

**Production of reducing sugars from leaves crown of pineapple, corn stalk and rose stalk using phosphoric acid: Kinetics and thermodynamics****Producción de azúcares reductores a partir de coronilla de piña, olote de maíz y tallo de rosa utilizando ácido fosfórico: cinética y termodinámica**N. Flores-Alamo¹, D. Gutiérrez-López^{1,2}, M. J. Solache-Ríos², F. Cuellar-Robles¹, M. del C. Carreño-de-León^{1*}¹Tecnológico Nacional de México/Instituto Tecnológico de Toluca, Av. Tecnológico S/N Col. Agrícola Bellavista, C.P. 52149, Metepec, México.²Instituto Nacional de Investigaciones Nucleares, Departamento de Química, Carretera México-Toluca S/N, La Marquesa, Ocoyoacac, Estado de México C.P. 52750, México.

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Abstract

The kinetics and thermodynamics of hydrolysis of diluted H_3PO_4 with three residual lignocellulosic materials (leaves crown of pineapple, LC; *Zea mays rachis*, CC; and rose stalk, RS) were used to study the production of reducing sugars. Three acid concentrations (1, 1.5, and 2M) and three temperatures (105, 120, and 150 °C) were tested for each material. An increase in acid concentration and temperature was conducive to sugar production. LC and the CC showed good capacity to produce reducing sugars in compared to RS. For LC and CC better conditions were 120 °C and 2.0 M; however, similar results were observed at 105 °C and 2.0 M. The best hydrolysis reaction time was 120 minutes to produce the greatest amount of reducing sugars. Hydrolysis kinetics showed that production exceeded the decomposition of sugars ($k_1 > k_2, k_r > 1$) with LC and CC. Thermodynamics analysis indicated that endothermic and non-spontaneous processes were involved for the production and decomposition of sugars. The magnitude of activation energy of RS was the highest of all three materials, this shows that RS was the most difficult material to hydrolyze. .

Keywords: hydrolysis, reducing sugars, thermodynamics, lignocellulosic materials, kinetics.

Resumen

Mediante la cinética y la termodinámica de la hidrólisis con H_3PO_4 diluido se estudió la producción de azúcares reductores de tres materiales lignocelulósicos residuales (hojas de la corona de piña, LC; olote de maíz, CC; y tallo de rosa, RS). Se probaron tres concentraciones de ácido (1, 1,5 y 2M) y tres temperaturas (105, 120 y 150 °C) para cada material. La temperatura y concentración mejoraron ligeramente la producción de azúcares. La LC y la CC mostraron una mejor producción de azúcares reductores en comparación con el RS. Las mejores condiciones de operación para LC y el CC fueron 120 °C y 2 M; sin embargo, se observaron resultados similares a 105 °C y 2 M. El tiempo de reacción al que la hidrólisis produjo la mayor cantidad de azúcares reductores fue de 120 minutos. La cinética de hidrólisis mostró que la rapidez de producción predominó sobre la descomposición de los azúcares ($k_1 > k_2, k_r > 1$) con la LC y el CC. El análisis termodinámico mostró un proceso endotérmico y no espontáneos para la producción y descomposición de azúcares. La energía de activación fue mayor para el RS que para la LC y el CC, lo que indica que el RS es un material recalcitrante ante el proceso de hidrólisis acida.

Palabras clave: hidrólisis, azúcares reductores, termodinámica, materiales lignocelulósicos, cinética.

* Corresponding author. E-mail: mcarrenod@toluca.tecnm.mx;

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1 Introduction

The need of energy supply led to search for environmentally friendly alternative sources to reduce the atmospheric pollution due to the use of fossil fuels (Antonio-Narcizo, *et al.*, 2023). The geographical location of the State of Mexico allows for a wide diversity of climates and soil types that allows the production of seeds, legumes, vegetables, fruits, agave, herbs (including medicinal ones) and, varied flower production, all these products generate residues such as shells, stems, leaves and petals that are not properly disposed causing soil erosion and the emission of polluting gases into the atmosphere due to their natural decomposition (Hernández-Teyssier, *et al.*, 2023). This is the case of residues such as corn cob stalks (*Zea mays rachis*), pineapple crown leaves and rose stems. These residues are the most abundant sources of renewable biomass globally (Contreras-Zarazúa *et al.*, 2022). They have a complex structure consisting of carbohydrate polymers, cellulose (35-50%), hemicellulose (15-25%) and a phenolic polymer, lignin (20-25%). The process of conversion of lignocellulose to reducing sugars consists of three stages, a pre-treatment stage by physical, chemical, physico-chemical processes that involve thermal and non-thermal effects, biological or enzymatic media that helps to alter the cellulose structure by releasing and extracting the hemicellulose from the lignocellulosic, in order to allow access to acid molecules. the cellulose structure by releasing and extracting the hemicellulose from the lignocellulosic material, to later allow the access of acid molecules and in a second stage of saccharification or hydrolysis, where simple sugars are obtained for later use in a third stage where the transformation of hexoses and pentoses to bioethanol takes place (Alvira *et al.*, 2010). Monomers, such as glucose, can be obtained from these polymers, and lignocellulosic biomass has great potential as a raw material for obtaining reducing sugars, which can be used in different industries (Cortes *et al.*, 2013).

