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Modeling of the Hydrolysis of Sugar Cane Bagasse with Hydrochloric Acid

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Abstract

Sugar cane bagasse was hydrolyzed under different concentrations of hydrochloric acid (2–6%), reaction times (0–300 min), and temperatures (100–128°C). Sugars obtained (xylose, glucose, arabinose, and glucose) and degradation products (furfural and acetic acid) were determined. Based on the Saeman model and the two-fraction model, kinetic parameters for predicting these compounds in the hydrolysates were developed. The influence of temperature was studied using the Arrhenius equation. The optimal conditions selected were 128°C, 2% HCl, and 51.1 min. Using these conditions, 22.6 g xylose/L, 3.31 g arabinose/L, 3.77 g glucose/L, 3.59 g acetic acid/L, and 1.54 g furfural/L were obtained.

Index Entries: Sugar cane; bagasse; xylose; modeling; acid hydrolysis.

Introduction

Xylose is a sugar that can be used as a carbon source in the fermentation process. The main application of xylose is its bioconversion to xylitol, a functional sweetener with important technological properties like anticarcinogenicity, low caloric value, and negative heat of dissolution *(1)*.

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The economic interest in xylitol production can be enhanced if the needed xylose solutions can be obtained from the hydrolysis of low-cost lignocellulosic wastes. Sugar cane bagasse is a potential xylose source. The hydrolysis of sugar cane bagasse to obtain xylose solutions has a double benefit: the elimination of wastes and the generation of value-added products that increases the economy of the process.

Dilute acids lead to a limited hydrolysis called prehydrolysis. This consists in the hydrolysis of the hemicellulosic fraction, leaving the cellulose and lignin fractions almost unaltered. Sulfuric, hydrochloric, hydrofluoric, or acetic acids are commonly employed as catalysts of the hydrolysis. The product of the hydrolysis is a solution containing primarily xylose, glucose, and arabinose. Oligomers, furfural, and acetic acid are also released. Bonds in the hemicellulosic fraction are weaker than in the cellulosic fraction. Therefore, by selecting operational conditions, it is possible to almost quantitatively hydrolyze the hemicelluloses, leaving the cellulose and lignin in the solid residue. Then, cellulose and lignin can be processed for the production of lactic acid or ethanol *(2–4)* through saccharification–fermentation or for the production of paper pulp *(5)*.

The xylose obtained from the hemicellulosic hydrolysis of sugar cane bagasse can be used for its conversion through chemical or biotechnology processes to xylitol *(6,7)* or single-cell protein *(8)*.

This work deals with the hydrolysis of sugar cane bagasse using hydrochloric acid. Kinetic models were developed to explain the time-course of the xylose, glucose, arabinose, acetic acid, and furfural generated. The hydrolysis was optimized to obtain xylose solutions with low concentrations of growth inhibitors.

Materials and Methods

Raw Material

The raw material used in these experiments was sugar cane bagasse collected from a local industry (Ingenio Azucarero de Mante, Tamaulipas, Mexico). Sugar cane bagasse was air-dried, milled, screened to select the fraction of particles with a size lower than 0.5 mm, homogenized in a single lot, and stored until needed.

Analysis of Samples

Analyses of the main fractions (glucan, xylan, araban, and klason lignin) were carried out using a quantitative acid hydrolysis under standard conditions *(9)*. Treatments were performed in the range 100–128°C in media containing 2, 4, or 6 g HCl/100 g liquor. All experiments were performed using a liquor/solid ratio (LSR) of 10 g liquor/g sugar cane bagasse on a dry basis. Samples were collected at 0, 20, 40, 60, 180, and 300 min. The experiments were performed in nine experimental sets corresponding to conditions shown in Table 1.

Samples of liquor were taken from the reaction media and centrifuged. The supernatant was used to determine the composition of the

Table 1
Operational Conditions Employed in This Work

Set	Temperature (°C)	[HCl] (%)	Time[a] (min)
1	100	2	0–300
2	100	4	0–300
3	100	6	0–300
4	122	2	0–300
5	122	4	0–300
6	122	6	0–300
7	128	2	0–300
8	128	4	0–300
9	128	6	0–300

[a]Samples taken at 0, 20, 40, 60, 180, and 300 min.

hydrolysates. The pellets were washed twice with sterile water and used to determine the insolubilized fraction and, by difference, the solubilized fraction (as dry weight).

The supernatant was diluted with water and analyzed by ultraviolet–visible (UV-vis) spectroscopy at 280 nm for furfural and by high-performance liquid chromatography (HPLC) for glucose, xylose, arabinose, and acetic acid. The HPLC analyses were carried out using a Transgenomic ION-300 column (oven temperature = 45°C) with isocratic elution (flow rate = 0.4 mL/min; mobile phase: H_2SO_4 0.005 *N*) and a refraction index (RI) detector.

