Revista Mexicana de Ingeniería Química

Low temperature hydrochloric acid hydrolysis of corn stover. Kinetic, thermodynamics and characterization

Hidrólisis con ácido clorhídirco del rastrojo de maíz a baja temperatura. Cinética, termodinámica y caracterización

J.C. Gómora-Hernández, M. del C. Carreño-de-León, N. Flores-Álamo*

Tecnológico Nacional de México/Instituto Tecnológico de Toluca, Av. Tecnológico s/n. Colonia Agrícola Bellavista, Metepec, Estado de México, C.P. 52149, México.

Abstract

Acid hydrolysis at high temperature is a technique to pretreat and produce monomeric sugars from lignocelluloses; however, its main disadvantage is the production of inhibitory aldehydes. In this paper, reducing sugars production was studied by acid hydrolysis of corn stover employing 2.2 M hydrochloric acid solution and low temperature range (60 - 80 ºC). Experimental data were great fitted to different kinetic models, thermodynamic parameters were calculated from first order, Saeman and Saeman biphasic kinetic models, rate constants showed similar values between each other demonstrating that corn stover hydrolysis is an endothermic and non-spontaneous process capable to produce thermodynamically stable products. FTIR and SEM analyses showed the breaking of lignocellulosic matrix and the depolymerization of polysaccharides after acid treatment. The proposed operational conditions were adequate to produce reducing sugars avoiding their decomposition into inhibitory aldehydes.

Keywords: Acid hydrolysis, corn stover, holocellulose, kinetic study, reducing sugars.

Resumen

La hidrólisis ácida a alta temperatura es un técnica tanto para pre-tratar como para producir azúcares monoméricos a partir de las lignocelulosas, sin embargo, su principal desventaja es la formación de aldehídos inhibidores. En el presente trabajo se propone la producción de azúcares mediante la hidrólisis ácida del rastrojo de maíz utilizando una solución 2.2 M de ácido clorhídrico y bajas temperaturas (60 - 80 °C). Los datos experimentales de la producción de azúcares se ajustaron adecuadamente a diferentes modelos cinéticos y los parámetros termodinámicos fueron calculados a partir de las constantes cinéticas determinadas con los modelos: de primer orden, Saeman y Saeman bifásico mostrando valores similares entre sí, y que la hidrólisis a baja temperatura del rastrojo de maíz con ácido clorhídrico es un proceso endotérmico y no espontáneo capaz de generar productos termodinámicamente estables. Los análisis realizados por FTIR y MEB mostraron el rompimiento de la matriz lignocelulósica y la depolimerización de los polisacáridos después del tratamiento ácido. Las condiciones de operación propuestas fueron adecuadas para producir azúcares reductores disminuyendo su transformación en aldehídos inhibidores.

Palabras clave: Azúcares reductores, estudio cinético, hidrólisis ácida, holocelulosa, rastrojo de maíz.

1 Introduction

The high demand of products obtained from fossil materials has contributed to environmental deterioration and human damage mainly caused to greenhouse gasses emission. In the last decade the petroleum reserves have diminished around the world increasing its cost. Due to the current environmental crisis one of the most beneficial solutions is the transition from fossil based to biobased sources (Mishra & Ghosh, 2019). Lignocellulosic biomass is the most abundant and cheap natural source, its annual production is around 200 billion of dry tons around the world and in recent years it has been used to produce a wide range of biobased products such as chemicals, textiles, drugs, biopolymers and biofuels (Camesasca *et al*., 2015; Dahmen *et al*., 2019; González-Leos *et al*., 2020). The direct fermentation of lignocelluloses is difficult mainly due to their recalcitrance, however, pretreatment methods focused on to increase the fermentability of these materials by two ways: In the first, lignocellulosic matrix is broken increasing surface area, enzyme-biomass contact and the subsequent fermentation yield.

The second one is associated to a transformation of cellulose and hemicellulose into easily fermentable sugars by chemical or biological methods (Bin-Bin *et al.*, 2018; Sánchez-Herrera *et al.*, 2018). Among all chemical methods, acid hydrolysis has been reported as a rapid technic to produce monomeric sugars mainly from the hemicellulose fraction (Texco-López *et al.*, 2018). Acid hydrolysis can be performed either at high temperature and low acid concentration or at low temperature and high acid concentration; last one has the capability to produce low amount of inhibitors from thermal dehydration of monomeric sugars and reduce cellulose cristalinity, however, the main disadvantage of high acid concentration is the increase in process cost due to reactor corrosion caused by high acid loadings (Siripong *et al.*, 2016). High temperature acid hydrolysis is usually used to depolymerize hemicellulose and solubilize lignin, maintaining cellulose almost unaltered for a subsequent enzymatic hydrolysis, the main disadvantage of this process is the decomposition of sugars into aldehydes such as furfural and 5-hydroxi methyl furfural (5-HMF), which have been considered toxic compounds for microbial growth (Camesasca *et al.*, 2015; Muñoz-Páez *et al.*, 2019; Vázquez *et al.*, 2007). Usually, acid hydrolysis at high temperatures is employed as lignocellulosic biomass pretreatment prior to enzymatic hydrolysis which improve enzymatic efficiency (Gaur *et al.*, 2016; Kuglarz *et al.*, 2018). Different types of organic and inorganic acids have been used for biomass hydrolysis; sulfuric acid has been the most studied option employing kinetic and statistical approaches (Chen *et al.*, 2015; Li *et al.*, 2016; Kuglarz *et al.*, 2018). Phosphoric acid is another type of inorganic acid employed for both purposes: fermentable sugars production by direct hydrolysis and as pretreatment of lignocelluloses, this acid is less corrosive and toxic than other inorganic acids and thus the production of inhibitory compounds is low (Lenihan *et al.*, 2010; Yu *et al.*, 2019). Mid-20th century, hydrochloric acid was used at pilot scale in liquid and gas phases, the reported sugars yields exceeded 70% with respect hemicellulose and cellulose content in three stage hydrolysis process. In addition to its high sugars yield, hydrochloric acid can be recovered easily by vacuum evaporation due to its high volatility (Fan *et al.*, 1987). In recent years, hydrochloric acid has been also used to hydrolyze a wide range of lignocellulosic materials such as cassava peels (*Manihot esculenta*) (Adeogun *et al.*, 2018), sea moss (*Kappaphycus alvarezii*) (Abd-Rahim *et al.*, 2014) and sorghum straw (Herrera *et al.*, 2003). As sulfuric acid, hydrochloric is a strong acid capable to produce inhibitors as by-products, however, acid hydrolysis performed at low reaction temperatures and acid concentrations > 0.5 M seems to be an adequate method to produce rapidly high amount of monomeric sugars avoiding aldehydes production. In this work was evaluated sugars and furfural production by low temperature hydrochloric acid hydrolysis employing corn stover as raw material and to determine kinetic and thermodynamic parameters of hydrolysis reaction. Severity of acid treatment was calculated and correlated to reducing sugars amount to understand the effect of hydrolysis variables on hydrolysis yield; moreover, characterization of raw and hydrolyzed corn stover by Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) was also reported and discussed.

