyophilized. The lyophilized samples were hydrolyzed to determine the concentration of total carbohydrate present, as detailed below in the Results section. Samples of 10 mg of lyophilized aliquots obtained from the sequential extraction were placed in a Pyrex tubes of 16x150 mm, 5 mL HCl 1 M was added to them, and were placed in a water bath at 100 ± 5 °C for 150 minutes, shaking the samples every 30 minutes. The tubes were cooled down with water jet to room temperature. The goal of acid hydrolysis with HCl is to break the oligomeric structure and release totally the carbohydrates present in each extracted fraction. The solutions obtained at the end of hydrolysis were filtered with Whatman paper # 4, after the aliquots were filtered with cartridges Sep Pack (C18); discarding the first 3 mL, the remaining 2 mL were collected. The aliquots collected were dried with constant air flow in a water bath at 45° C on a heating plate. The result was a solid dried sample that was reconstituted in 1 mL distilled water. The reconstituted solution was analyzed by HPLC to determine the concentration of monosaccharides present in the extracted fractions. The HPLC Dionex unit used a column anion-exchange CarboPac PA1 (4x250 mm) and pre-column CarboPA1 (4x50 mm). The column was operated at room temperature using water as eluent at flow rate of 1.0 mL/min and 0.3 mL/min NaOH 1 M developing solution on post-column. The Dionex pulsed amperometric detector unit used an AgCl electrochemical cell. The purpose was to determine the concentration of monosaccharides in the reconstituted solutions of each fraction of the cell wall; therefore, calibration curves were made with the carbohydrates present in the lignocellulosic materials. The standards used for the calibration curves were arabinose, glucose, galactose, mannose, rhamnose and xylose (Aldrich CAT-29387-3). The amounts of carbohydrates obtained were averaged and considered for the determination of the composition of hemicellulose, lignin and cellulose. The initial composition of hemicellulose is a parameter considered within the kinetic model called stoichiometric factor, which represents the moles of xylose contained in one mole of hemicellulose.

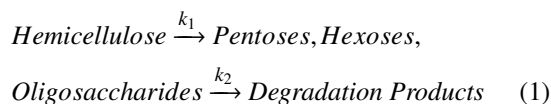
Table 1. Insoluble fraction recovered at each chemical extraction stage.

	Run			
	1	2	3	Average
	Mass (g)			
Water-Thimerosal	0.343	0.352	0.363	0.352
CDTA	0.66	0.64	0.651	0.650
Sodium carbonate	0.233	0.235	0.237	0.235
KOH 4%	0.255	0.255	0.256	0.255
24%	0.51	0.521	0.521	0.517
Residue	0.999	0.998	0.972	0.989

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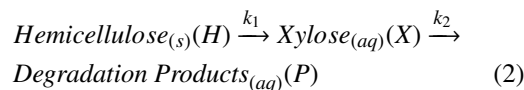
## 2 Kinetic model

The first kinetic model of acid hydrolysis was focused on cellulose. Subsequently, considering the importance of hemicellulose in the production of potential sugars to ferment, several kinetic models were developed. Some authors were focused in recovering the sugars in this portion, since hemicellulose is easier to hydrolyze than cellulose by high selectivity to dilute acid hydrolysis (Maloney, 1986; Jacobsen, 2000; Saha B. C., 2003; Canettieri E. V., 2007). The hemicellulose hydrolysis models were adapted from the first-order pseudo-homogeneous kinetic model of cellulose hydrolysis developed by Seaman in 1945 in a dilute acid batch system and then modified including two fractions of hemicellulose (Saeman, 1945). Hemicellulose hydrolysis and degradation reaction of sugars can be considered as a pseudo-first-order process. The high selectivity of the pretreatment allows maximizing the ratio of the rate constants,  $k_1$  and  $k_2$ , as shown in Equation 1 (Morinelly, 2009).



Usually, hemicellulose hydrolysis models are based on the action of an acid catalyst that breaks down the long chains of hemicellulose and forms short chain oligomers that continue to break down to form monomeric carbohydrates. These models apply for pH conditions below 2, since at higher values the hydronium ion competes with the hydroxyl ion catalysis. All the papers found in the literature use one of three models that describe the hemicellulose

hydrolysis: simplified model, hemicellulose fractions and oligomers formation. The simplified model describing the kinetics of hemicellulose hydrolysis is based on an approach proposed by Seaman to a two-step first order reaction (Saeman, 1945; Jacobsen, 2000). It proposes that hemicellulose is hydrolyzed to xylose, in a second reaction xylose is degraded to other undesirable products (Kim, 1986; Brennan, 2004; Canettieri E. V., 2007; Morinelly, 2009). Hemicellulose decomposition to xylose is rigorously a heterogeneous process. This process is treated as pseudo-homogeneous; it was adopted to describe hemicellulose hydrolysis and includes the stoichiometric ratio of the hemicellulose which reacts in the process, noting that this would depend on the composition of the hemicellulose of each species. A kinetic model of diluted acid pretreatment of hemicellulose is essential for understanding the causes that enhance its hydrolysis. The pseudo-homogeneous process approach is widely used because it describes the hydrolysis reaction reasonably well, mainly for two reasons: (1) it predicts xylose production and other monosaccharides from raw materials and (2) it optimizes the operating conditions of hemicellulose degradation by means of statistical techniques (Brennan, 2004) 33.