Statistical Analysis

All experimental data were carried out in triplicate and average results are given. Nonlinear regression analyses of experimental data were performed with a commercial optimization routine dealing with the Newton's method (Solver, Microsoft Excel 2000, Microsoft Corporation, Redmond, WA, USA) by minimizing the sum of the squares of deviations between experimental and calculated data, as reported previously *(10)*. Values of r^2 were used as criteria of fitting for selecting the better kinetic models.

Kinetic Models

Several reactions take place during the hydrolysis of sugar polymers with dilute acids. The substrate is in the solid phase and the catalyst in the liquid phase. It is usual to apply simple models to study the kinetic of the hydrolysis. The first model successfully applied was used for the hydrolysis of fir wood with sulfuric acid *(11)*:

$$\text{Cellulose} \longrightarrow \text{Glucose} \longrightarrow \text{Decomposition products} \quad (1)$$

This model is called the Saeman model and it was also applied to the hydrolysis of the hemicellulosic fraction *(12,13)*. Therefore, it can be generalized to:

$$\text{Polymers} \xrightarrow{k_1} \text{Monomers} \xrightarrow{k_2} \text{Decomposition products} \quad (2)$$

where k_1 is the rate of the generation reaction and k_2 is the rate of the decomposition reaction (min^{-1}). Solving the differential equations, the following model predicts the concentration of monomers:

$$M = M_0 e^{-k_2 \cdot t} + P_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (3)$$

where M and P are concentrations of monomer and polymer, respectively, expressed in grams per liter, t is time, and the subscript 0 indicates initial conditions. In this work, Eq. (3) was applied to model the hydrolysis of sugar cane bagasse with hydrochloric acid.

Results and Discussion

The composition obtained for the sugar cane bagasse was (weight percent on dry basis) as follows: glucan, 38.9%; xylan, 20.6%; araban, 5.56%; klason lignin, 23.9%; others, 11.0% (average values of three replicates, error minor than 1% in all compounds). These values are in the range found for this kind of material.

The yield of the hydrolysis at 300 min varied in a narrow range (44.9–56.9%). Figure 1 shows the experimental results for concentration of xylose. The potential concentration of xylose (corresponding to the quantitative conversion of xylan to xylose without degradation reactions) was 23.4 g/L. The highest xylose concentration obtained was 23.5 g/L in the experiment of set 7 during 40 min, which corresponding to 100.5% of potential concentration. In experiments performed at 122°C and 128°C can be observed that xylose concentration reached a maximum value and then decreased with reaction time. This suggests decomposition reaction, probably to furfural.

During the hydrolysis, other sugars were released to the liquor, mainly glucose and arabinose. Glucose originates from both cellulosic and hemicellulosic fractions, whereas arabinose is a pentose found only in hemicelluloses. The determination of these monomers is of interest because of their potential application as carbon sources for microbial growth. Figure 2 shows the experimental results for the concentration of glucose.

In general, analyzing the results, it can be established that the concentration of glucose increased with reaction time and reached maximum values for each experiment as a function of temperature and HCl concentration. The maximum values for glucose concentration were 4.03 g/L at 100°C, 5.88 g/L at 122°C, and 6.58 g/L at 128°C. Under severe conditions (high temperature and a long time), a slight decrease in glucose concentra-

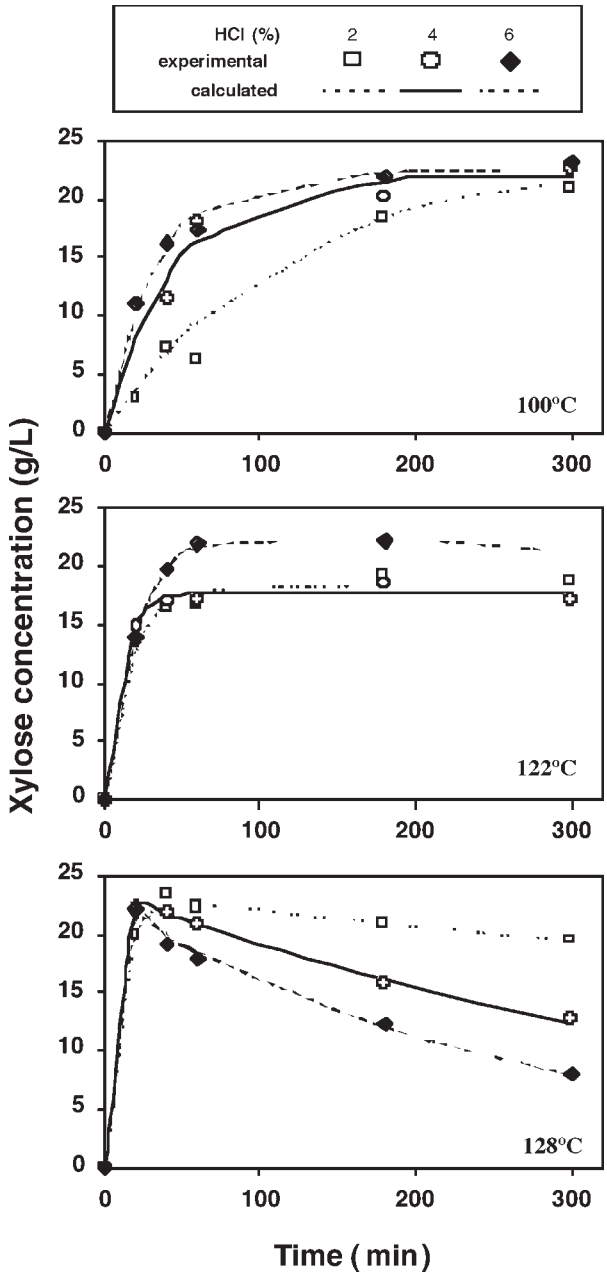

Fig. 1. Comparison between experimental and calculated xylose concentrations.