2 Materials and methods

2.1 Raw materials

Corn stover samples were obtained from crops located at Mexico State, the crops employed in this study used for their growth neither chemical fertilizers nor pesticides. Samples were air dried and milled into powder by mechanical milling; after that, particles with a diameter less than 250 μm were recovered by sieving, dried at 45 °C for 48 hours and employed in this study. Prior acid hydrolysis, milled and dried corn stover was characterized to determine its main physicochemical parameters: Moisture employing 45 °C as dried temperature (AOAC, 2005), total volatile solids and ashes (APHA, 2005), holocellulose (Wise *et al.*, 1946) and acid-insoluble lignin (ASTM, 2013). To eliminate extractive compounds such as chlorophyll, terpenes and resins that interfere in physicochemical parameters determination, a soxhlet extraction with ethanol-toluene 1:2 mix was carried out before initial characterization.

2.2 Hydrochloric acid hydrolysis

Acid hydrolysis tests were performed in batch without stirring. In 20 mL vials, 1 g of dried and milled corn stover was mixed with 15 mL of 2.2 M hydrochloric acid solution and homogenized. The vials were placed into a furnace and heated at different reaction temperatures: 60, 70 and 80 °C. The hydrolysis times were set at: 15, 30, 45, 60, 75, 90, 105 and

120 minutes. After these times, two samples were taken and cooled at room temperature for 10 minutes and then, phases were separated by filtration. The liquid phase also known "hydrolysate" was recovered and employed to determine the total amount of reducing sugars, furfural, pH and the severity of hydrolysis process. Severity Factor (SF) correlates the impact of reaction time and temperature on lignocellulosic biomass hydrolysis (Eq. 1); however, for acid hydrolysis Combined Severity Factor (CSF) is most appropriate (Eq. 2), it involves the effect of reaction time, temperature and acid concentration into a single factor and has been defined as a measure of hydrolysis effectiveness (Pappas *et al.*, 2014).

$$SF = \log\left[t \cdot e^{\frac{T-T_r}{14.75}}\right] \tag{1}$$

$$CSF = SF - pH \tag{2}$$

where t is the reaction time in minutes, T the hydrolysis temperature, T_r a reference temperature most often 100 °C, 14.75 an activation energy constant and pH the potential of hydronium ions at the end of the hydrolysis.

The hydrolyzed corn stover samples were washed with hot distilled water until a final pH of 7; they were dried overnight at 45 °C and milled for their subsequent characterization by FTIR and SEM.

2.3 Kinetic and thermodynamic parameters calculation

The mechanism of acid hydrolysis is difficult caused by simultaneous presence of serial and parallel reactions. Saeman (1945) developed the first kinetic model for sulfuric acid hydrolysis of wood cellulose considering a sequence of pseudo-homogeneous irreversible firs order reactions. This model has been used for glucose production from cellulose fraction, hemicellulose hydrolysis employing different inorganic acids and lignocellulosic materials: *Manihot esculenta* peels (Adeogun *et al.*, 2018), sorghum straw (Vázquez *et al.*, 2007), waste mushroom medium (Byeong-Il & Jae-Won, 2015) and barley straw (Aguilar-Rivera & Canizales-Leal, 2004). The kinetic equation proposed by Saeman is shown in Eq. 3.

$$M = \frac{P_o \cdot k_1}{k_2 - k_1}\left[e^{-k_1 \cdot t} - e^{-k_2 \cdot t}\right] \tag{3}$$

where M and P_o are the amount of reducing sugars at the reaction time t (min) and the initial amount of polysaccharide respectively, in this paper both are given in g per each 100 g raw corn stover. The k_1 rate constant is associated to reducing sugars production while k_2 is related with sugars decomposition; k_1 and k_2 are given in min^{-1}.

The k_2 rate constant observed in Saeman model corresponds to thermal decomposition of sugars into aldehydes, however, if this decomposition phase is not appreciated in experimental data first order kinetic model (Eq. 4) can be used as was reported by Swati *et al.* (2013).

$$M = P_o[1 - e^{-k_1 \cdot t}] \tag{4}$$

In recent years, another kinetic model known as Saeman biphasic has been employed to study xylose production from acid hydrolysis of hemicelluloses. This model assumes that hydrolysis proceeds through two parallel first order reactions, in which one reaction occurs faster than other (Tizazu & Moholkar, 2018). The generalized equation of Saeman biphasic model is shown in Eq. 5.

$$M = \frac{\alpha \cdot P_o \cdot k_f}{k_2 - k_f}\left[e^{-k_f \cdot t} - e^{-k_2 \cdot t}\right] + \frac{(1-\alpha) \cdot P_o \cdot k_s}{k_2 - k_s}\left[e^{-k_s \cdot t} - e^{-k_2 \cdot t}\right] \tag{5}$$

where P_o, t and k_2 have the same meaning that described previously, while k_f and k_s were the rate constants for the easy to hydrolyze and the difficult to hydrolyze fractions, respectively, both are given in min^{-1}. The easy to hydrolyze fraction is denoted as α.

Sugars production data were fitted to all kinetic models described above. For furfural production, only first order kinetic model was tested.

Activation Energy (AE) and frequency factor (A) were determined by Arrhenius equation (Eq. 6), furthermore, the change in enthalpy (ΔH) and entropy (ΔS) were calculated by Eyring equation (Eq. 7). Finally, Gibbs free energy (ΔG) was obtained employing Eq. 8.

$$\ln(k) = \ln(A) - \frac{E_a}{R \cdot T} \tag{6}$$

$$\ln\left[\frac{k}{T}\right] = \ln\left[\frac{k_B}{h_v}\right] + \frac{\Delta S}{R} - \frac{\Delta H}{R \cdot T} \tag{7}$$

$$\Delta G = \Delta H - (T \cdot \Delta S) \tag{8}$$

where, R is the ideal gas constant (8.3144 J mol^{-1} K^{-1}), T the absolute temperature in K, k_B the Boltzmann constant (1.3807×10^{-23} J K^{-1}) and hp the

Planck constant (6.6261×10^{-34} J s). For Arrhenius and Eyring equation, the rate constant k is given in min^{-1} and s^{-1} respectively. All fittings were performed in Origin 8.6.

2.4 Analytical techniques

The total amount of reducing sugars in each hydrolysate was determined by 3-5 dinitro salicylic acid method (Miller, 1959) in a *Perkin Elmer Lambda XLS* Uv-Vis spectrometer employing 540 nm as wavelength. Prior reducing sugars determination; hydrolysates were diluted 1:15 with distilled water. For furfural, hydrolysate samples were diluted 1:150 with distilled water and furfural concentration was determined in the same instrument at 277 nm. Glucose and furfural analytical grade chemical reagents were used for calibration curves. Hydrolysate pH was determined in a *Hanna HI 2221* potentiometer and CSF was calculated according to Eq.2.