For this study the following considerations were taken: (a) perfect mixing in a batch reactor, (b) volume and temperature are constant in the liquid phase, (c) all reactions are irreversible and first-order kinetics with respect to reactants. The model described begins with the reaction that represents hemicellulose hydrolysis; a first order kinetics with respect to the concentration



of the reactants, given the differential concentration of hemicellulose and xylose in batch reactor, as shown in equations (3) and (4).  $\omega_H$  represents the stoichiometric factor that means moles of xylose per mole of hemicellulose.

$$\frac{dH}{dt} = -k_1H \quad (3)$$

$$\frac{dX}{dt} = \omega_H k_1 H - k_2 X \quad (4)$$

$H_0$  -the hemicellulose present at  $t = 0$  when the system reached the experimental temperature-, was calculated by solving  $C_1$  and substituting in it Equation 5. The xylose concentration at  $t = 0$  upon reaching the desired temperature, is calculated from  $C_1$ . Finally, Equation 6 is the mathematical model that was used to predict the xylose concentration.

Initial conditions:

$$t = 0, \quad H_0 = H_i - \frac{X_0}{\omega_H}, C_1 = X_0 - \frac{\omega_H k_1 H_0}{k_2 - k_1}$$

The mathematical expression that describes xylose formation ( $X$ ) as a function of time was obtained by solving simultaneously Equations 3 and 4:

$$X(t) = \frac{\omega_H k_1 H_0}{k_2 - k_1} e^{-k_1 t} + C_1 e^{-k_2 t} \quad (5)$$

$$X(t) = \frac{\omega_H k_1 H_0}{k_2 - k_1} e^{-k_1 t} + \left[ X_0 - \frac{\omega_H k_1 H_0}{k_2 - k_1} \right] e^{-k_2 t} \quad (6)$$

The rate constants  $k_1$  and  $k_2$  represent xylose formation and degradation, respectively. Due to a strong dependence on temperature, the rate constants can be calculated with the Arrhenius equation.

$$k_i = A_i \exp\left(\frac{Ea_i}{RT}\right) \quad (7)$$

Where,  $k_i$  is the reaction rate constant,  $A_i$  is the pre-exponential term [ $\text{min}^{-1}$ ],  $Ea_i$  is the apparent activation energy [ $\text{kJ}\cdot\text{mol}^{-1}$ ],  $T$  is the absolute temperature [ $\text{K}$ ] and  $R$  is the gas constant [ $8.3143 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\text{K}^{-1}$ ]. It should be noticed that the values of  $k_i$ ,  $Ea_i$  and  $A_i$  will be approximate due to the assumptions made, such as a) pseudo-homogeneous process, b) nature and complex of raw material and c) the model just describes the hemicellulose hydrolysis process. Based on the chemical study done of the composition of *Ipomoea arborescens* and average weight percent, the maximum amount of hemicellulose in 50 grams of *Ipomoea arborescens* was  $3.413 \times 10^{-3}$  mole, which represents the initial amount of hemicellulose in the experiments of acid hydrolysis.

The system of differential equations was set up and their corresponding initial conditions were determined. The values of  $k_1$  and  $Ea_i$  and  $A_i$  were calculated as follows. First, an initial set of parameter values ( $k_1$  and  $k_2$ ) was chosen and Equations 3-6 were solved numerically with Euler's method using a time step of  $\Delta t = 5 \times 10^{-2}$  min; the total integration time was 60 min. The values of  $k_i$  at time  $t$  were computed from Equation 7. The results predicted by the model were compared with the experimental results obtained at each time, using the squared predictor error. If the error was close to zero the values of  $k_1$  and  $k_2$  were accepted, otherwise the procedure was repeated.