tion was observed, suggesting that decomposition reactions occur, probably to 5-hydroxymethylfurfural.

Figure 3 shows the experimental results for concentration of arabinose. The concentration increased quickly and reached stable values without evidence of degradation reactions. The maximum values achieved were 2.59 g/L for set 3 and 5.43 g/L for set 7.

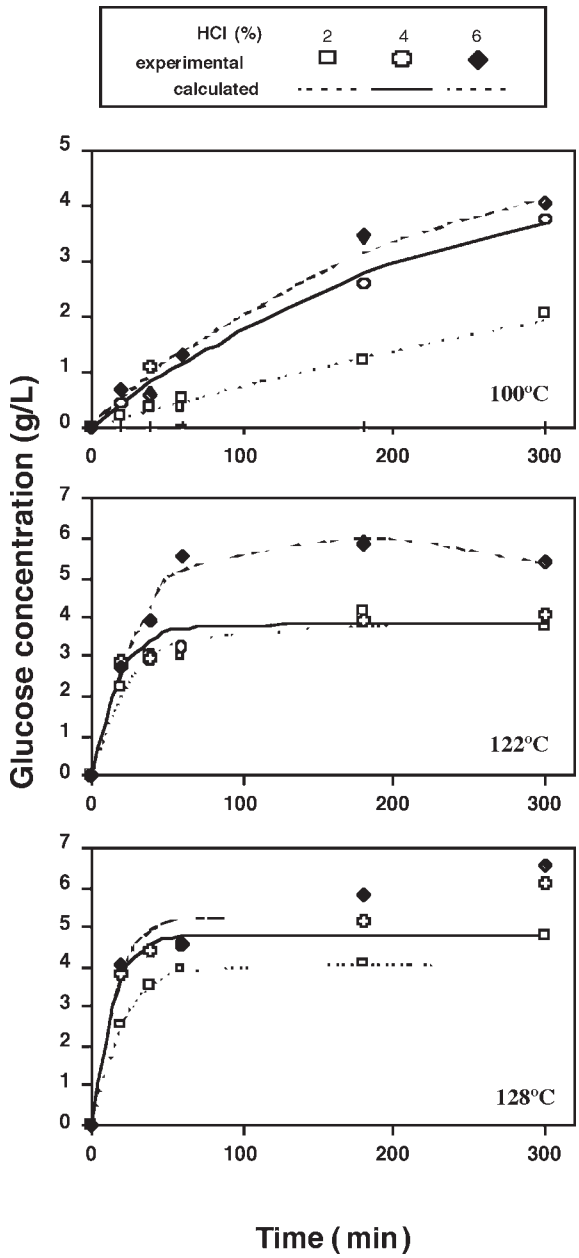

Fig. 2. Comparison between experimental and calculated glucose concentrations.

Acetic acid is generated from the hydrolysis of acetyl groups linked to hemicellulosic sugars. Figure 4 shows the experimental results for concentration of acetic acid. In the experiments performed, it was observed that acetic acid showed a similar behavior as arabinose, establishing maximum concentration values between 4.1 and 5.3 g/L. Acetic acid (4–10 g/L) can be an inhibitor of microbial growth *(14,15)* because it goes through the