To determine and observed changes in functional groups and the morphology after acid hydrolysis, raw and hydrolyzed corn stover samples were characterized by FTIR and SEM. FTIR analyses were performed in a *Varian 640* IR spectrometer employing a spectral range of 600 to 4000 cm^{-1}, 16 scans and a resolution of 4 cm^{-1}. The morphological studies were carried out in a *Jeol JSM-6610LV Oxford Instruments* electron microscope operated at 20 kV and a low vacuum of 30 Pa.

3 Results and discussion

3.1 Raw corn stover composition

The pH and dry basis composition of raw corn stover was: $87.25 \pm 0.47\%$ total volatile solids, $12.75 \pm 0.47\%$ ashes, $64.17 \pm 0.66\%$ holocellulose, $16.33 \pm 0.11\%$ lignin and a pH value of 6.77 ± 0.053. The moisture content in corn stover was $4.40 \pm 0.23\%$. The holocellulose percentage obtained in this work was higher to that reported by Chen *et al.* (2015), Lu *et al.* (2008) and Zhang et al, (2011) who studied dilute sulfuric acid hydrolysis of Chinese corn stover, however the lignin percentage determined by each of them was higher to that obtained in this study. The high content of holocellulose and total volatile solids coupled to the low amount of lignin suggests that corn stover can be an alternative material for production of reducing sugars.

3.2 Corn stover acid hydrolysis

The total amount of reducing sugars was measured; involving xylose, arabinose, galactose and glucose as hemicellulosic, glucose and cellobiose as cellulosic sugars (Arslan *et al.*, 2012). Cellobiose is considered as reducing sugar since it is composed by two glucose molecules but in aqueous solution only one molecule acts as reducing agent, if this carbohydrate is hydrolyzed can split into two reducing molecules (Saqib & Whitney, 2011).

As seen in Figure 1, after 120 minutes of reaction time at 80 ℃, maximum reducing sugars production yield was achieved (18.16 g/100 g raw corn stover equivalent to 12.11 g/L). The lowest reducing sugars yields were observed at the lowest reaction time and at the lowest hydrolysis temperature being 2.05 g/100 g raw corn stover the minimum value observed at 60 ℃ and after 15 minutes reaction time. The amount of reducing sugars increased as the reaction time and hydrolysis temperature raise. For furfural, the highest yield at 60 °C was 0.45 g/100 g raw corn stover obtained after 120 minutes (Figure 1a), this yield increased to 0.50 and 0.52 g/100 g raw corn stover for hydrolysis at 70 and 80 °C respectively (Figure 1b and 1c). This last yield is equivalent to a furfural concentration of 0.34 g/L. As reducing sugars, furfural production increased as a function of temperature and reaction time, showing the highest values at 80 ℃ and 120 minutes (Figure 1c). The effect of hydrolysis temperature on furfural production was lower in comparison to that observed for reducing sugars, suggesting that the operational temperatures employed in this study improving the production of reducing sugars over their decomposition into aldehydes.

The maximum reducing sugars and furfural production yields obtained in this work were similar to reported by Chen *et al.* (2015) and Zhang *et al.* (2011) using dilute sulfuric acid hydrolysis of Chinese corn stover; however maximum sugars yield was lower in comparison with some data reported in literature employing other kind of lignocelluloses and working conditions (Adeogun *et al.*, 2018; Lenihan *et al.*, 2010). The amount of furfural obtained here was less than reported by Byeong-II & Jae-Won (2015) using waste mushroom, Guerra-Rodríguez *et al.* (2012) in wheat straw and Tizazu & Moholkar (2018) in sugarcane bagasse, which is beneficial for the subsequent hydrolysates fermentation.
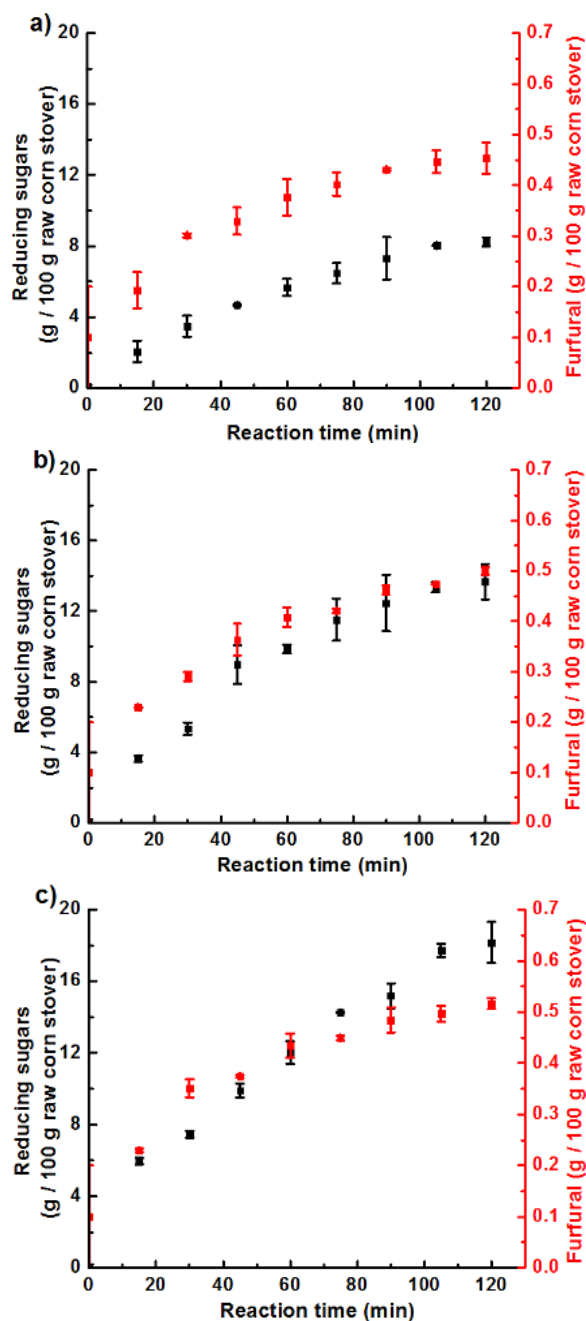
Fig. 1. Reducing sugars and furfural production by acid hydrolysis of corn stover at a) 60 °C, b) 70 °C and c) 80 °C.