### 3 Results and discussion

The aliquots obtained after each extraction of *Ipomoea arborescens* hydrolysis were analyzed by HPLC, which represents a fraction of the *Ipomoea arborescens* cell wall (cellulose, hemicellulose and pectin). The amount of carbohydrates in the analyzed aliquots is shown in Table 2, presented as weight percent (wt %). In the results of the analysis of the fractions, some carbohydrate represents a relative majority. Basically, the heterogeneous composition of pectin consists of the combination of arabinose, galactose and rhamnose monomers; the presence of these carbohydrates was during the extractions with water, CDTA and sodium carbonate. The heterogeneous composition of the hemicellulose that has as main component a backbone of xylose units occurs during the extractions with 4 and 24% KOH. From initial weight, the hemicellulose portion extracted was 70.6 wt % with 4% and 24% KOH. The residue composition was about 60% glucose which represents the cellulose present, it should be noted that the second component was xylose, indicating that part of the hemicellulose was not extracted in the previous step. The amount of the hemicellulose present in *Ipomoea arborescens* was determined at 25.68 wt %. The calculation of the empirical formula of the hemicellulose is based on the molar masses and weight percentage of galactose, glucose and xylose in the fraction extracted with potassium hydroxide. Therefore, the hemicellulose in the *Ipomoea arborescens* particles may be represented by an empirical formula consisting of 21 molecules of xylose, 5 molecules of glucose and 1 molecule of galactose; because of this, Reaction 2 may be rewritten as Reaction 8.

Table 2. Carbohydrate amounts in aliquots of soluble fractions during sequential chemical extraction analyzed and determined by HPLC; average quantities expressed in wt %.

	Carbohydrate (wt %)					
	Arabinose	Galactose	Glucose	Mannose	Xylose	Rhamnose
Water-thimerosal	14.41	19.15	53.43	4.51	7.85	0.65
CDTA	16.96	20.75	44.05	1.27	16.97	ND
Sodium Carbonate	30.63	50.74	9.57	ND	7.06	2.00
KOH 4%	2.66	1.75	10.83	ND	84.76	ND
24%	9.15	6.68	27.92	ND	56.24	ND
Residue	9.33	13.02	59.45	2.79	24.74	ND

ND - Not detected at least in 2 experiments or amount less than 0.50 wt %.

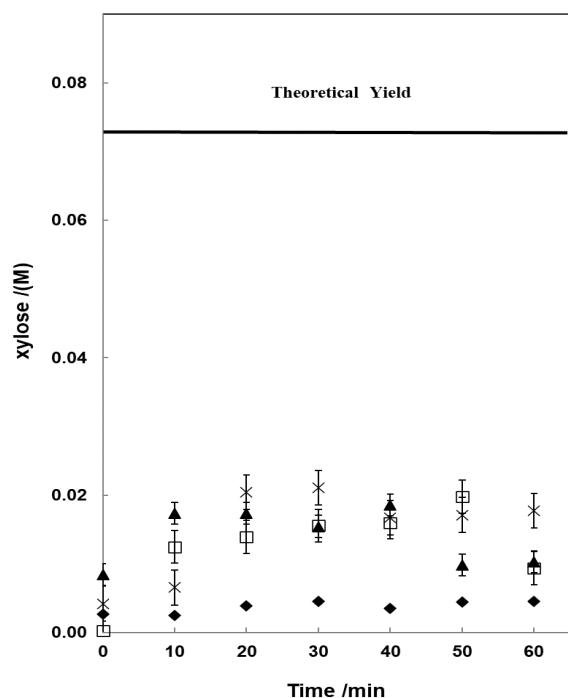
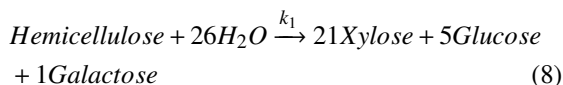


Figure 2. Xylose produced using different concentrations of sulfuric acid ( $\blacklozenge$ ; 0.25,  $\square$ ; 0.50,  $\blacktriangle$ ; 0.75 and  $\times$ ; 1 wt%), particle sizes smaller than 0.595 mm at 160 °C.

The empirical molecular weight of the hemicellulose was determined at 3762 grams per mole.



With a sulfuric acid concentration of 0.25 wt %, xylose production was scarce during all the time of reaction; whereas with 0.50 wt % sulfuric acid a large increase in xylose concentration was obtained at 10

min and reached its maximum value at 50 minutes. In experiments carried out with 0.75 and 1 wt %  $\text{H}_2\text{SO}_4$ , xylose concentration showed a considerable increase during the first 30 min, but after 40 min xylose degradation was observed. The production of xylose after 10 min of reaction with a sulfuric acid concentration of 0.75 wt % was the highest found in all studies of the acid effect, reaching approximately a concentration of 0.017 M. According to the results presented in Figure 2, the amount of sulfuric acid that produces significant xylose for reaction times between 20 and 50 min is between 0.5 and 1 wt %. Acid concentrations of 0.75 wt % allows relatively high yields of xylose, in other words, the hemicellulose degradation was considerable. The theoretical yield represents the amount of xylose that is expected according to the initial amount of hemicellulose.