Zea mays rachis (CC), rose stalk (RS), and leaves crown of pineapple (LC) were considered as residues which are disposed into the environment, burned or used to feed farm animals (Fritsch *et al.*, 2017). The energy potential of agricultural residues can be harvested and used industrially. It is, therefore, necessary to develop methods to extract their maximum energy potential, for this reason, the hydrolytic capacity of agricultural residues (CC, RS, LC) was evaluated in the present work using phosphoric acid at three concentrations (1, 1.5 and 2 M) and three temperatures (100, 110 and 150 °C).

2 Materials and methods

2.1 Substrate from agricultural residues

The residues were obtained from local producers in Toluca, a state of Mexico, they were subjected to rinsing using distilled water, dried in a recirculation oven until constant weight, and sieved to a mesh size of 100 mesh. The extracts (chlorophyll, resins, and terpenes) were eliminated as follows: 4 g of dry residue was placed in contact with a mixture of ethanol and benzene (1:2) for 4 h, followed by hot water in a soxhlet extraction apparatus, then the solids were dried until constant weight. Finally, the substrates (samples) were dried for 24 h at 50 °C. The amount of extract present in the sample was determined from the weight difference (Zheng *et al.*, 2014).

2.2 Substrate characterization

The contents of lignin and holocellulose present in each sample were determined and the residues were performed using FTIR spectroscopy, using a Varian 640 instrument in the wavenumber 500-4000 cm^{-1} and a JEOL JSM-590-LD low-vacuum scanning electron microscope (SEM).

2.3 Holocellulose and lignin

The substrates were refluxed with a mixture of acetylketone, 1,4-dioxane and HCl for 30 min (6, 2 and 1.5 mL respectively). The mixture was filtered and washed with 10 mL of each one next solvent: ether, dioxane, methanol and finally with distilled water. After that they were dried at 103 °C for a period of 16 hours, and the final weight was assumed to be cellulose (TAPPI T17/ m-55). Separately, another sample was contacted by 15 mL of 72% sulfuric acid and stirred for 2 h, then was diluted to 3% by distilled water (350 mL), was kept in reflux for 4 h and the solid was dried at 103 °C using an oven in 16 h. The weight of this residue was taken as acid-insoluble lignin (Bagby *et al.*, 1971).

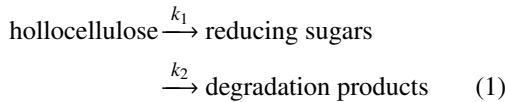
2.4 Kinetics of the acid hydrolysis experiments

Acid hydrolysis was carried out using three concentrations of H_3PO_4 (1.0, 1.5 and 2.0 M) at three temperatures (105, 120 and 150 °C). The kinetics of sugar production were determined in duplicate for each material and samples were taken every 30 min for 5 h. In each run, 20 test tubes with screw caps were put in a Hanna brand COD digester at the desired temperature. Each tube contained 0.5 g of residue with 7.5 mL of solution at the desired

concentration. At the end of the reaction, each sample was cooled at 20°C (local temperature) and separated by filtration the solid and liquid phases (hydrolyzed). The dinitrosalicylic acid method (DNS) was used to determine the reducing sugar content in the hydrolysates (Miller, 1959). The furfural was measured as follows: 200 μ L of each hydrolysate was diluted with distilled water to a volume of 10 mL, subsequently the samples were homogenized and analyzed on a Thermo Scientific Evolution Array Uv-Vis spectrometer using a wavelength of 277 nm (Saien *et al.*, 2017). The solid phase was characterized using FTIR and SEM.

2.5 Kinetic and thermodynamic calculations

Sugar production data were adjusted to the Saeman (1945) kinetic model, which was the first kinetic model applied to the sulfuric acid hydrolysis of wood. It has been used satisfactorily with other residues (Tizazu & Moholkar, 2018; Sarkar & Aikat, 2013), considering that the process involves a series of reactions related to the production of monomeric sugars and their transformation into aldehyde inhibitors (Equation 1):



According to Saeman (1945) the reactions presented in Equation 1 were first-order, irreversible and proposed a kinetic model to predict the concentration of monosaccharides as a function of the reaction time (Equation 2):

$$M = \left[\frac{k_1 P_0}{k_2 - k_1} \right] (e^{-tk_1} - e^{-tk_2}), \quad (2)$$

where M represents the weight (g) of sugar per 100 g of raw material, P_0 the initial weight (g) of holocellulose per 100 g of raw material, t is the reaction time (min), k_1 and k_2 represents the kinetic constants in min^{-1} .