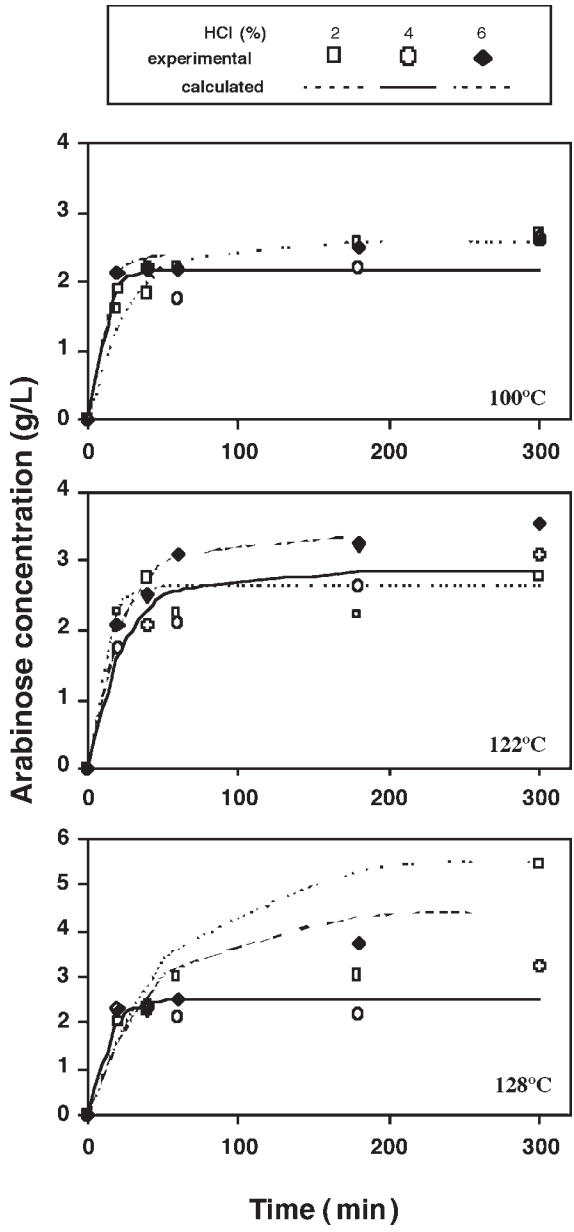

Fig. 3. Comparison between experimental and calculated arabinose concentrations.

cellular membranes and decreases the intracellular pH, which affects the metabolism of the microorganism *(16,17)*. However, it has been reported that an acetic acid concentration of 9–10 g/L can stimulate the growth of the microorganism *(18)*. In our study, the maximum acetic acid concentrations were below the low limit of the toxic effect.

Furfural has also been reported to be a growth inhibitor. Figure 5 shows the experimental results for concentration of furfural. The amount

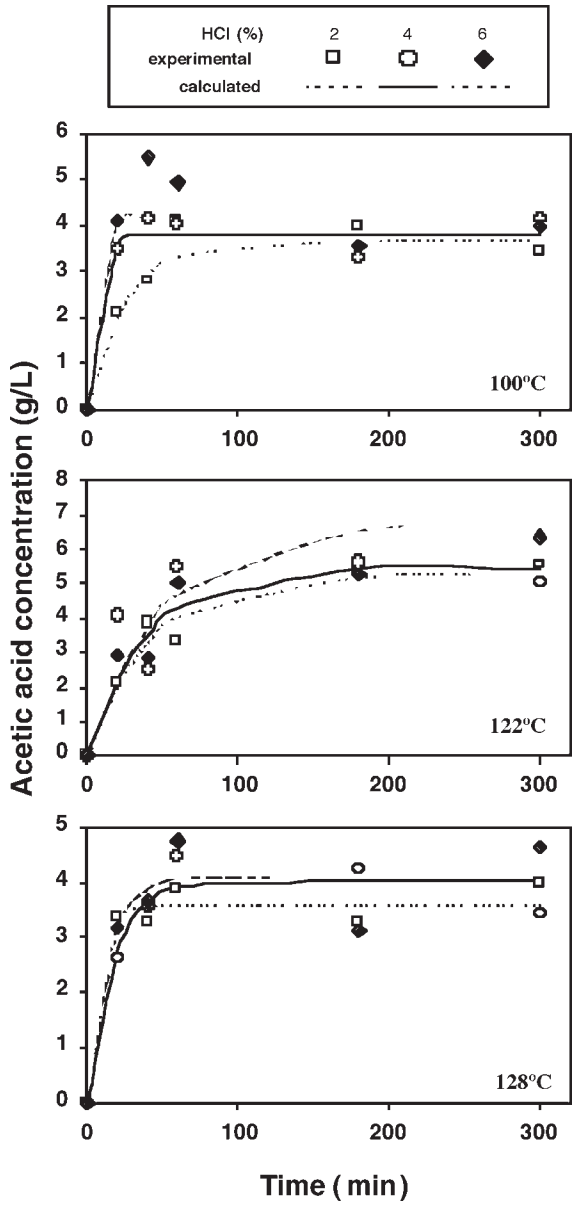

Fig. 4. Comparison between experimental and calculated acetic acid concentrations.

of furfural increased with reaction time, catalyst concentration, and temperature. The maximum value reached was 7.97 g/L, obtained in experiments performed under severe conditions (set 8, 300 min).

For comparative purposes, we can selected the optimum values for each set based on higher xylose concentrations and lower concentrations of the potential growth inhibitors acetic acid and furfural. It can be observed that it is possible to obtain hydrolysates with xylose concentration higher