The experimental results of glucose concentration produced during acid hydrolysis of *Ipomoea arborescens* as a function of reaction time with 0.25, 0.5, 0.75 and 1.0 wt %  $\text{H}_2\text{SO}_4$  at 160°C, are shown in Figure 3. Maximum glucose production was recorded at 0.75 wt % sulfuric acid at 10 min reaction, around 0.077 M. In the acid hydrolysis with concentrations of 1 wt %  $\text{H}_2\text{SO}_4$ , glucose is produced in the heating stage of the reactor; when the study temperature is done, the glucose reaches its maximum concentration and the degradation stage begins.

Under conditions of 0.75 and 1 wt %  $\text{H}_2\text{SO}_4$  concentrations, glucose production increases at  $t = 0$ , it is when it has reached a reaction temperature of 160 °C, the maximum molar concentration determined at 10 min for 0.75 wt % and at 20 min for 1.0 wt % of acid concentration. However, an acid concentration of 0.75 wt % corresponded to the increase in glucose production, which, at the same time, shows a similar result as if it were exposed to more time to heat and to

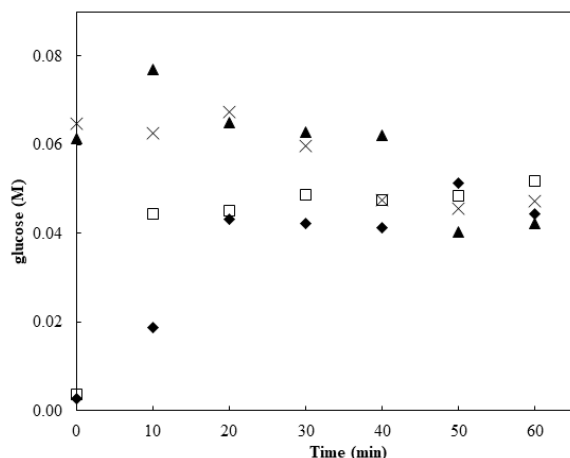


Figure 3. Glucose concentration profile at different concentrations of sulfuric acid (♦; 0.25, □; 0.50, ▲; 0.75 and ×; 1 wt.%) using particle sizes smaller than 0.595 mm at 160 °C.

potential acid degradation. At 0.25 and 0.5 wt % acid concentrations, glucose generation was more stable and remained in values between 0.04 and 0.05 M. The acid effect was more evident at concentrations higher than 0.50 wt % of sulfuric acid, despite the selectivity it has over hemicellulose; when the acid is slightly in excess, the reaction mechanism of the reaction promotes the hydrolysis of the cellulose (Jacobsen, 2000; Saha B. C., 2003; Canettieri E. V., 2007).

It is important to clarify that the attack carried out by sulfuric acid in concentrations higher than 0.5 wt % is carried out on polysaccharides containing glucose that is accessible to this attack.

The aim of the studies that evaluated particle sizes was to find the size at which the acid hydrolysis reactions had better conversions of hemicellulose to xylose, avoiding the degradation of xylose and the formation of degradation products. The experimental data obtained for xylose molar concentration for different particle sizes is shown in Figure 4. In the reactions for particle sizes 2.00-1.41 and 1.41-0.841 mm xylose concentration was kept constant throughout the reaction without ever reaching a clear maximum. As particle size decreases, xylose production increases as seen for sizes range of 0.841-0.595 mm where xylose is obtained at a 0.005M concentration after 20 minutes of reaction. Standing out is the maximum xylose concentration of 0.02 M in 50 minutes of reaction with particle sizes less than 0.595 mm. In contrast, the larger particle sizes (2.00-1.41 and 1.41-0.841 mm) obtained did not exceed concentrations of 0.008 M for 1 h of reaction, in this

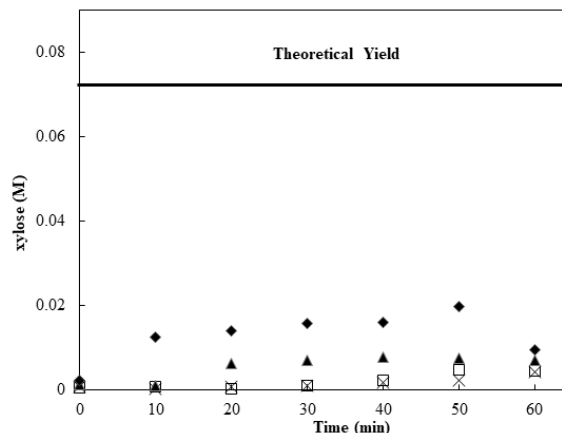


Figure 4. Xylose produced at 160°C using different particle sizes and 0.5% wt % H<sub>2</sub>SO<sub>4</sub>, ×; 2.00-1.41 mm, □; 1.41-0.841 mm, ▲; 0.841-0.595 mm, ♦; smaller than 0.595 mm.