According with Saeman (1945) and Ranganathan *et al.*, (1985), the kinetic constants obtained from the Saeman model can be used to calculate the relationship between the two constants (k_r), which shows the effect of temperature and acid concentration and can be used to determine the reaction time at which the production of sugars reaches a maximum (Equation 3).

$$t_m = \frac{1}{k_2(k_r - 1)} \ln(k_r) \quad (3)$$

The experimental sugar production data were fitted to the kinetic model using nonlinear regression in Origin 8.1 software.

The rate constants determined from the kinetic model were used to determine the thermodynamic parameters: E_a (activation energy), ΔH (enthalpy), ΔS (entropy) and ΔG (Gibbs free energy). They were calculated to know the energetic changes at the molecular level and elucidate the process of the acid hydrolysis of agricultural residues. The Arrhenius equation was used to calculate E_a and A . Equations 4 and 5 are exponential and linear equations, respectively.

$$k = A e^{-E_a/(RT)} \quad (4)$$

$$\ln(k) = \ln(A) - \frac{E_a}{RT}, \quad (5)$$

where k is the kinetic constant (min^{-1}), A a factor of frequency (min^{-1}), E_a the activation energy (J mol^{-1}), T temperature (K) and R the constant of ideal gas ($8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$). The thermodynamic parameters were calculated from the plot of T^{-1} vs $\ln(k)$.

The calculation of ΔH and ΔS was carried out using the Eyring equation:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h_p}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (6)$$

where k is in s^{-1} , h_p the Planck constant ($6.6261 \times 10^{-34} \text{ J s}$), ΔS the entropy ($\text{J mol}^{-1} \text{ K}^{-1}$), ΔH the enthalpy (J mol^{-1}), k_B is the Boltzmann constant ($1.3807 \times 10^{-23} \text{ J K}^{-1}$) and R and T are the same in the Arrhenius equation.

ΔS and ΔH were calculated from the graph of $\ln(k/T)$ vs $1/T$ and ΔG was determined by using the Equation 7 (Saratale *et al.*, 2008).

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

2.6 Factorial analysis

Factorial analysis by using Minitab 17 software was carried out with a confidence level of 95% for the production of reducing sugars using three factors at three levels. The factors (with two replicates) were the type of material (LC, CC and RS), concentration (1, 1.5 and 2M) and temperature (105, 120 and 150 °C). The significance of each factor and the interactions between them were determined.

3 Results and discussion

3.1 Substrate characterization

The percentages of holocellulose in CC, LC and RS were 70.17, 69.36 and 63.80% and the lignin contents were 17.61, 17.85 and 20.14 %w, respectively. These values were similar to those reported by Ventura-Cruz & Tecante, (2019), 71.08% holocellulose, and 16.36%

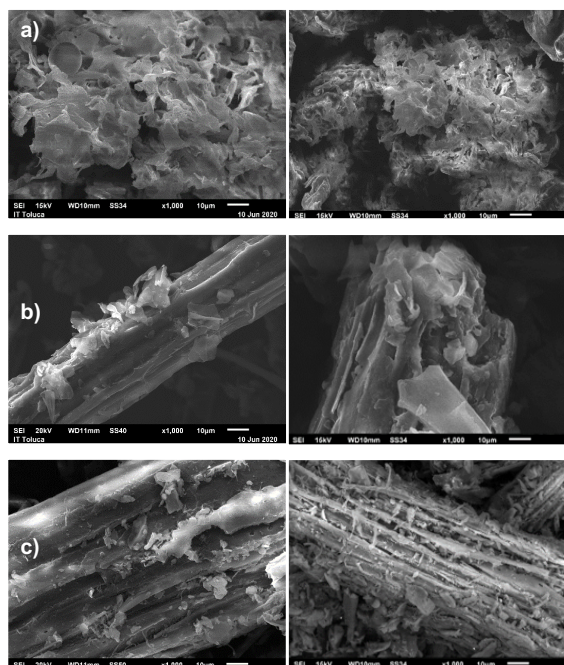


Figure 1. Micrographs of lignocellulosic materials, before (left) or after (right) hydrolysis a) CC, b) LC and c) RS.

of lignin from rose stem, besides Sun & Cheng, (2002) reports 45% of cellullose, 35 % hemicellulose and 15 % of lignin for corn cobs. According to these values, the highest yield of sugars can be expected for CC and LC because it had a higher holocellulose content and the lower percentage of lignin than RS.

3.2 SEM analysis

The morphology of each non-hydrolyzed material (Figure 1, right) shows a surface with an organized, smooth, and uniform structure; lignocellulosic materials (lignin and hemicellulose), provide rigidity and protection to cellulose fibers. After hydrolysis (Figure 1, left) at 150 °C with 2 M acid concentration, pores were evident in CC as a result of chemical and thermal attack on the cell wall. A rough and scaly surface was evident in LC and RS (b and c) due to the partial rupture of the lignin and hemicellulose chains. Similar results have been reported by Imman *et al.*, (2021) with pineapple leaves at 143.2 °C and 0.61 M of sulfuric acid, Adeogun *et al.*, (2019) using sulfuric acid at 5% and 121 °C, and Brígida *et al.*, (2010) with green coconut fiber, H₂O₂ solutions at 30% v/v and 85 °C.