CSF was determined in each hydrolysate considering operational temperature, reaction time and the hydrolysate pH determined at the end of the hydrolysis. CSF increased with rise in temperature, reaching the highest values at 80 °C. Moreover, CSF increased in logarithmic way as a function of reaction

time, trend described by Eq. 2. Reducing sugars and furfural production data were well fitted to an exponential model with respect to CSF; furthermore the maximum yields were associated to the highest CSF values. The effect of CSF on sugars yields (Figure 2a) was higher in comparison to furfural yields (Figure 2b), this behavior is in agreement to that observed in Figure 1 and is associated to low hydrolysis temperatures which are suitable for reducing sugars production diminishing transformation of sugars into aldehydes; this last reaction is favored at temperatures higher than 100 °C (Saucedo-Luna *et al.*, 2010; Tizazu & Moholkar, 2018).

For each temperature, furfural production data were correlated to reducing sugars production by linear fitting (R^2 values obtained were higher than 0.95). The slope of line straight relates the amount of furfural that is produced per g of obtained sugars.
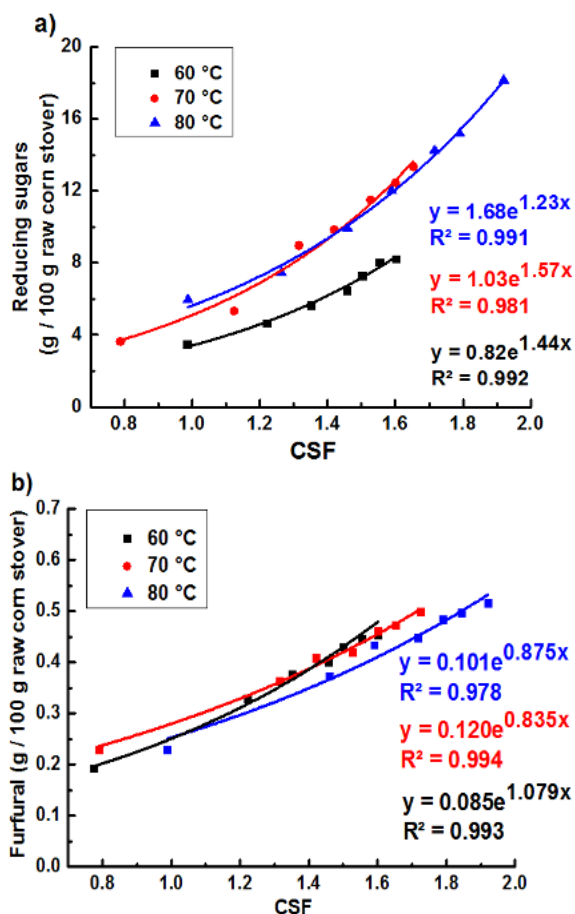

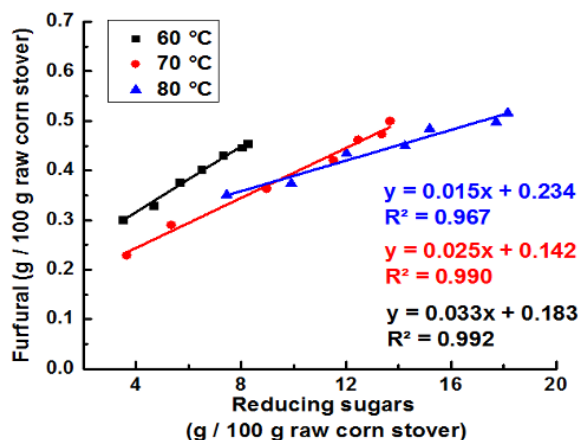Fig. 2. Effect of CSF on a) reducing sugars and b) Furfural production.

Fig. 3. Linear relationship between reducing sugars and furfural production.

To produce only 1 g of furfural from corn stover by hydrochloric acid hydrolysis at 60, 70 and 80 ºC are necessary 30.30, 40 and 66.67 g of reducing sugars respectively. These relationships between furfural and sugars must be taken carefully, since a change in operational conditions and lignocellulosic source can modify either sugars or furfural production yields. For the conditions employed in this study an increased in reaction temperature improve the amount of reducing sugars; however this trend can be modified if temperature rises up a lot accelerating thermal decomposition of sugars.

3.3 Kinetic and thermodynamic study

For acid hydrolysis, the most employed kinetic model was developed by Saeman (1945). This model involves two serial first order and pseudo-homogeneous reactions; the first is associated to monomeric sugars production and the second one to sugars decomposition (Eq. 3). Moreover, from Saeman model and in agreement to Swati *et al.* (2013), acid hydrolysis of lignocellulosic materials can also be studied employing first order kinetic model (Eq. 4).

The modified Saeman biphasic model (Eq. 5) was developed in recent years considering the effect of amorphous-crystalline structure of lignocellulosic materials on sugars production efficiency. This model is based on two parallel depolymerization reactions of polysaccharides into monomeric sugars, which one reaction occurs faster than each other. The fast hydrolyze fraction usually is denoted as α. Zhang *et al.* (2011) assigned α=0.65 during dilute sulfuric acid hydrolysis of corn stover, this value was employed for Saeman biphasic model fittings.
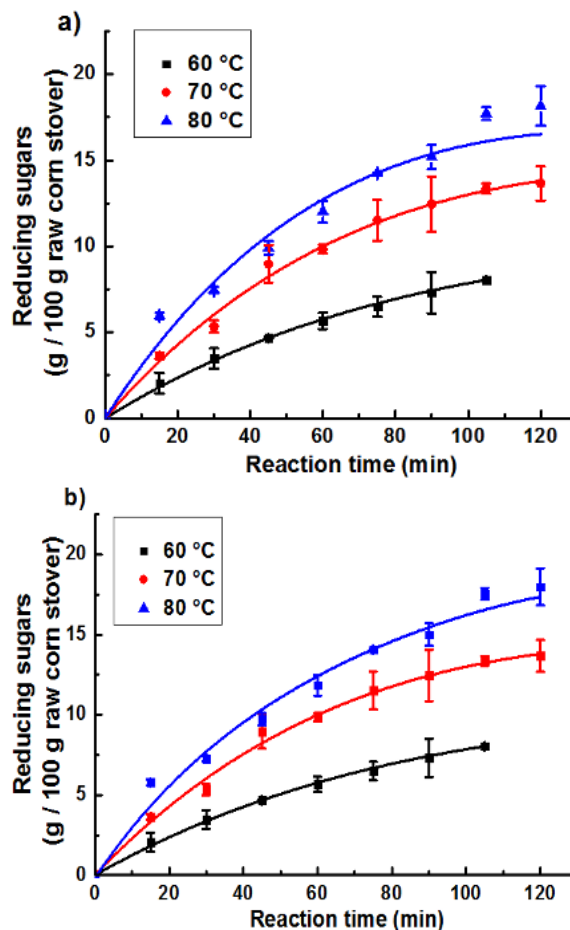

Fig. 4. Reducing sugars production data fitted to a) Saeman and b) Saeman biphasic models.

Reducing sugars production data were fitted to all models described previously. As seen in Figure 4, sugars data were good fitted to both Saeman and Saeman biphasic models showing R^2 values higher than 0.990.