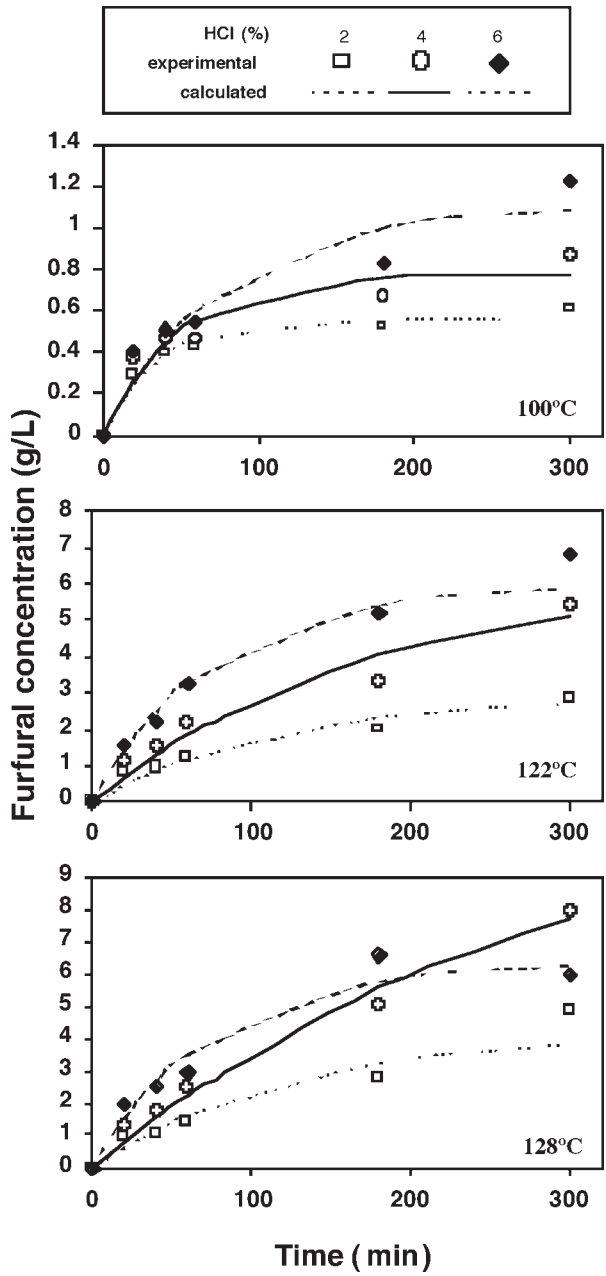

Fig. 5. Comparison between experimental and calculated furfural concentrations.

than 20 g/L, furfural concentration around 1 g/L, and acetic acid acetic lower than 4 g/L. Furthermore, the glucose concentration was normally lower than 4 g/L at optimal conditions, which indicates low degradation of the cellulosic fraction. This is favorable because the solid residue can be posteriorly processed for paper pulp or for the generation of glucose solutions by enzymatic hydrolysis.

Table 2
Kinetic and Statistical Parameters for Xylose Concentration in the Hydrolysis of Sugar Cane Bagasse with Hydrochloric Acid

	Fitting the Saeman model			Fitting the two-fraction model			
Set	k_1 (min^{-1})	$k_2 \times 10^3$ (min^{-1})	r^2	α (g/g)	k_1 (min^{-1})	$k_2 \times 10^3$ (min^{-1})	r^2
1	0.009	0.158	0.997	1.00	0.009	0.000	0.997
2	0.020	0.264	0.973	0.935	0.023	0.000	0.975
3	0.028	0.129	0.985	0.955	0.031	0.000	0.988
4	0.033	1.02	0.955	0.787	0.060	0.000	0.992
5	0.041	1.78	0.950	0.763	0.089	0.000	0.996
6	0.047	0.320	0.999	1.00	0.047	0.320	0.999
7	0.099	0.645	0.997	1.00	0.099	0.645	0.997
8	0.207	2.14	0.994	1.00	0.209	2.14	0.999
9	0.698	3.76	0.994	0.968	0.698	3.52	0.996

Kinetic Modeling of Xylose Concentration

Xylose is the main product in the hydrolysis of sugar cane bagasse. To apply the Saeman model *(11)*, the value of M_0 was 0 g/L and P_0 was determined using Eq. (4), assuming a total conversion of xylan to xylose in the raw material without degradation:

$$P_0 = \frac{150}{132} \cdot \frac{CXn_0/100}{LSR} \times 1000 = 23.4 \text{ L/g xylose} \quad (4)$$

CXn_0 is the initial composition of xylan (20.6 g xylan/100 g sugar cane bagasse on dry basis), LSR is the liquid/solid ratio (10 g water/g sugar cane bagasse), and 150/132 is the ratio of the stoichiometric factors.

Results of fitting experimental data to Eq. (3) are shown in Table 2. The values of the statistical parameter r^2 were suitable except for sets 4 and 5. Therefore, the kinetic model was modified to include the presence of two fractions in the polymer of xylan with different reaction rates. Evidence of two fractions for the hydrolysis of xylan was also reported by other authors *(19)*. Moreover, it is usual to find that one of these fractions does not react in some experimental conditions *(9,10)*. The ratio between the susceptible xylan and total xylan in the raw material is designated α (g of susceptible xylan/g of total xylan). The values of α are usually in the range 0.5–1 g/g. Equation (3) was modified to yield Eq. (5) according with the model of two fractions:

$$M = M_0 e^{-k_2 \cdot t} + \alpha P_0 \frac{k_1}{k_2 - k_1} (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (5)$$

Data were fitted applying Eq. (5) for each set to obtain the optimal values for α, k_1, and k_2. Table 2 also shows the results of fitting the model of two

fractions and the correlation coefficient r^2. Better fitting was obtained using the two-fraction model as compared with the Saeman model.

