



**Sugar production by dilute acid hydrolysis of oat bagasse with three different acids: kinetics and thermodynamics**

**Producción de azúcares por hidrólisis ácida diluida del bagazo de avena con tres ácidos diferentes: cinética y termodinámica**

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**Abstract**

Acid hydrolysis is used as a treatment method to hydrolyze the polysaccharides present in biomass to fermentable sugars. In this research the hydrolysis of oat bagasse was studied employing different inorganic acids (HCl, H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) at low temperatures (90 - 110 °C) in a long-term process. Sulfuric acid showed a high potential to produce reducing sugars reaching the maximum production yields at 110°C, while hydrochloric acid at 110°C was the most catabolic acid promoting sugars transformation into furfural. FTIR and relative transmittance analyses suggested that major impact on lignin polymer was made by phosphoric acid hydrolysis at Combined Severity Factors (CSF) higher than 1.5. Kinetic constants calculated from conventional Saeman model allowed to determine thermodynamic parameters for each inorganic acid. Decomposition of sugars occurred most frequently when the Activation Energies (Ae) were low than calculated for sugar production, being aldehydes, the most stable products obtained during hydrolysis. Thermodynamic parameters show an endothermic and non-spontaneous oat bagasse hydrolysis reaction for different inorganic acids.

*Keywords:* kinetics, thermodynamics, oat bagasse, reducing sugars, acid hydrolysis.

**Resumen**

La hidrólisis ácida se utiliza como tratamiento para hidrolizar los polisacáridos presentes en la biomasa y convertirlos en azúcares fermentables. Se estudió la hidrólisis del bagazo de avena empleando diferentes ácidos inorgánicos (HCl, H<sub>2</sub>SO<sub>4</sub> y H<sub>3</sub>PO<sub>4</sub>) a bajas temperaturas (90 - 110 °C) en un proceso de larga duración. El ácido sulfúrico mostró un alto potencial para producir azúcares reductores alcanzando un rendimiento máximo de producción a 110°C, mientras que el ácido clorhídrico a 110°C fue el ácido más catabólico al promover la conversión de los azúcares reductores en furfural. Los análisis FTIR y de transmitancia relativa sugirieron que el mayor impacto sobre la lignina lo tuvo la hidrólisis con ácido fosfórico para factores de severidad combinados (CSF) superiores a 1.5. Las constantes cinéticas calculadas a partir del modelo convencional de Saeman permitieron determinar los parámetros termodinámicos para el proceso de hidrólisis con cada ácido inorgánico. La descomposición de los azúcares se produjo con mayor frecuencia para valores de Energías de Activación (Ae) más bajos que los calculados para la producción de azúcar, siendo los aldehídos, los productos más estables obtenidos durante la hidrólisis. Los parámetros termodinámicos muestran una reacción de hidrólisis endotérmica y no espontánea del bagazo de avena para los diferentes ácidos inorgánicos.

*Palabras clave:* cinética, termodinámica, bagazo de avena, azúcares reductores, hidrólisis ácida.

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## 1 Introduction

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Chemical products produced from fossil sources are non-easily biodegradable and have a negative impact on both environment and human health during their life cycle; moreover, they have contributed to petroleum reserves depletion and to climate change by their wrong final disposal and treatment. Currently, renewable feedstocks have been used as alternative sources for value-add chemicals production with lower environmental damage being lignocellulosic biomass the most promising material (Láinez *et al.*, 2018; Jia *et al.*, 2022; Ramos-Ibarra *et al.*, 2021). It is well known that lignocelluloses are the most abundant natural sources around the world, they comprise a wide range of materials such as organic fraction of municipal solid waste, agro-industrial and forestry residues, garden wastes and crop residues (Cai *et al.*, 2017). Lignocellulosic biomass is mainly composed of three complex carbohydrates; cellulose, hemicellulose and lignin, from which cellulose and hemicellulose can be depolymerized into monomeric sugars for subsequent green chemicals production by biochemical or chemical methods (Qi *et al.*, 2018). Acid hydrolysis is a chemical method that has demonstrated to be highly efficient to treat, disrupt and modify lignocellulosic matrix. Acid hydrolysis can be performed to achieve two goals; the first, disrupt lignocellulosic matrix, increase surface area and to reduce cellulose crystallinity improving the subsequent enzymatic hydrolysis, while the second is to produce monomeric and oligomeric sugars by polysaccharides glycosidic bond cleavage mainly from hemicellulosic fraction (Láinez *et al.*, 2018; Solarte-Toro *et al.*, 2019). Acid hydrolysis is a complex heterogeneous process; it involves both physical and chemical factors. In agreement with Tizazu & Moholkar, 2018 and Xiang *et al.*, 2003, cellulose and hemicellulose acid hydrolysis in lignocellulosic materials proceeds in three main steps: (1) diffusion of acid protons through material, (2) protonation of glycosidic oxygen, cleavage of the C-O bonding and carbonium ion formation coupled with rapid addition of water to produce free sugar, (3) and diffusion of products throughout liquid phase.