The k_2 rate constants determined from Saeman model were higher than k_1 rate constants, this trend suggests that sugars decomposition reaction (aldehydes production) is faster than sugars production, however experimental data showed a low production of furfural after hydrolysis and a low rise on its concentration when reaction temperature increased, thus, Saeman rate constants behavior can be due to the low reaction temperatures which promotes reducing sugars production and stabilizes quickly furfural concentration; around 45 minutes reaction time. Moreover, both rate constants (k_1 and k_2) increased their values with rise in reaction temperature. From Saeman kinetic constants, the

maximum sugars concentration (Sugmax) and the time on which this maximum concentration is achieved (topt) can be determined employing mathematical models reported previously (Alves *et al.*, 2012); these models are shown in Eq. 9 and Eq. 10.

$$S ug_{max} = P_o \left(\frac{k_2}{k_1}\right)^{\left[\frac{k_2}{k_1-k_2}\right]} \tag{9}$$

$$t_{opt} = \left[\frac{\ln(k_2) - \ln(k_1)}{k_2 - k_1}\right] \tag{10}$$

Table 1 summarizes the kinetics and statistical parameters obtained from Saeman kinetic model, and as can be seen in this table the maximum sugars concentrations determined for each temperature were similar to that observed in Figure 4, the calculated optimum reaction times were higher than the maximum time tested, furthermore when reaction temperature increased the optimum time diminished showing a minimum of 140 minutes at 80 °C. Increasing reaction temperature not only the highest reducing sugars yield was achieved but also the lowest operational time was needed, moreover the concentration of furfural did not increased

considerably when reaction temperature changed from 60 to 80 °C.

The k_2 rate constants calculated with Saeman model were similar to that obtained for sugars decomposition employing Saeman biphasic model, while k_1 rate constants from Saeman model were similar to fast to hydrolyze (k_f) rate constants determined with Saeman biphasic model. Both k_f and k_2 rate constants (Saeman biphasic model) increased as reaction temperature rises, and with exception to 80 °C k_f and k_s showed similar values to each other. The value of k_s was lower than k_f at 80 °C which was expected cause k_s is associated to the slow to hydrolyze fraction in biomass. Similar behavior to that observed in this paper was reported previously during dilute sulfuric acid hydrolysis of corn stover in a cycle spray reactor employing a low temperature range of 90 to 100 °C (Zhang *et al.*, 2011).

Employing first order kinetic model only sugars production rate constants are calculated. According to Swati *et al.* (2013), this model can be used for hydrolysis processes despising sugars decomposition, as shown in Table 2 rate constants obtained with first order model were lower in comparison to that obtained with Saeman and Saeman biphasic models, furthermore R^2 coefficients diminished.

Table 1. Kinetics and statistical parameters of corn stover acid hydrolysis obtained from Saeman model.

Temp. (°C)	k_1 (min^{-1})	k_2 (min^{-1})	R^2	$S ug_{max}$ (g / 100g)	t_{opt} (min)
60	2.05×10^{-3}	8.63×10^{-3}	0.999	9.74	218.45
70	3.79×10^{-3}	8.95×10^{-3}	0.996	14.46	166.53
80	5.12×10^{-3}	9.58×10^{-3}	0.993	16.71	140.48

Table 2. Kinetics and statistical parameters of corn stover acid hydrolysis obtained from Saeman biphasic and first order models.

	Saeman biphasic model				First order model	
Temp. (°C)	k_f (min^{-1})	k_s (min^{-1})	k_2 (min^{-1})	R^2	k (min^{-1})	R^2
60	2.05×10^{-3}	2.05×10^{-3}	8.63×10^{-3}	0.999	1.29×10^{-3}	0.942
70	3.79×10^{-3}	3.79×10^{-3}	8.95×10^{-3}	0.996	2.50×10^{-3}	0.964
80	6.29×10^{-3}	2.95×10^{-3}	9.28×10^{-3}	0.992	3.36×10^{-3}	0.983

Table 3. Kinetics and statistical parameters of furfural production obtained with first order model.

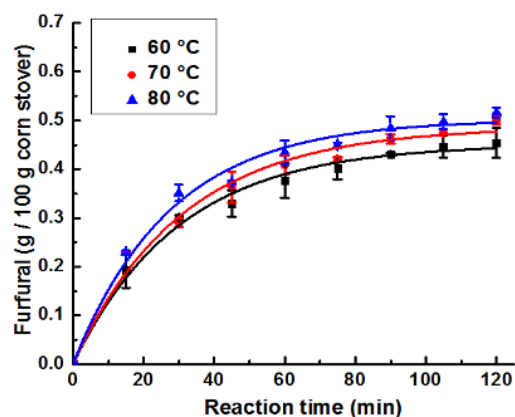| Temp. (°C)	P_o (g/100 g)	k (min^{-1})	R^2
60	0.451	3.32×10^{-2}	0.99
70	0.478	3.44×10^{-2}	0.996
80	0.501	3.61×10^{-2}	0.987

Fig. 5. Furfural production data fitted to first order kinetic model.

Experimental data for Furfural production were fitted to first order kinetic model (Figure 5), P_o did not correspond to initial amount of holocellulose. In agreement to Rafiqul & Sakinah (2012), P_o is the potential concentration of furfural and is a parameter calculated by non-linear regression.

As seen in Table 3, the correlation coefficient was $R^2 > 0.985$ for all temperatures. The highest value of P_o was 0.501 g/100 g raw corn stover determined at 80 °C and lowest was for 60 °C (0.45 g/100 g raw corn stover). Furfural production rate constants were higher than k_2 constants determined with Saeman and Saeman biphasic model, this trend was found by Rafiqul & Sakinah, (2012), caused by the accelerated furfural production in the initial reaction times. After 45 minutes the concentration slightly increased until the end of experiment, both P_o values and rate constants increase slightly when reaction temperature rises.

Thermodynamic parameters of hydrolysis process were estimated employing Arrhenius (Eq. 6), Eyring (Eq. 7) and Free Gibbs energy (Eq. 8) equations. Both reducing sugars and furfural rate constants obtained by different kinetic models were used for thermodynamic study. The k_1 and k_f rate constants respectively determined with Saeman and Saeman biphasic model as well as sugars production rate constants calculated with first order kinetic model fitted to linear form of Arrhenius equation are shown in Figure 6a.

On the other hand, linear fittings of both k_2 and furfural production rate constants are presented in Figure 6b. The k, k_1, and k_f rate constants fitted to linear form of Arrhenius equation (Figure 6a) show similar slopes between each other, thus the expected AE and A are similar in all cases for reducing sugars production. Sugars decomposition rate constants obtained from all kinetic models showed similar slopes in Arrhenius curve, since furfural production rate constants were higher than those calculated with Saeman and Saeman biphasic model its Arrhenius plot was observed 1.5 units above (Figure 6b). Thermodynamic and statistical parameters of low temperature hydrochloric acid hydrolysis of corn stover are presented in Table 4.