Comparing values of k_1 with k_2, it can be concluded that the rate for xylose generation is around 150-fold higher than the rate for xylose degradation. In sets 1–5, k_2 values were actually negligible. In general, values of kinetic coefficients increased with temperature and hydrochloric acid concentration.

The value of parameter α was in the range 0.76–1.00 g/g, with an average of 0.93 g/g. This value is in accordance with others reported for acid hydrolysis using other lignocellulosic materials. For example, values of α in the range 0.58–0.80 g/g for hydrolysis of oak *(20)*, 0.84 g/g for corn, and 0.86 g/g for sunflower seeds *(21)*. It is usual to find that the parameter α depends on the operational conditions. In the hydrolysis of *Pinus pinaster* at atmospheric pressure, the values of α were in the range 0.57–0.63 g/g, whereas at autoclave pressure and temperature, they were in the range 0.86–0.87 g/g *(22,23)*. Figure 1 shows experimental data and the prediction of the model with two fractions. A good agreement between them can be observed.

The kinetic coefficients can be correlated to obtain an equation that explains the influence of the temperature on the hydrolysis. Traditionally, the equation of Arrhenius is used for this purpose:

$$k_1 = k_{10} \cdot e^{-E_a/RT} \tag{6}$$

where k_1 is the kinetic coefficient, k_{10} is a pre-exponential factor (same units as for k_1), E_a is the activation energy (kJ/mol), R is the gas constant (8.3143×10^{-3} [kJ/mol·K]), and T is the temperature (K).

Equation (6) was applied to the kinetic coefficient previously obtained. The values of k^2 were too small and it was not possible to get a good fitting because they are greatly affected by experimental errors. This behavior is frequently found in this kind of hydrolysis *(24,25)*. Table 3 shows results of fitting the kinetic coefficients k_1 to the equation of Arrhenius. The fitting was performed for each HCl concentration, sets 1–4–7, 2–5–8, and 3–6–9. The average value obtained for E_a was 102 kJ/mol, and for $\ln(k_{10})$, it was 28.9 (k_{10} in min^{-1}). These values are in the range found for other lignocellulosic substrates in the literature. In models with two fractions for xylan, E_a of the easy fraction showed values around 127 kJ/mol *(26)*, 120 kJ/mol *(27)*, and 96.3 kJ/mol for hard woods *(20)* and 80.3 kJ/mol and 92.3 kJ/mol for agricultural wastes *(21)*.

Kinetic Modeling of Glucose Concentration

Glucose is a secondary product in the acid hydrolysis of lignocellulosic materials. It has a double origin: cellulose and hemicellulosic heteropolymers that contain glucose. It is not possible to distinguish if the glucose originates from cellulose or hemicelluloses, but it likely originates from hemicelluloses because cellulose is a polymer very resistant to dilute acids.

Table 3
Parameters Obtained Fitting the Equation of Arrhenius for Xylose Concentration

Set	[HCl] (%)	$\ln(k_{10})$ (k_{10} in min^{-1})	E_a/R (K^{-1})	r^2
1–4–7	2	30.1	13,022	1.000
2–5–8	4	25.8	11,069	0.973
3–6–9	6	30.6	12,805	0.758
Average	—	28.85	12,299	—

Table 4
Kinetic and Statistical Parameters of Glucose Concentration in the Hydrolysis of Sugar Cane Bagasse with Hydrochloric Acid

	Fitting the Saeman model			Fitting the two-fraction model			
Set	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	r^2	α_G (g/g)	k_1 (min^{-1})	$k_2 \times 10^3$ (min^{-1})	r^2
1	0.158	0.000	0.996	0.138	0.001	0.000	0.991
2	0.390	1.65	0.966	0.139	0.004	0.464	0.990
3	0.601	3.87	0.981	0.125	0.005	0.030	0.979
4	2.28	16.4	0.941	0.088	0.037	0.000	0.971
5	2.76	17.9	0.847	0.090	0.054	0.000	0.963
6	3.29	13.5	0.969	0.163	0.024	1.05	0.988
7	2.61	15.4	0.879	0.097	0.046	0.147	1.000
8	3.11	13.3	0.785	0.111	0.074	0.000	0.987
9	2.84	11.3	0.829	0.123	0.066	0.000	0.967

The Saeman model and the two-fraction model were used to model the glucose concentration. In this case, 5-hydroxymethylfurfural (HMF) was the main decomposition product. The value for potential concentration of polymers cannot be calculated because it originates from both cellulose and hemicelluloses. In a first approach, it was fixed using the concentration obtained for the quantitative conversion of glucan to glucose, 43.2 g/L. This is the same approach used for xylan in Eq. (4). The result of the fitting for the Saeman model is shown in Table 4. The values obtained for the coefficient r^2 were lower than 0.9 in some cases. Therefore, the fitting was not good.