The micrographs of CC and RS after hydrolysis with H₃PO₄ shows porous surface of the material, possibly due to the decomposition of the holocellulosic fraction. Hydrolysis causes the rupture of the carbohydrate fibers, exposing the material for subsequent transformation. This suggests that the sugars produced came mainly

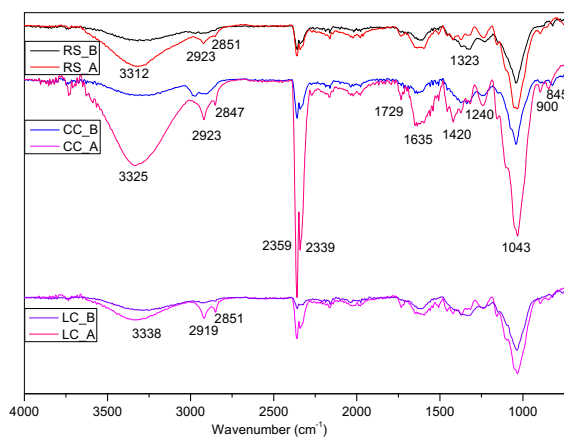


Figure 2. Infrared spectra for lignocellulosic material before (B) and after (A) hydrolysis at 150 °C and 2 M concentration.

from carbohydrate fibers that were not intertwined, i.e., from the amorphous phase of cellulose. To make most of the RS and LC for the production of reducing sugars, hydrolysis with concentrated acid or subsequent enzymatic treatment could be a promising alternative (Jang & Choi, 2018). The results show that phosphoric acid interacted preferably with cellulose and hemicellulose, rather than lignin.

The morphological and structural changes shown in the micrographs in Figure 1 are similar to those previously reported by Boontum *et al.*, (2019), Li *et al.*, (2016), Sahoo *et al.*, (2018) and Sun *et al.*, (2015), who observed the rupture and rearrangement of carbohydrate microfibrils due to acid or alkaline hydrolysis, in addition to an increase in the pore size, which favors subsequent enzymatic hydrolysis.

3.3 FTIR analysis

The FTIR spectra for the three materials before (B) and after (A) the hydrolysis process under the most severe operating conditions (2 M, 150 °C, 300 min) are shown in Figure 2.

The bands between 3312 and 3338 cm⁻¹ were ascribed to vibrations of the -OH groups in cellulose (Coates, 2006). The peaks at 2919-2923 cm⁻¹ and 2847-2851 cm⁻¹ were attributed to C-H bond by stretching vibrations (Lu & Hsieh, 2010). The bands between 2339 and 2359 cm⁻¹ suggested the presence of silanes (Si-H), which are typical of the nutrient adsorption processes of plants. The band at 1729 cm⁻¹ was assigned to the C=O bonds of non-conjugated ketones found in the hemicellulose, and the peaks at 1635 were assigned to the bending of the O-H bond of adsorbed water (Dai & Fan, 2010). The 1043 cm⁻¹ peak may be due to the OH bond of the C-OH groups, corresponding to hemicellulose and lignin. Finally, band at 900 cm⁻¹ was for C-H bond, which corresponds to the aromatic hydrogens of the lignin. As can be seen in the IR spectrum after hydrolysis,