All thermodynamic parameters (Table 4) calculated for reducing sugars production were higher in comparison to that observed for sugars decomposition. From AE and A values can be concluded that reducing sugars production from corn stover needed more energy than sugars dehydration, this result was similar that reported previously employing hazelnut shells and corn stover with sulfuric acid (Arslan *et al.*, 2012; Zhang *et al.*, 2011).

Table 4. Thermodynamic and statistical parameters of hydrochloric acid hydrolysis of corn stover calculated with different kinetic model rate constants.

|	AE (kJ mol^{-1})	A (min^{-1})	R^2	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	R^2	Gav (kJ mol^{-1})
	Sugar production						
First order (k)	46.98	3.17×10^4	0.96	44.13	-202.28	0.955	113.54
Saeman (k_1)	44.9	2.35×10^4	0.969	42.05	-204.74	0.964	112.31
S. biphasic (k_f)	54.87	8.31×10^5	0.998	52.02	-175.11	0.998	112.11
	Sugar decomposition						
First order (k)	4.03	1.42×10^{-1}	0.991	1.18	-304.67	0.917	105.73
Saeman (k_2)	5.09	5.39×10^{-2}	0.964	2.24	-312.72	0.845	109.55
S. biphasic (k_2)	3.55	3.10×10^{-2}	0.999	0.69	-317.31	0.998	109.58
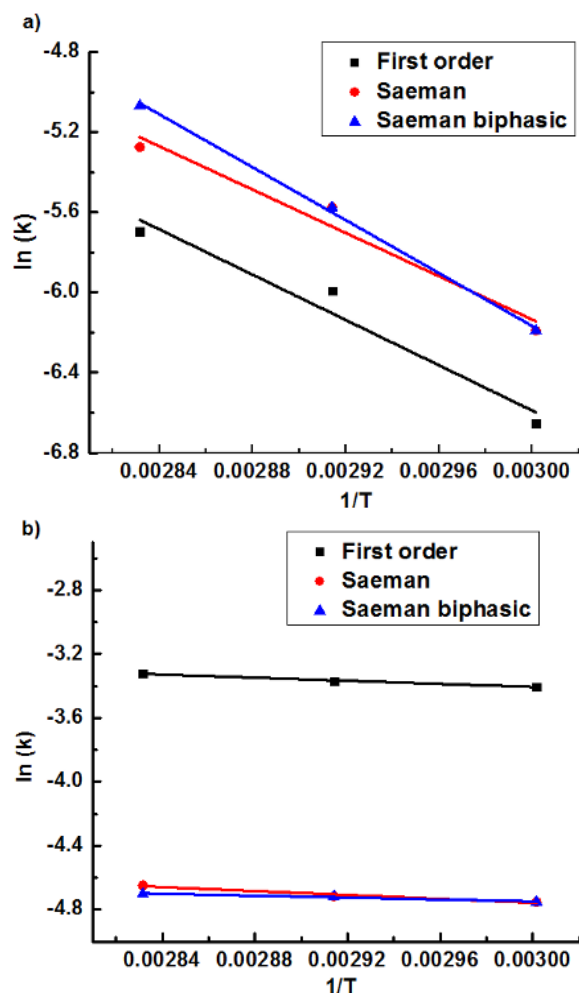
Fig. 6. a) Reducing sugars production and b) sugars decomposition rate constants fitted to linear form of Arrhenius equation.

For reducing sugars decomposition, the low AE and A values can be due to a rapid transformation of xylose present in raw corn stover into furfural before 45 minutes reaction time, after this time furfural concentration stabilized until the end of the experiment showing a little effect of temperature on furfural yield. Both AE and A for sugars decomposition was in the range reported by Adeogun *et al.* (2018) who studied hydrochloric acid hydrolysis of *Manihot esculenta* peels.

The positive values of ΔH and ΔG (Table 4) suggest that acid hydrolysis of corn stover is an endothermic and non-spontaneous process respectively; it means that the process requires an external energy source to perform it. According to Tizazu *et al.* (2018), negative values of ΔS indicate that maximum amount of energy is in the reactants side

prior to cellulose-water-acid complex formation and the generated products are thermodynamically stable. Sugars decomposition has more negative entropy than sugars production, thus furfural is the most stable product formed during corn stover hydrolysis.

The behavior of ΔH, ΔG and ΔS is in agreement with some papers reported previously. Swati *et al.* (2013) determined kinetic and thermodynamic parameters of sulfuric acid hydrolysis of *Parthenium hysterophorus* employing first order kinetic model. They observed that the production of reducing sugars is an endothermic and non-spontaneous reaction capable to produce stable sugars (negative entropies). Years after, similar trend was reported for sulfuric acid hydrolysis of sugarcane bagasse (Tizazu *et al.*, 2018).

3.4 FTIR and SEM characterization of raw and hydrolyzed corn stover

FTIR analyses were performed to determine the main changes in functional groups attributed to acid hydrolysis. The intensity of the main vibrational bands of hemicellulose located around 1240 and 1740 cm^{-1} diminished after acid hydrolysis, which is caused by the formation of monomeric sugars from hemicellulosic fraction and the deacetylation of corn stover (Gaur *et al.*, 2016). β-glycosidic bond was observed in each spectrum at 896 cm^{-1}, the intensity of this vibrational band related to C−O−C bond in cellulose and hemicellulose raised after acid treatment. For lignin, the main vibrational bands of aromatic ring were observed at 1432, 1510 and 1590 cm^{-1} (Li *et al.*, 2016), these bands became more defined as reaction time increased, new band appeared at 1064 cm^{-1} and according to Hsu *et al.* (2010) this band is attributed to C-O-H bond of primary and secondary alcohols presents in lignin structure.
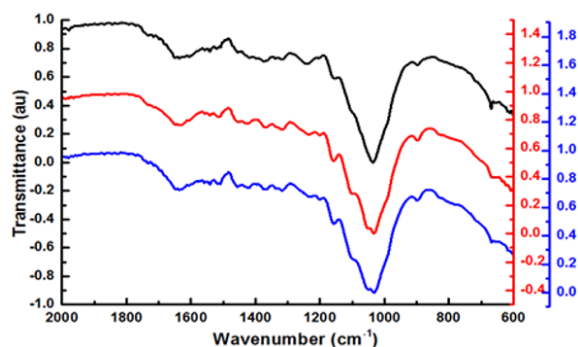