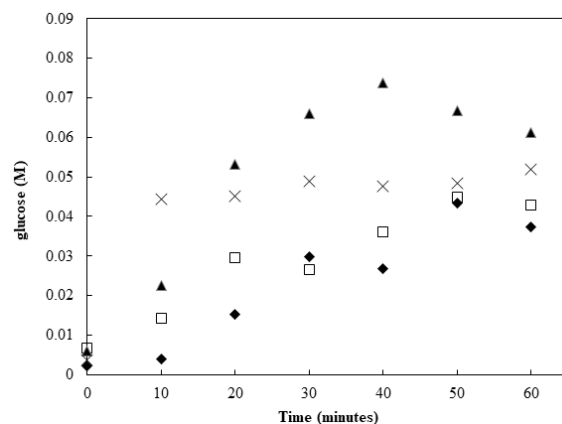


Figure 5. Glucose concentration produced at 160°C using four different particle sizes and 0.5 wt % H<sub>2</sub>SO<sub>4</sub>, ×; 2.00-1.41 mm, □; 1.41-0.841 mm, ▲; 0.841-0.595 mm, ♦; smaller than 0.595 mm.

case the surface area of contact with the acid was the limiting factor to obtain higher yields of xylose in the acid hydrolysis. The four particle size conditions showed a significant difference among them; better xylose yields are obtained by reducing particle size.

The experimental data for glucose production in acid hydrolysis with different particle sizes are presented in Figure 5. Glucose concentration increases after 20 min of reaction as can be observed with particle sizes of 2.00-1.41 mm, while with 1.41-0.841 mm the same can be observed after 10 min, reaching a maximum yield of 0.04 M and 0.044M at 50 min, respectively.



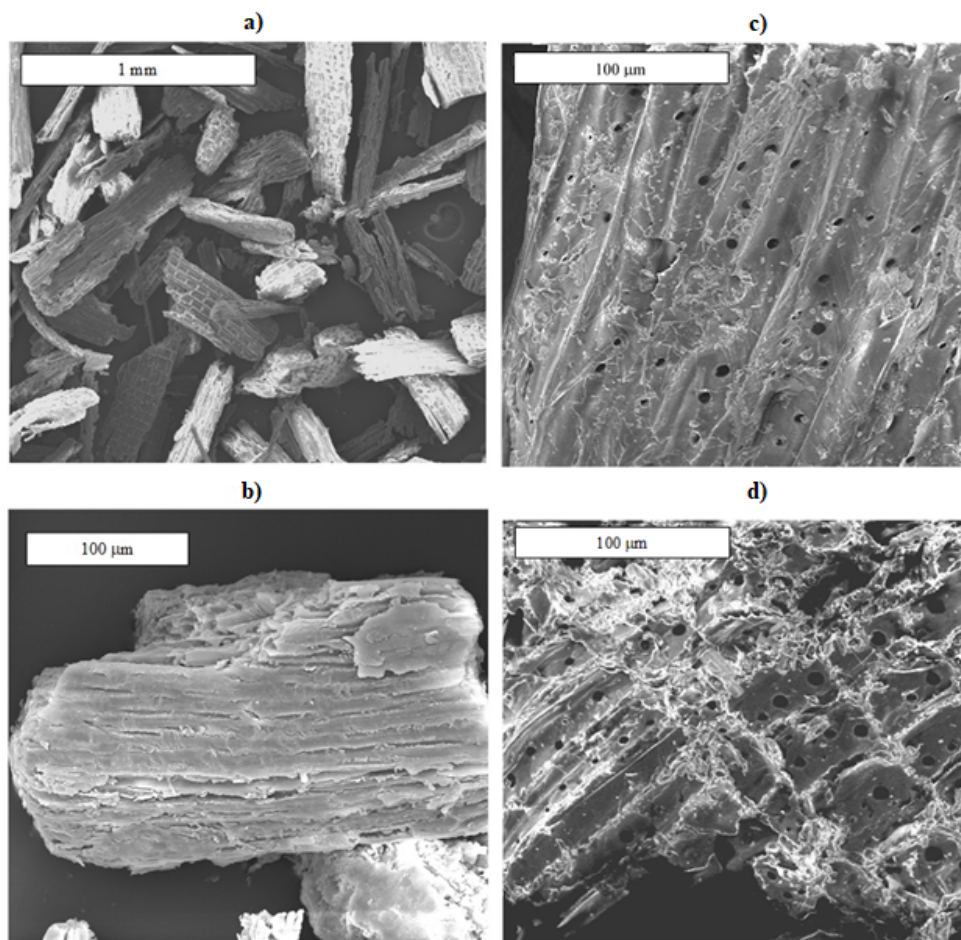


Figure 6. SEM images of *Ipomoea arborescens* particles prior and after to reacted with 0.5 wt % sulfuric acid. the acid hydrolysis at two different temperatures. General view of particles smaller than 0.595 mm: a) 50x and b) 350x, c) 120°C and d) 160°C