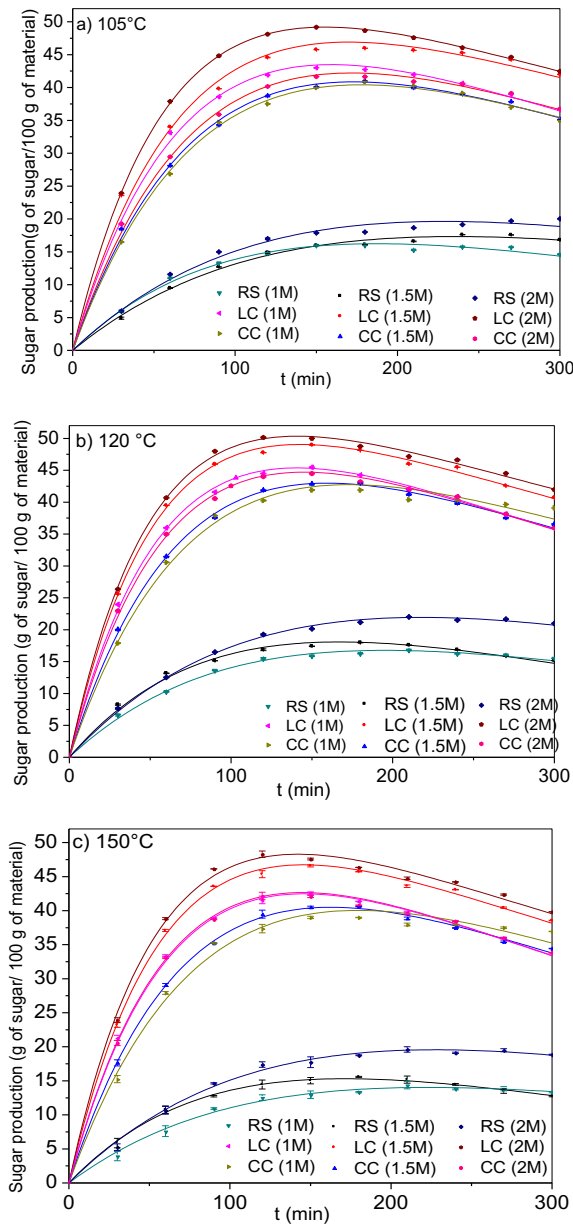


Figure 3. Production of reducing sugars using H₃PO₄ at three temperatures a) 105°C, b) 120°C and c) 150°C.

some bands intensified, possibly due to the breaking of the chains of the lignocellulose components (Figure 2).

3.4 Reducing sugars after acid hydrolysis

The production of reducing sugars from agricultural residues was performed under different experimental conditions. Figure 3 shows the curves for each residue tested with H₃PO₄ at three concentrations (1M, 1.5 M, 2 M) and three temperatures (105 °C, 120 °C, 150 °C). The highest amount of sugar was 50.14 g/100 g from LC at 120 °C, at 2 M and after 120 min of reaction.

In general, the lowest quantity of sugars was obtained from RS (Figure 3) in comparison to LC (17.85%) and CC (17.61%), which can be attributed to the higher content of lignin present in the RS (20.14%). This inhibits the hydrolysis process of the cellulosic fraction. The reaction time using H₃PO₄ was lower than 180 and 500 minutes reported by Gutiérrez-Lopez *et al.*, (2022) using H₂SO₄. Using sulfuric acid involves the use of corrosion resistant material for construction of reactors, which increases the cost of the process (Woiciechowski *et al.*, 2020). The best temperatures for acid hydrolysis were observed at 105 °C and 120 °C.

The production of reducing sugars predominates up to a reaction time of 120 min., after the degradation of these sugars predominates. The best conditions for the three materials were found at 120 °C and 2M of H₃PO₄. The maximum yields were 50.14, 44.48 and 21.54 g sugar/100 g of LC, CC or RS, respectively (Table 1). The quantities of sugar produced were similar to those obtained at the same acid concentration and 105 °C at the same reaction times (LC 48.10, CC 40.60 and RS 16.98 g/100 g of material). Rising temperatures require an increased energy supply, it would be better to consider this last temperature of 105 °C. Sugar production decreased slightly for the three materials with the increase in temperature from 120 °C to 150 °C, because sugar degradation increases at higher temperatures and longer reaction times (Saha *et al.*, 2018).

Table 1. Reducing sugars production (g /100 g) with a reaction time of 120 min.

Molar concentration		1 M	1.5 M	2 M
Temperature and material		H ₃ PO ₄ , 120 minutes		
105°C	LC	42.16	44.56	48.10
	CC	37.50	38.74	40.60
	RS	14.76	14.89	16.98
120°C	LC	44.48	47.75	50.14
	CC	40.26	41.89	44.48
	RS	15.43	16.85	21.54
150°C	LC	41.58	45.35	45.29
	CC	37.36	39.49	42.15
	RS	12.52	14.45	17.4

Díaz-Blanco *et al.*, (2018), reported that the production of sugars from Agave using sulfuric acid increase with the rise of acid concentration. This behavior was similar to that reported by Cao *et al.*, (2018), who observed the same trend at 120 °C. However, in the current study, the sugar production yield increased when the temperature increased from 105 to 120 °C. Saha *et al.*, (2018) reported that the production of sugars from fruit residues using acetic acid was higher at low temperature (62.5 °C), with a time of 30 min and an acid concentration of 0.2 M. Castro *et al.*, (2014) reported that for hydrolysis of *Eucalyptus benthamii* with H₃PO₄, the highest production of sugars was obtained at 200 °C and the average level of acid concentration of 0.75 %w/w. Jung *et al.*, (2013), evaluated the production of sugars using acid hydrolysis of fruit bunches and concluded that an increase in both the acid concentration and the temperature were associated with a decrease in operation times, favoring yield. Both behaviors were observed in the current study. The differences in sugar production between the aforementioned investigations and the present study can be attributed mainly to the nature of the biomass, type of acid and hydrolysis conditions used.

A decrease in furfural production was observed using H₃PO₄ in LC and CC at 105 and 120 °C. Gutiérrez-Lopez *et al.*, (2022) used sulfuric acid; the yield of sugars, the decrease in the reaction time, and the decrease in the decomposition of the produced sugars confirmed that H₃PO₄ has a higher potential for the hydrolysis process than sulfuric acid (Table 2).

However, when the temperature was increased to 150 °C, furfural production increases substantially, possibly due to the degradation of sugars at this temperature. A slight increase in furfural production was observed in RS with the addition of phosphoric acid, which was associated with a decrease in sugar production (Figure 3).