Fig. 7. FTIR spectra of raw (black line) and hydrolyzed corn stover at 80 °C and after 60 (red line) and 120 (blue line) minutes reaction time.
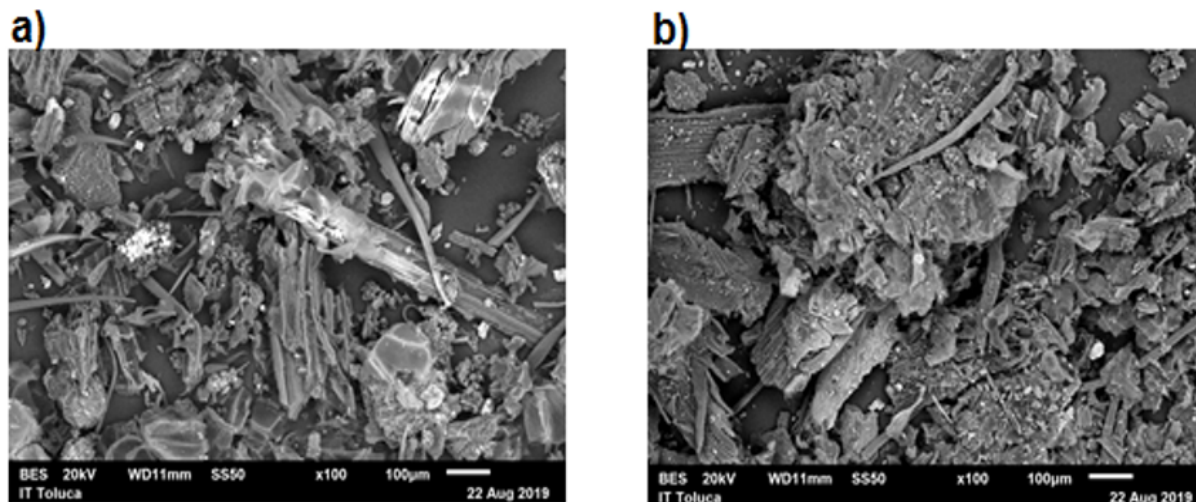
Fig. 8. Micrographs with 100X magnification of a) raw and b) hydrolyzed corn stover with hydrochloric acid at 80 °C and after 120 minutes reaction time.

Characteristic vibrations of cellulose observed between 1000 and 1200 cm^{-1} diminished slightly their amplitude and intensity after acid hydrolysis suggesting the depolymerization of this carbohydrate, similar behavior was reported previously in *Manihot esculenta* peels hydrolysis (Adeogun *et al*., 2018). Figure 7 shows FTIR spectra of raw and hydrolyzed corn stover at 80 °C and for different reaction times.

Micrograph of milled corn stover before acid hydrolysis showed intact carbohydrate fibrils and irregular morphology caused by pulverization and milling. As can be seen in Figures 8a and 8b, some fibrils in both raw and hydrolyzed corn stover are covered by many layers, which in agreement to Siripong *et al*. (2016) are associated to hemicellulose and cellulose content. After acid hydrolysis these layers were disrupted and the biomass was observed rougher and more disordered than raw material. As consequence of this fact, the porosity of corn stover increased after acid hydrolysis. Morphological changes observed in this work were similar to that reported by Li *et al*. (2016) in sulfuric acid pretreatment of corn residues and Sánchez-Herrera *et al*. (2018) during liquid hot water pretreatment of sugarcane straw. The white particles detected in micrographs correspond to elements such as potassium, calcium, silicon and aluminum which are present in corn stover matrix and after acid hydrolysis they can be better appreciated due to a decomposition of carbohydrates.

Conclusions

Hydrochloric acid hydrolysis of corn stover performed at low temperature was an efficient method to produce reducing sugars avoiding furfural production. Reducing sugars yields raises as an increase in hydrolysis temperature, reaching their maximum yields at the highest reaction temperature and at the longest reaction time. Despite an increase in reaction temperature favoured both sugars and furfural yields, the major effect of this variable was on sugars production demonstrating that low temperature hydrolysis not only produced reducing sugars but also diminished their decomposition. Rate constants calculated from Saeman and Saeman biphasic models were similar to each other, and according to thermodynamic parameters hydrolysis of corn stover with 2.2 M hydrochloric acid is an endothermic and non-spontaneous reaction which generates stable products being furfural the most stable compound formed throughout the process. FTIR and SEM analyses showed a decrease in cellulose and hemicellulose content after acid hydrolysis suggesting that the produced sugars came from both fractions. The low concentrations of furfural suggest that reducing sugars present in hydrolysates can be employed for value-add products production such as bioethanol, biohydrogen and bio-plastics by biotechnological processes.

References

Abd-Rahim F., Wasoh H., Zakaria M. R., Ariff A., Kapri R., Ramli N., Siew-Ling L. (2014). Production of high yield sugars from Kappaphycus alvarezii using combined methods of chemical and enzymatic hydrolysis. *Food Hydrocolloids 42*, 309-315.

Adeogun A. I., Idowu M. A., Oladeji O. B., Ofudje E. A., Akinloye A. O. (2018). Kinetic, thermodynamic and optimization studies of dilute acid hydrolysis of Manihot esculenta peels for glucose production. *Waste and Biomass Valorization 1-10*.

Aguilar-Rivera N., Canizales-Leal M. J. (2004). Barley straw acidic hydrolysis kinetics. *Revista Mexicana de Ingeniería Química 3*, 257-263.

Alves G. L. V., Marabezi K., Zanbom M. D., Silva C. A. A. (2012). Dilute acid hydrolysis of sugar cane bagasse at high temperatures: A kinetic study of cellulose saccharification and glucose decomposition. Part 1: Sulfuric acid as the catalyst. *Industrial & Engineering Chemistry Research 51*, 1173-1185.

AOAC. (2005). *Official method of Analysis of the Association of Analytical Chemists*. Determination of Moisture, ash, protein and fat. AOAC. Washington DC.

APHA. (2005). Standard Methods for Water and Wastewater Examination 21 st ed. American Public Health Association-American Water Works Association. *Water Environmental Federation Publication*. Washington DC.

Arslan Y., Takac S., Eken-Saracoglu N. (2012). Kinetic study of hemicellulosic sugar production from hazelnut shells. *Chemical Engineering Journal 185-186*, 23-28.

ASTM. (2013). American Society for Testing and Materials. ASTM D1106-96, *Standard Test Method for Acid-Insoluble Lignin in Wood*, ASTM International, West Conshohocken.

Bin-Bin H., Ming-Yuan L., Yu-Tao W., Ming-Jun Z. (2018). Enhanced biohydrogen production from dilute acid pretreated sugarcane bagasse by detoxification and fermentation strategy. *International Journal of Hydrogen Energy 43*, 19366-19374.

Byeong-Il N., Jae-Won L. (2015). Kinetic study on the dilute acid catalysed hydrolysis of waste mushroom medium. *Journal of Industrial and Engineering Chemistry 25*, 176-179.

Camesasca L., Ramírez M. B., Guigou M., Ferrari M. D., Lareo C. (2015). Evaluation of dilute acid and alkaline pretreatments, enzymatic hydrolysis and fermentation of napiergrass for fuel ethanol production. *Biomass & Bioenergy 74*, 193-201.