Low yields of glucose production indicate that covers and protectors of the hemicellulose to cellulose in the cell wall are not being removed, therefore glucose, as product of cellulose hydrolysis, was not released. However, the most remarkable aspect to emerge from the results is that a maximum glucose production of 0.073 M was obtained with particle sizes of 0.841-0.595 mm at 40 min of reaction time. The glucose production is favored by size reduction, shown in Figure 5; the particles smaller than 0.595 mm impregnated with acid in a larger contact area enable higher production of xylose, i.e., the hemicellulose was more degraded and cellulose was released, and by breaking the glycosidic bond  $\beta$  (1-4), glucose production occurs at higher rates.

Reviewing the morphology of the particles, Figure 6 shows SEM images for *Ipomoea arborescens*

particles smaller than 0.595 mm. In order to have a general view and to be able to observe the surface of the particles. The morphology of the particles predominates in the form of rectangular thin flakes, a series of pictures that suggest the presence of the xylem block in the wood of *Ipomoea arborescens*. The particles appear to be formed of rods that agglomerate to form a set. This suggests that the shape of the *Ipomoea arborescens* particles was determined by the disk saw, the saw teeth formed the thin chips causing ruptures, and disengages of the solid and hard wood structures. This suggests that the shape of the *Ipomoea arborescens* particles was determined by the saw blade, the teeth of the saw formed the thin chips causing ruptures and breakup of the solid and hard structures. Furthermore, the above suggests a variability in the chemical composition of the *Ipomoea*

*arborescens* particles; this is because the chemical composition of the particle surface and the core of the flakes are different. The surface is rough and irregular, solid but with small slits that will be decisive to understand that the acid hydrolysis reaction occurs on the surface of the particles, having the possibility of penetrating through the cracks. Figure 6 b) shows that smaller size particle adheres to the larger surfaces.

Figure 6 shows the effect of acid hydrolysis on the surface of the particles of *Ipomoea arborescens* with a 0.5 wt% concentration of sulfuric acid at 120 °C and 160 °C. To emphasize the morphological changes in the surface of the particles of *Ipomoea arborescens* the images are magnified, the reacted particles show their original geometric form. There is an external layer covering the surface, it is irregular at some of the surface sites, which suggests that the attack of the acid solution may leave exposed some sites before others. The hydrolysis reaction occurs at the surface of the particles, hydrogen ions break the interactions of the hemicellulose releasing xylose into the fluid. When the external layer of the hemicellulose is removed, the acid and the reaction temperature cause damage to the surface, forming pores; these pores lead to the internal diffusion of the acidic solution into the particles. This internal diffusion of the acid causes the breaking of the cellulose fibers releasing glucose. In Figure 6 b) the surface of the particle was exposed at a 160 °C reaction temperature, the external layer covering the surface of the particle was largely removed, creating a greater number of pores and leaving the surface exposed. It should be noted that, the relevance of the images is to observe that the external film that covers the surface was affected by the treatment at a higher temperature; this suggests that the hemicellulose is removed mostly.

Data obtained before from different experiments was presented in order to better explain how parameters were chosen to find optimal conditions. It was tested with different acid concentrations as well as different particle sizes of *Ipomoea arborescens*. In order to find acid concentration in which the hemicellulose hydrolysis is better developed, in other words to obtain a maximum xylose and avoid the formation of degradation products. In this way, kinetic conditions for the study were set with particle sizes smaller than 0.595 mm and 0.5 wt % sulfuric acid concentration at which the highest yields of xylose are obtained, namely the optimum conditions to the hemicellulose degradation. The kinetic experiments were conducted by varying the temperature from 100 to 180 °C.