3.5 Kinetic and thermodynamic parameters of acid hydrolysis

The kinetic parameters and hydrolysis time to produce the reducing sugars with H₃PO₄ were calculated using the Saeman model (Table 3). The Saeman kinetic model (Equation 2) was used to study the production of sugars from lignocellulosic biomass, with a correlation coefficient (*R*²) above 0.98. The two kinetic constants of the model were associated with the formation of hexoses and pentoses from cellulose and hemicellulose (*k*₁), and to the thermal decomposition of sugars into aldehydes and low-molecular-weight organic acids (*k*₂) (Fan *et al.*, 2010; Kumar *et al.*, 2015).

The values of the kinetic constant, *k*₁, increased as a function of temperature, with a minimum value of 4.91×10⁻³ min⁻¹ for RS at 2M and 105 °C; the highest value was 18.76 ×10⁻³ min⁻¹ for LC at 2M H₃PO₄ and 120 °C. The relationship between temperature and the kinetic constant of sugar production was studied by Sarkar & Aikat (2013) and Zhang *et al.*, (2011), who observed an increase in the kinetic constant at higher temperatures. Guerra-Rodríguez *et al.*, (2012) conducted the hydrolysis of wheat straw using diluted H₂SO₄ and observed an increase in the rate constant as a function of temperature. The same response was observed in the current study.

The *k_r* factor observed in Table 3 is defined as the numerical relationship (*k*₁/*k*₂) between the kinetic constants and denotes the reactions (formation or decomposition) that predominate during the hydrolysis process. If *k_r* > 1, the production of sugars predominates over decomposition (Thakur *et al.*, 2013).

The production of reducing sugars predominated under all the temperature and concentration conditions for LC and CC but improves with the increase of temperature for LC. This also occurred for CC, suggesting that the best conditions using H₃PO₄ were 2M and 105 °C for both materials.

Table 2. Production of furfural (g of furfural/100 g of material) at three temperatures and three concentrations.

Temperature and material		1 M			1.5 M			2 M		
		60 min	120 min	300 min	60 min	120 min	300 min	60 min	120 min	300 min
105°C	LC	0.09	0.45	0.84	0.1	0.6	0.95	0.12	0.76	1
	CC	0.07	0.4	1.06	0.11	0.76	0.98	0.13	0.85	0.74
	RS	0.05	0.12	0.21	0.05	0.18	0.3	0.08	0.25	0.45
120°C	LC	0.12	0.75	1.1	0.12	0.79	1.11	0.12	0.8	1.16
	CC	0.1	0.7	1.12	0.13	0.9	1.21	0.11	1	1.14
	RS	0.05	0.3	0.5	0.06	0.35	0.4	0.1	0.5	1.25
150°C	LC	0.15	1.59	1.69	0.13	1.41	1.78	0.19	1.5	1.69
	CC	0.14	1.3	1.45	0.13	1.25	1.65	0.15	1.35	1.48
	RS	0.06	0.6	0.8	0.08	0.48	0.6	0.13	0.5	0.7

Table 3. Acid hydrolysis kinetic parameters calculated.

Experimental concentration and temperature	Lignocellulosic material	k_1 (min^{-1}) $\times 10^{-3}$	k_2	k_r	t_m (min)
(1M, 105°C)	LC	13.69	1.82	7.52	169.9
	CC	10.91	2.58	4.23	173.1
	RS	6.85	3.75	1.83	194.3
(1.5M,105°C)	LC	16.32	1.68	9.71	155.3
	CC	11.5	2.41	4.77	171.9
	RS	5.54	3.17	1.75	235.5
(2M,105°C)	LC	12.96	2.41	5.38	159.4
	CC	10.46	2.58	4.05	177.6
	RS	4.91	3.67	1.34	234.7
(1M, 120°C)	LC	15.67	2.43	6.45	140.7
	CC	11.64	2.32	5.02	173
	RS	7.31	3.71	1.97	188.4
(1.5M,120°C)	LC	17.66	1.86	9.49	142.4
	CC	12.73	2.49	5.11	159.3
	RS	7.57	4.66	1.62	166.7
(2M,120°C)	LC	18.76	1.69	11.1	141
	CC	14.86	2.46	6.04	145
	RS	5.16	4.21	1.23	214.2
(1M, 150°C)	LC	13.85	2.79	4.96	144.9
	CC	10.23	2.61	3.92	179.3
	RS	6.79	2.76	2.46	223.4
(1.5M,150°C)	LC	15.89	2.15	7.39	145.6
	CC	10.56	2.8	4.09	162.7
	RS	8.32	3.89	2.14	171.6
(2M,150°C)	LC	17.23	1.97	8.75	142.1
	CC	13.66	2.8	4.88	145.9
	RS	5.2	3.68	1.41	227.5

The highest values of the kinetic constants were observed at 120 °C with phosphoric acid, and in the case of CC and LC, for each temperature and type of acid, the constant, k_1 , was higher than the constant k_2 , suggesting that the proposed hydrolysis conditions favored the production of sugars over their decomposition.