Chen L., Zhang H., Li J., Lu M., Guo X., Han L. (2015). A novel diffusion-biphasic hydrolysis coupled kinetic model for dilute sulfuric acid pretreatment of corn stover. *Bioresource Technology 177*, 8-16.

Dahmen N., Lewandowski I., Zibek S., Weidtmann A. (2019). Integrated lignocellulosic value chains in a growing bioeconomy: Status quo and perspectives. *GCB Bioenergy 11*, 107-117.

Fan L. T., Gharpuray M. M., Lee Y. H. (1987). *Cellulose Hydrolysis*. Editorial Springer, Germany.

Gaur R., Soam S., Sharma S., Gupta R. P., Vansal V.R., Kumar R., Tuli D. K. (2016). Bench scale dilute acid pretreatment optimization for producing fermentable sugars from cotton stalk and physicochemical characterization. *Industrial Crops and Products 83*, 104-112.

González-Leos A., Bustos-Vázquez M. G., Rodríguez-Castillejos G. C., Rodríguez-Durán L. V., Del Ángel-Del Ángel A. (2020). Kinetics of lactic acid fermentation from sugarcane bagasse by *Lactobacillus pentosus*. *Revista Mexicana de Ingeniería Química 19*, 377-386.

Guerra-Rodríguez E., Portilla-Rivera O. M., Jarquín-Enríquez L., Ramírez J. A. Vázquez M. (2012). Acid hydrolysis of wheat straw: A kinetic study. *Biomass & Bioenergy 36*, 346-355.

Herrera A., Téllez-Luis S. J., Ramírez J. A., Vázquez M. (2003). Production of xylose from sorghum

straw using hydrochloric acid. *Journal of Cereal Science 37*, 267-274.

Hsu T. C., Guo G. L., Chen W. H., Hwang W. S. (2010). Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis. *Bioresource Technology 101*, 4907-4913.

Kuglarz M., Alvarado-Morales M., Dabkowska K., Angelidaki I. (2018). Integrated production of cellulosic bioetanol and succinic acid from rapeseed straw after dilute-acid pretreatment. *Bioresource Technology 265*, 191-199.

Lenihan P., Orozco A., O'Neill E., Ahmad M. N. M., Rooney D. W., Walker G. M. (2010). Dilute acid hydrolysis of lignocellulosic biomass. *Chemical Engineering Journal 156*, 395-403.

Li P., Cai D., Luo Z., Qin P., Chen C., Wang Y., Zhang C., Wang Z., Tan T. (2016). Effect of acid pretreatment on different parts of corn stalk for second generation ethanol production. *Bioresource Technology 206*, 86-92.

Lu X. B., Zhang Y. M., Liang Y., Yang J., Dan H. B. (2008). Modelling and optimization of the dilute sulphuric acid treatment on corn stover at low temperature. *Chemical and Biochemical Engineering Quarterly 22*, 134-142.

Mishra A., Ghosh S. (2019). Bioethanol production from various lignocellulosic feedstocks by a novel "Fractional hydrolysis" technique with different inorganic acids and co-culture fermentation. *Fuel 236*, 544-553.

Muñoz-Páez K. M., Alvarado-Michi E. L., Buitrón G., Valdez-Vázquez I. (2019). Distinct effects of furfural, hydroxymethylfurfural and its mixtures on dark fermentation hydrogen production and microbial structure of a mixed culture. *International Journal of Hydrogen Energy 44*, 2289-2297.

Pappas I. A., Koukoura Z., Tananaki C., Goulas C. (2014). Effect of dilute acid pretreatment severity on the bioconversion efficiency of Phalaris aquatica L. Lignocellulosic biomass into fermentable sugars. *Bioresource Technology 166*, 395-402.

Rafiqul I.S.M., Sakinah A. M. M. (2012). Kinetic studies on acid hydrolysis of Meranti wood

sawdust for xylose production. *Chemical Engineering Science 71*, 431-437.

Saeman J. F. (1945). Kinetics of wood saccharification: Hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature. *Industrial and Engineering Chemistry 37*, 43-52.

Sánchez-Herrera D., Sánchez O., Houbron E., Rustrian E., Toledano T., Tapia-Tussel R., Alzate-Gaviria L. A. (2018). Biomethane potential from sugarcane straw in Veracruz, Mexico: Combined Liquid hot water pretreatment and enzymatic or Biological hydrolysis. *Revista Mexicana de Ingeniería Química 17*, 1105-1120.

Saqib A. A. N., Whitney P. J. (2011). Differential behaviour of the dinitrosalicylic acid (DNS) reagent towards mono and di-saccharide sugars. *Biomass & Bioenergy 35*, 4748-4750.

Saucedo-Luna J., Castro-Montoya A. J., Rico J. L., Campos-García J. (2010). Optimization of acid hydrolysis of bagasse from *Agave tequilana* Weber. *Revista Mexicana de Ingeniería Química 9*, 91-97.

Siripong P., Duangporn P., Takata E., Tsutsumi Y. (2016). Phosphoric acid pretreatment of Achyranthes aspera and Sida acuta weed biomass to improve enzymatic hydrolysis. *Bioresource Technology 203*, 303-308.

Swati G., Haldar S., Ganguly A., Chatterjee P. K. (2013). Investigations on the kinetics and thermodynamics of dilute acid hydrolysis of *Parthenium hysterophorus* L. substrate. *Chemical Engineering Journal 229*, 111-117.

Texco-López A., Cadena-Ramírez A., Álvarez-Cervantes J., Tovar-Jiménez X., Gómez-Aldapa C. A., Castro-Rosas J., Téllez-Jurado A. (2018). Optimization of the acid hydrolysis of cladodes of *Opuntia ficus*-indica by response surface methodology. *Revista Mexicana de Ingeniería Química 17*, 1095-1104.

Tizazu B. Z., Moholkar V. S. (2018). Kinetic and thermodynamic analysis of dilute acid hydrolysis of sugarcane bagasse. *Bioresource Technology 250*, 197-203.

Vázquez M., Oliva M., Téllez-Luis S. J., Ramírez J. A. (2007). Hydrolysis of sorghum straw using phosphoric acid: Evaluation of furfural production. *Bioresource Technology 98*, 3053-3060.

Wise L. E., Murphy M., D'Adieco A. (1946). Chlorite holocellulose, its fractionation and beating on summative wood analysis and on studies on the hemicelluloses. *Paper Trade Journal 122*, 35-45.

Yu H., Xiao W., Han L., Huang G. (2019). Characterization of mechanical pulverization/phosphoric acid pretreatment of corn stover for enzymatic hydrolysis. *Bioresource Technology 282*, 69-74.

Zhang H., Jin Q., Xu R., Yan L., Lin. (2011). Kinetic studies of xylan hydrolysis of corn stover in a dilute acid cycle spray flow-through reactor. *Frontiers of Chemical Science and Engineering 5*, 252-257.