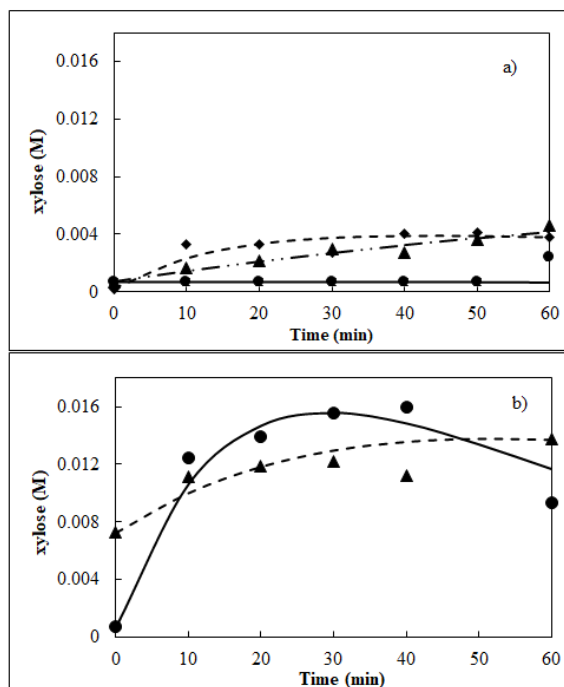


Figure 7. Predicted and experimental values of xylose concentration during sulfuric acid hydrolysis of *Ipomoea arborescens* particles. Experimental conditions: <0.595 mm, 0.5 wt % H<sub>2</sub>SO<sub>4</sub>. a) Xylose experimental at 100°C, ●; xylose calculated at 100°C, solid line; xylose experimental at 120°C, ▲; xylose calculated at 120°C, long dash dot, ◆; xylose experimental at 140°C, xylose calculated at 140°C, dash line. b) xylose experimental at 160°C, ●; xylose calculated at 160°C, solid line; xylose experimental at 180°C, ▲; xylose calculated at 180°C, dash line.

Analysis of the form of graphs shows two types of behaviors. In the first group shown in Figure 7a, the xylose concentration increases mostly linearly with time, until the concentration reaches a maximum value approaching an asymptotic at the end of the reaction. The experiments were conducted at low temperature, Figure 8a describes in terms of a chemical reaction, the first part of the Equation 7 where the hemicellulose begins to produce carbohydrates, mainly xylose, with null or insignificant degradation of xylose. On the other hand, in experiments conducted at high temperatures, Figure 7b shows a significant increase in xylose concentration at the beginning of the reaction, noting that the reactor has a pre-heating period to reach the study temperature during which xylose was produced. A considerable increase in the amount of xylose produced during the reaction is observed; associated this behavior with the chemical

reaction, the second part of Equation 7 is shown where xylose reaches a maximum in the fluid and then the concentration decreases due to degradation by effect of the temperature and amount of acid. Otherwise, the correlation between experimental data and xylose calculate by mathematical model presents good fit under experimental conditions of temperature.

The mathematical model used to determinate xylose and the experimental results obtained at 160 °C shows a good correlation, and presented a variation at  $t = 50$  min. During the first 10 min of reaction, an increase is observed, continuing an increasing trend that reaches a maximum concentration at  $t = 50$  min, then a degradation process on the xylose molecules starts due to the temperature and the xylose concentration starts decreasing at  $t = 60$  min of reaction. Moreover, the experiment at 180 °C, Figure 8 b) dashed line, it is shown the comparison of the concentrations obtained during  $t = 60$  min of reaction to mathematical model. First, it was observed that at  $t = 0$  the xylose produced was  $7.5 \times 10^{-3}$  M; this amount was produced in the time reactor set up after the reaction temperature was reached. Besides this, the experimental data for xylose shows a growth until  $t = 30$  min of reaction. Then there was an increase in the xylose concentration to 0.018 M at  $t = 50$  min of reaction as it was in the experiments performed at other temperatures. The mathematical model used to calculate xylose and the experimental xylose obtained from acid hydrolysis at 160 °C shows a good correlation, and presented a variation after  $t = 50$  min of reaction. Comparing the experimental xylose concentration and the calculated concentration from the mathematical model, the apparent rate constants  $k_1$  and  $k_2$ , where calculated with least squares regression; the results are shown in Table 3.

The values of the constant rates suggest that; the reaction is governed by two reaction mechanisms at different temperature ranges; one from 100 to 160°C, and the second one from 160°C to 180°C.

Table 3. Apparent rate constants for the formation and degradation reactions obtained from experimental data at different temperatures.

Temperature, °C	Apparent rate constants [ $\text{min}^{-1}$ ] $\times 10^{-3}$	
	Formation $k_1$	Degradation $k_2$
100	0.0023	0.232
120	1.178	8.628
140	4.3358	65.48
160	20.492	51.22
180	7.887	24.43

The acid hydrolysis of *Ipomoea arborescens* at between 100 and 140 °C showed xylose formation; on the other hand, the reactions made at 160 and 180 °C temperature indicate xylose degradation. In fact, it was observed an increase from 100°C to 140°C and a decrease from 160°C to 180°C on the values of the rate constants; it implies a change in the reaction mechanism at temperatures higher than 160°C. From the linear form of the Arrhenius equation, values can be obtained for the: activation energy and the pre-exponential factor. The inverse of the temperature is plotted against the natural logarithm of the apparent rate constant. Apparent rate constants determined with data obtained during acid hydrolysis between 100-140 °C were used to determine  $E_{a1}$  and  $A_{app1}$  for the xylose formation; for the xylose degradation  $E_{a2}$  and  $A_{app2}$  were determined at temperatures of 140-180 °C.