The kinetic constants were used to calculate the thermodynamic parameters (Table 4) for sugar production (k_1) and decomposition (k_2), and the linear Arrhenius and Eyring equations were used. E_a values were relatively low in the case of LC (0.37 to 6.96 kJ/mol) and CC (2.38 to 6.50 kJ/mol). This indicates that the hydrolysis may have occurred more easily in comparison with the E_a values of RS between 10.63 to 11.53 kJ/mol (Figure 3). With low production of sugars in the temperature range used, this phenomenon was also indicated by the enthalpy values both for the production and decomposition process. This indicated a relatively high energy required for RS, compared to

LC and CC (Lavarack *et al.*, 2002).

These results suggest that LC and CC can be hydrolyzed at temperatures below 105 °C and acid concentrations lower than 1 M (Ajala *et al.*, 2020). For CC the results were like those of Adeogun *et al.*, (2019) who reported an E_a of 6.12 kJ/mol for CC treated with NaOH and 19.19 kJ/mol for CC minus pretreatment; both were hydrolyzed by H₂SO₄ at a concentration of 0.5 to 5%, between 70 and 95 °C. The positive values of ΔH and ΔG of acid hydrolysis for the production of sugars from the residues indicated that the processes were endothermic and non-spontaneous (Adeogun *et al.*, 2019). The entropy values obtained for the experimental conditions showed that the formation process predominates over decomposition for hydrolysis (Sarma *et al.*, 2014).

The ΔG magnitude for degradation shows that this process was minus favorable than the reducing sugars production (Adeogun *et al.*, 2019; Gurgel *et al.*, 2012).

Table 4. Acid hydrolysis of LC, CC and RS; thermodynamic parameters.

Acid concentration and material	T (°C)	Production (kJ/mol)				Decomposition (kJ/mol)			
		E_a	ΔH	ΔS	ΔG	E_a	ΔH	ΔS	ΔG
1.0M, LC	105	0.37	3.69	-0.33	119.5	-11.8	-8.56	-0.31	125.8
	120				124.4				130.5
	150				134.2				139.8
1.5M, LC	105	1.27	4.60	-0.33	119.0	-7.22	3.89	-0.32	126.3
	120				123.9				131.1
	150				133.7				140.8
2.0M, LC	105	6.96	3.64	-0.31	119.5	-4.43	-7.76	-0.35	125.5
	120				124.1				130.8
	150				133.3				141.4
1.0M, CC	105	2.38	5.71	-0.33	120.3	-0.94	-2.40	-0.34	125.1
	120				125.3				130.1
	150				135.3				140.2
1.5M, CC	105	3.24	6.57	-0.33	120.1	-4.55	-1.22	-0.33	125.2
	120				125.3				130.1
	150				135.3				140.2
1.5M, CC	105	3.24	6.57	-0.33	120.1	-4.55	-1.22	-0.33	125.2
	120				125.0				130.1
	150				135.0				139.9
2.0M, CC	105	6.50	3.17	-0.31	120.2	-2.83	0.50	-0.33	125.0
	120				124.8				130.0
	150				134.2				140.0
1.0M, RS	105	10.63	3.96	-0.33	121.8	9.60	12.93	-0.36	123.6
	120				126.8				129.0
	150				136.8				139.9
1.5M, RS	105	11.12	7.80	-0.30	122.4	4.36	1.02	-0.32	123.9
	120				127.0				128.7
	150				136.0				138.5
2.0M, RS	105	11.53	1.79	-0.33	123.0	0.66	3.99	-0.34	123.6
	120				127.9				128.7
	150				137.8				138.8

Table 5. Factorial ANOVA to obtain the reducing sugars.

Source of variation	Degree of freedom	Sum of squares	Mean square	F value	P value
Model	26	18442.7	709.34	29.72	0
Lineal	6	16767.8	2794.63	117.08	0
Material (A)	2	16524.8	8262.42	346.14	0
Concentration (B)	2	224.9	112.46	4.71	0.012
Temperature (C)	2	18	9.02	0.38	0.686
2 interactions	12	948.8	79.07	3.31	0.001
AB	4	546.5	136.63	5.72	0
AC	4	359.1	89.76	3.76	0.007
BC	4	43.3	10.82	0.45	0.77
3 interactions	8	726.1	90.76	3.8	0.001
ABC	8	726.1	90.76	3.8	0.001
Error	81	1933.5	23.87		
Total	107	20376.2			