Some models have been developed to study the kinetic approach of acid hydrolysis (Chen *et al.*, 2015; Swati *et al.*, 2013; Tizazu & Moholkar, 2018; Yan *et al.*, 2014), most of them are based on Saeman equation (Saeman, 1945) and consider

that hydrolysis of lignocellulosic biomass follows first-order behaviour in which glucan and xylan are solubilized prior chemical reaction (pseudo-homogeneous process) (Rafiqul & Mimi Sakinah, 2012; Yan *et al.*, 2014). In addition to sugars, some compounds also known as inhibitors are produced during acid hydrolysis of lignocelluloses being furfural and hydroxymethylfurfural (HMF) the most undesirable products. One alternative to diminish inhibitors production is performing acid hydrolysis at relatively low temperatures and long residence times (Jin *et al.*, 2011).

In this study, the effect of three different inorganic acids; hydrochloric, sulphuric and phosphoric on hydrolysis rates and thermodynamic behaviour was investigated employing relatively low temperatures. The total reducing sugars amount was fitted to conventional Saeman model estimating the kinetic constants. The effect of pH and Combined Severity Factor (CSF) on sugars production was analysed, and the physicochemical properties changes in hydrolysed material due to reaction conditions were also reported and discussed. The main idea of this paper is to show the production of reducing sugars and the hydrolysis reaction behaviour from oat bagasse, a scarcely reported lignocellulosic biomass.

## 2 Materials and methods

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### 2.1 Raw material

Oat bagasse samples were collected in the municipality of Metepec located at Mexico State, Mexico. These were air-dried and milled into mechanical milling (SWISSMEX model Junior) to a particle size smaller than 250  $\mu\text{m}$ , these were used for initial characterization and hydrolysis assays. Before oat bagasse characterization, a Soxhlet extraction with ethanol-toluene mixture (1:2) was carried out to eliminate extractives such as terpenes and resins. The percentage of holocellulose and lignin in dry basis were determined by chlorite method (Wise *et al.*, 1946) and method for acid insoluble lignin (ASTM, 2001) respectively. The percentage of moisture, ash, and total volatile solids (TVS) in oat bagasse were determined using standard methods.

## 2.2 Acid hydrolysis assays

The acids employed for acid hydrolysis of oat bagasse were hydrochloric, sulphuric and phosphoric at the same concentration (2.2 M) while the reaction temperatures were set at: 90, 100 and 110 °C. The reaction times proposed were in the range from 0 to 300 minutes. For each experiment, 1 g of raw corncob was mixed with 15 mL of each acid solution in a 20 mL vial. The mixtures were then slowly homogenised, then the vials were sealed and heated for different reaction times. After hydrolysis, vials were cooled at room temperature for 15 minutes and phases were separated by filtration. Hydrolysates (liquid phase) were used to determine pH, reducing sugars and furfural concentration. The severity of hydrolysis reaction was determined by the calculation of CSF, which involves the effect of reaction time, temperature and acid concentration into a single numerical value and according to (Sun *et al.*, 2015), it can be mathematically defined as shown in Eq. 1.

$$CSF = \log \left[ t \cdot \exp \left( \frac{T - T_r}{14.75} \right) \right] - pH \quad (1)$$

where  $t$  is the reaction time in minutes,  $T$  the hydrolysis temperature,  $T_r$  the reference temperature (100 °C), 14.75 an empirical constant associated to activation energy and pH the acidity of hydrolysate after hydrolysis.

The hydrolysed oat bagasse was washed with hot distilled water to remove the acid excess, dried at 45 °C and characterized to observe physicochemical changes attributed to reaction conditions.