In a second approach, the potential concentration of glucose was considered a variable; consequently, only a fraction of glucan is considered reactive. Therefore, a new variable was introduced, α_G (meaning the glucose fraction susceptible to hydrolysis), similar to Eq. (5) leading to Eq. (7), which gives the concentration of glucose as a function of time:

$$G = G_0 e^{-k_2 \cdot t} + \alpha_G \cdot Gn_0 \cdot \frac{k_1}{k_2 - k_1} (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) \quad (7)$$

where G_0 is the glucose concentration at time 0 (0 g/L), Gn_0 = 43.2 g/L (corresponding to a hypothetical quantitative conversion of glucan to glucose); k_1 is the kinetic coefficient of hydrolysis of glucan to glucose, and k_2 is the kinetic coefficient of glucose decomposition.

The fitting of glucose concentration using the model of two fractions [Eq. (7)] is shown also in Table 4. Better coefficients (r^2) than using the one-fraction model were obtained. These data are shown in Fig. 2. A negligible decomposition of glucose was observed, the coefficient k_2 being close to 0 or very much lower than k_1 (approx 130-fold lower).

The value of α_G was not significantly affected by temperature and HCl concentration. It varied from 0.088 g/g in set 4 to 0.139 g/g in set 2, with an average of 0.119 g/g. This corresponds to a susceptible glucan of 4.64 g /100 g sugar cane bagasse (on dry basis) and means that the treatment with hydrochloric acid is very selective toward the xylan hydrolysis, leaving the cellulose almost unaltered because 4.64 g/100 g can be considered the glucose that occurs in the hemicellulosic fraction.

Kinetic Modeling of Arabinose Concentration

Arabinose is a pentose that is generated from hemicelluloses. It appears mainly in agricultural materials, such as sugar cane bagasse, but in lower concentration than xylose. The same models used for modeling glucose were used to model the behavior of arabinose. These are a first model considering that all araban is hydrolyzed (called Saeman model) and a second model considering two fractions of araban and only one susceptible to hydrolysis (two-fraction model). The parameter α_A is the ratio between susceptible araban and total araban.

Table 5 shows the results of fitting both models. Only in four sets did the fitting using the Saeman model show statistical significance ($r^2 > 0.9$). However, the model of two fractions fitted better. Figure 3 shows the experimental and calculated values using the two-fraction model.

Kinetic coefficients for arabinose decomposition (probably to furfural) were zero in the two-fraction model. The value of α_A varied from 0.395 g/g in set 2 to 1.000 g/g in set 7. The fraction of susceptible araban was affected by temperature. The average values were 0.431 g/g at 100°C, 0.531 g/g at 122°C, and 0.751 g/g at 128°C.

Kinetic Modeling of Acetic Acid Concentration

Acetic acid is a byproduct because of the hydrolysis of the acetyl groups present in the hemicellulosic heteropolymers. The following simple model was applied *(13,24,25)*:

$$\text{Acetyl groups} \xrightarrow{k_1} \text{Acetic acid} \qquad (8)$$

Table 5
Kinetic and Statistical Parameters of Arabinose Concentration in the Hydrolysis of Sugar Cane Bagasse with Hydrochloric Acid

	Fitting the Saeman model			Fitting the two-fraction model			
Set	$k_1 \times 10^3$ (min^{-1})	$k_2 \times 10^3$ (min^{-1})	r^2	α_A (g/g)	k_1 (min^{-1})	$k_2 \times 10^3$ (min^{-1})	r^2
1	10.7	3.90	0.889	0.467	0.0369	0.000	0.979
2	10.9	4.62	0.620	0.395	0.102	0.000	0.915
3	13.1	4.21	0.930	0.432	0.0992	0.000	0.994
4	14.4	3.47	0.513	0.477	0.0973	0.000	0.837
5	10.8	3.29	0.831	0.511	0.0398	0.000	0.936
6	16.7	2.42	0.973	0.604	0.0418	0.000	0.996
7	14.5	0.00	0.987	1.000	0.0177	0.000	0.978
8	12.2	3.58	0.587	0.458	0.0767	0.000	0.853
9	15.6	2.93	0.931	0.794	0.0221	0.000	0.910

Table 6
Kinetic and Statistical Parameters of Acetic Acid Concentration in the Hydrolysis of Sugar Cane Bagasse with Hydrochloric Acid

Set	Ac_0 (g AcH/L)	k (min^{-1})	r^2
1	3.69	0.0386	0.981
2	3.82	0.134	0.960
3	4.14	0.316	0.930
4	5.25	0.0241	0.944
5	5.47	0.0258	0.834
6	6.72	0.0201	0.882
7	3.59	0.129	0.958
8	4.04	0.0571	0.940
9	4.11	0.0743	0.860

Based on this reaction model and solving differential equation leads to Eq. (9), which expresses the acetic acid concentration (AcH) as a function of time (t):

$$AcH = Ac_0(1 - e^{-k_1 \cdot t}) \tag{9}$$

Ac_0 is the potential concentration of acetyl groups and k_1 the rate of acetic acid generation (min^{-1}). Ac_0 was expressed as acetic acid and introduced as a regression parameter.