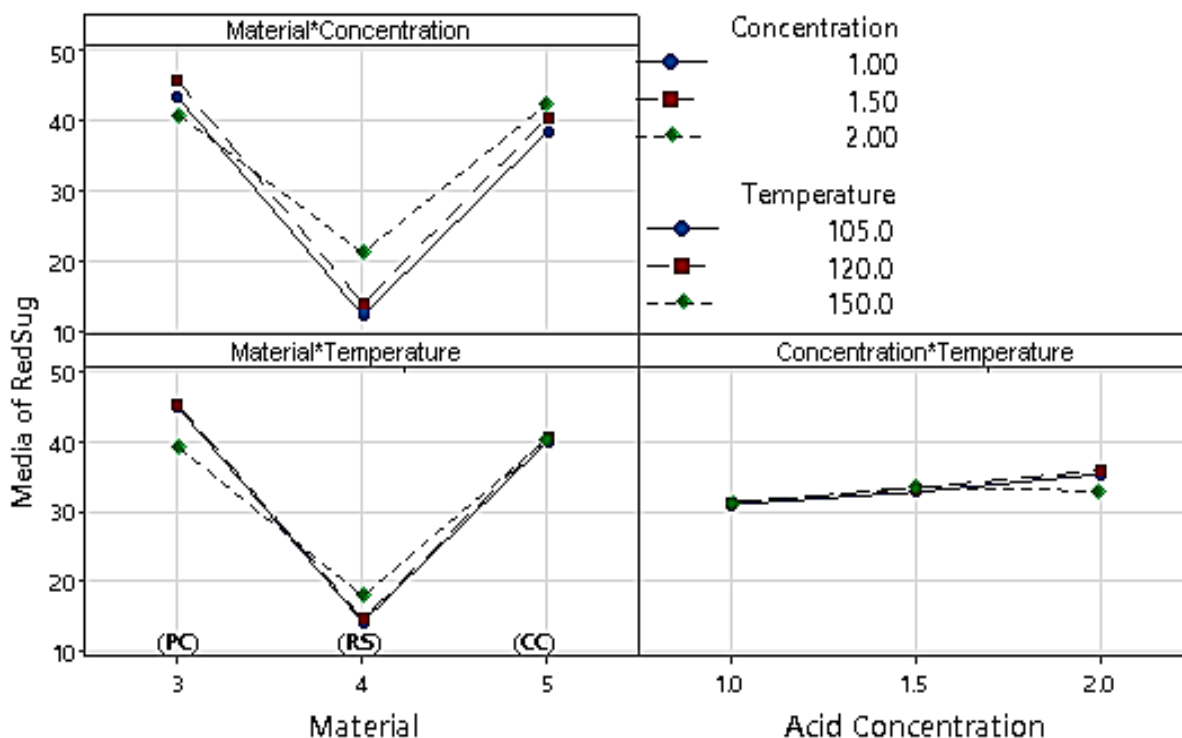


Figure 4. Interactions for the production of reducing sugars.

The E_a and ΔH were positive for the degradation of RS, in contrast with the values obtained using LC and CC, what may be due to the lack of sugar degradation in LC and CC (Figure 3). Degradation can be considered as a simultaneous process to the production of sugars (Saeman, 1945; Tizazu & Moholkar, 2018).

3.6 Analysis of factorial variance of acid hydrolysis

A factorial variance analysis was performed for the production of reducing sugars at a confidence level of 95%, considering three factors, each at three different levels. The factors were the type of material (LC, CC and RS), acid concentration (1, 1.5 and 2M) and temperature (105, 120 and 150 °C), each with two replicates (18 experiments). The maximum amount of reducing sugars (Table 1) was selected as the dependent variable or response (Table 5 and Figure 4).

Temperature (C) had the least influence ($P > 0.05$) on the production of reducing sugars within the interval in which the work was performed, whereas the type of lignocellulosic material (A) and concentration of acid (B) were significant ($P < 0.05$). AB and AC interactions were present ($P < 0.05$; Figure 4).

Conclusions

The yield of reducing sugars was favored with the raise in the H_3PO_4 concentration (1 to 1.5M) and temperature (from 105 to 120 °C). At these conditions, hydrolysis times were reduced. The results at 150 °C were similar to those obtained at 120 °C. LC and CC showed a higher capacity to produce reducing sugars in comparison to RS. The best conditions for produce sugars from LC and CC were 120 °C and 2.0M of phosphoric acid. Similar results were achieved with less severe conditions (105 °C and 2.0M), so a cost-benefit analysis should be performed to establish the most appropriate operating conditions.

Comparing the results with those reported using sulfuric acid, a decrease in furfural production was observed using H_3PO_4 for LC and CC. H_3PO_4 improved the sugar yield and decreased the reaction times and is more effective than sulfuric acid for the hydrolysis of the residues treated in this study.

According to the production profiles, decomposition of reducing sugars predominates over production after 120 min with H_3PO_4 . The hydrolysis kinetic data were analyzed by the Saeman model; k_1 and k_2 showed that the production of sugars predominated over the decomposition of sugars ($k_1 > k_2, k_r > 1$) using LC and CC.

The process for production and decomposition of reducing sugars were endothermic and not spontaneous for the three materials. For RS the

E_a was higher than LC and CC, showing that RS is a recalcitrant material causing a low production of reducing sugars. The thermodynamics indicated that temperature influence more on the production and decomposition of sugars than phosphoric acid concentration for LC and CC; but to RS the influence was similar.

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