In order to provide a reference, the results obtained by other authors who investigated the acid hydrolysis in a variety of species of trees, crop residues and fodder were compared to the results of this project; Table 4 shows that comparison. The activation energies obtained for the reaction of formation of xylose in different species are found in the range of 95-179 kJ/mole, while for agricultural and forestry residues were in the range of 65-171 kJ/mole for different conditions of temperature and acid concentrations. These ranges of activation energies are due to the differences in the nature of the species studied; specifically, the contents and arrangement of cell wall components are different within the treated biomass. Overall, the activation energy found in this project is comparable with results in previous works. *Ipomoea arborescens* has lower activation energy  $E_a = 100.85$  kJ/mole,  $A = 2.79 \times 10^{10} \text{ min}^{-1}$  compared with other wood species studied previously.

## Conclusions

The combination of the study of the composition of *Ipomoea arborescens* particles, the experimental data obtained in acid hydrolysis and the comparison of the calculated data from the solution of the pseudo-homogeneous kinetic model for the acid hydrolysis allowed to correlate adequately the acid hydrolysis under controlled laboratory conditions. From the composition, the stoichiometric factor for the hemicellulose was obtained, which is included in the acid hydrolysis reaction as well as the values of the apparent rate constants for the formation

Table 4. Activation energies calculated from particles of different species of trees, agricultural and forestry residues under acid hydrolysis conditions.

Material	Temperature, H <sub>2</sub> SO <sub>4</sub> (wt % o mol)	kinetic model	activation energy [kJ/mol]
red oak*	140-160°C, 0.1-0.2%	xylan $\xrightarrow{1}$ xylose $\xrightarrow{2}$	$Ea_1=65.40, Ea_2=106$
corn cobs*	50-90°C 0.2-3.2 mol <sup>a</sup>	oligomers $\xrightarrow{1}$ xylose $\xrightarrow{2}$	$Ea_1=129.7, Ea_2=108.8$
wheat straw*		xylan $\xrightarrow{1}$ xylose $\xrightarrow{2}$	$Ea_1=167, Ea_2=141$
switchgrass*			$Ea_1=169, Ea_2=99.5$
"Panicum virgatum"			
corn residues*	no isothermal 0.49-1.47 %	xylan $\xrightarrow{1}$ xylose $\xrightarrow{2}$	$Ea_1=171.6, Ea_2=133.9$
residues <sup>o</sup>	130-160°C 0.65 %	xylan $\xrightarrow{1}$ xylose	$Ea_1=101.3$
"Eucaliptus grandis"			
birchwood*	100-170°C 0.04-0.18 mol	xylan fractions	$Ea_1=126.7, Ea_2=156.5$
		$xylan_f \searrow^1$	
		$xylan_d \nearrow^2$	
"Betula papyrifera"			
		$xylan_f \searrow^1$	
		$xylan_d \nearrow^2$ xylose $\xrightarrow{3}$	$Ea_1=120.1, Ea_2=118.0, Ea_3=112.6$
red Oak*	120-140°C, 1.0-5.0%		
aspen <sup>γ</sup>	160-190°C	Hemicellulose $\xrightarrow{1}$ xylose $\xrightarrow{2}$	$Ea_1=97\sim 151, Ea_2=155.3$
red maple <sup>γ</sup>	0.25-1.0 %		$Ea_1=88.6\sim 149.4, Ea_2=129.6$
switchgrass <sup>γ</sup>			$Ea_1=65.9\sim 167.9, Ea_2=165.59$
basswood <sup>γ</sup>			$Ea_1=102.6\sim 179.13$
"Tilia americana"			$Ea_2=165.59$

<sup>o</sup> (Canettieri E. V., 2007) \* (Yat, 2006) <sup>γ</sup> (Canettieri E. V., 2007)

and degradation of xylose. The mathematical model adequately predicted the experimental concentrations, presenting mainly an adequate correlation with the study temperature.

The best results for the hemicellulose acid hydrolysis, represented by the xylose formation, were found with conditions of 160°C, 0.50 wt % of H<sub>2</sub>SO<sub>4</sub>, particle sizes less than 0.595 mm at t = 20 min of reaction time. The selectivity of the hydrolysis leans toward the cellulose degradation under acid conditions greater than 0.75 wt % and temperatures above 160 ° C. The optimum operating temperature for scaling the acid hydrolysis process of *Ipomoea arborescens* is between 120 and 160 ° C.

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### Abbreviations

HPLC, high performance liquid chromatography, SEM, scanning electron microscopy, CDTA, 1,2-Cyclohexylenedinitrilotetraacetic acid, wt %, weight percent.

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