Table 6 shows the coefficients obtained in the fitting. Figure 5 represents the experimental data and the prediction of the model. Ac_0 varied in the range 3.59–6.72 g/L, with an average of 4.54 g/L. Based on materials

Table 7
Kinetic and Statistical Parameters
of Furfural Concentration in the Hydrolysis
of Sugar Cane Bagasse with Hydrochloric Acid

Set	F_0 (g/L)	k (min^{-1})	r^2
1	0.560	0.0296	0.97
2	0.779	0.0207	0.92
3	1.11	0.0131	0.91
4	2.94	0.00866	0.95
5	5.96	0.00631	0.95
6	5.98	0.0134	0.96
7	4.16	0.0840	0.87
8	12.0	0.00349	0.99
9	6.35	0.0135	0.94

balances, it was calculated that acetyl groups are 3% in raw material. This value is in accordance with others reported in literature *(26)*.

Kinetic Modeling of Furfural Concentration

Furfural is generated as a decomposition product of pentoses in the hydrolysis of lignocellulosic materials. Based on furfural results from Fig. 5, a similar model to that used for acetic acid can be considered. Equation (10) expresses the furfural concentration (F) as a function of time (t):

$$F = F_0(1 - e^{-k_1 \cdot t}) \tag{10}$$

F_0 is the potential concentration of furfural and k_1 is the rate of furfural generation (min^{-1}). F_0 was introduced in the model as a regression parameter. Table 7 shows the kinetic and statistical parameters obtained in the fitting of furfural generated in the hydrolysis. Figure 5 shows the comparison between experimental and predicted data.

The value of F_0 increased with the temperature. It was in a wide range, 0.560–12.0 g/L, in accordance with other works using sorghum straw *(13)*.

Comparison with Sulfuric Acid Hydrolysis

In other work (data unpublished), the hydrolysis of sugar cane bagasse with sulfuric acid was studied as catalyst instead of hydrochloric acid. The same operational conditions (liquid/solid ratio, temperature, and time) were used.

In general, higher concentrations were obtained using hydrochloric acid. The maximum concentration of xylose was 21.3 g/L using HCl versus 18.1 g/L using H_2SO_4. The application of the equation of Arrhenius gave E_a = 102 kJ/mol using HCl versus 109 kJ/mol using H_2SO_4. The pre-exponential factor was lower using HCl, ln k_0 = 28.9 versus ln k_0 = 31.1 (k_0 in min^{-1}).

Table 8
Composition of the Hydrolysates in the Optimal Conditions Found for Each Set

Set	Temperature (°C)	[HCl] (%)	Time (min)	Xylose (g/L)	Arabinose (g/L)	Glucose (g/L)	Acetic acid (g/L)	Furfural (g/L)
1	100	2	300	21.7	2.59	1.94	3.69	0.560
2	100	4	300	21.8	2.20	3.67	3.82	0.787
3	100	6	300	22.3	2.40	4.14	4.14	1.09
4	122	2	300	18.4	2.65	3.82	5.25	2.71
5	122	4	300	17.9	2.84	3.87	5.46	5.06
6	122	6	107.1	22.6	3.32	6.04	5.93	4.55
7	128	2	51.1	22.6	3.31	3.77	3.59	1.54
8	128	4	22.2	22.3	2.08	3.88	2.10	0.892
9	128	6	7.6	22.1	0.686	2.09	1.77	0.623

The glucose concentration was low using both treatments: 3.7 g/L using HCl and 3.4 g/L using H_2SO_4. This suggests that both treatments are selective and the cellulose was almost unaltered.

Optimization of Results

If the hydrolysates of sugar cane bagasse are going to be used as fermentation media, the target should be to obtain sugar solutions (xylose, glucose, and arabinose) with low concentration of inhibitor (furfural and acetic acid), leaving the cellulosic fraction unaltered for further processing.

Conditions for temperature, time, and HCl concentration that lead to a maximum xylose concentration in each set were obtained using the kinetic models. For each condition selected, the values predicted for the other compounds were also calculated. Table 8 shows these results. The maximum xylose concentration varied between 17.9 (set 4) and 22.6 g/L (set 7).

The sugar concentrations obtained were high, especially the xylose concentration (values close to 100% of the potential xylose). Concentrations of growth inhibitors are under the lower limit. The optimal conditions selected were 128°C, 2% HCl (set 7), and 51.1 min. Under these conditions, 22.6 g of xylose/L, 3.31 g of arabinose/L, 3.77 g of glucose/L, 3.59 g of acetic acid/L, and 1.54 g of furfural/L were obtained. HCl was a good catalyst for hydrolysis of sugar cane bagasse. It was selective for the hemicelluloses and could be used to obtain xylose solutions with low concentrations of furfural and acetic acid.

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