## 2.3 Analytical techniques

The amount of reducing sugars of hydrolysates was determined by 3-5 Dinitrosalicylic acid (DNS) method reported by (Miller, 1959). The hydrolysates obtained with hydrochloric and sulphuric acids were diluted 1:15 with distilled water and phosphoric acid hydrolysates were dilute 1:30. The difference in dilution ratio is associated with the nature of inorganic acids since hydrochloric and sulphuric are strong acids while phosphoric is a triprotic weak acid. After that, 500  $\mu$ L of each dilution were mixed with 500  $\mu$ L of DNS reagent in 12 mL test tubes which were sealed and heated in water bath during 5 minutes at 92 °C, then vials were cooled at room temperature for 10 minutes and each mixture was diluted with 10 mL of distilled water. The absorbance of samples was determined with a Spectro Array Thermo Scientific Uv-Vis spectrometer at 540 nm. Furfural

concentration was measured for each hydrolysate by using Uv-Vis spectrometer at 277 nm and 1:150 dilutions with distilled water. Hydrolysates pH's were determined with Hanna HI 2221 potentiometer and CSF was calculated employing Eq. 1.

The raw and hydrolysed oat bagasse was analysed by Fourier Transform Infrared spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) to observe the main physicochemical changes on oat structure due to reaction conditions. FTIR analyses were performed in a Varian 640 IR spectrometer employing a spectral range from 600 to 4000  $\text{cm}^{-1}$ . The morphological studies were carried out in a Jeol JSM-6610LV Oxford Instruments electron microscope operated at 20 kV and low vacuum (30 Pa).

## 2.4 Determination of kinetic and thermodynamic parameters

Saeman kinetic model has been used in acid hydrolysis processes with different lignocellulosic materials (Gómora-Hernández *et al.*, 2020; Han *et al.*, 2019; Jin *et al.*, 2011; Rafiqul & Mimi Sakinah, 2012). This model assumes a series of two pseudo-homogeneous, irreversible and first order reaction in which mass transfer does not affect the reaction rates. The first reaction ( $k_1$ ) corresponds to cellulose and hemicellulose transformation into monomeric sugars, mainly glucose, galactose, xylose and arabinose. The second reaction ( $k_2$ ) is related to the decomposition of hexoses and pentoses into HMF and furfural respectively which are inhibitory for microbial growth. Usually, Saeman and modified Saeman kinetic models are used to estimate kinetic parameters employing experimental data obtained from individual sugars, previous works showed that reducing sugars production data can also be applied to study the kinetics of acid hydrolysis (Gómora-Hernández *et al.*, 2020) being the general scheme of the reaction as follows (Fig. 1):

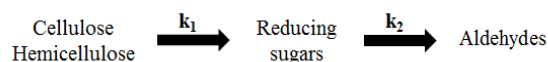


Fig. 1. Simplified scheme of Saeman kinetic model.

From the reaction scheme shown before and solving the differential equation, the total amount of reducing sugars as a function of reaction time is

obtained (Eq. 2).

$$M = \frac{P_o \cdot k_1}{k_2 - k_1} [e^{-k_1 \cdot t} - e^{-k_2 \cdot t}] + M_o e^{-k_2 t} \quad (2)$$

where  $P_o$  and  $M_o$  are respectively the amount of holocellulose and reducing sugars in oat bagasse given in g / 100 g raw material,  $t$  the reaction time in minutes,  $k_1$  and  $k_2$  the kinetic constants associated to production and decomposition of sugars in  $\text{min}^{-1}$  and  $M$  the concentration of reducing sugars at different times ( $t$ ). Since the concentration of reducing sugars in raw material is very low,  $M_o$  can be approximated to 0 and the final model results as follows (Eq. 3):

$$M = \frac{P_o \cdot k_1}{k_2 - k_1} [e^{-k_1 \cdot t} - e^{-k_2 \cdot t}] \quad (3)$$

From  $k_1$  and  $k_2$  rate constants the maximum sugar production (Eq. 4) and the time ( $t_{opt}$ ) at which this maximum concentration is achieved (Eq. 5) can be calculated according to the following equations (Gurgel *et al.*, 2012; Saeman, 1945):

$$Sug_{max} = P_o \left( \frac{k_2}{k_1} \right)^{\left[ \frac{k_2}{k_1 - k_2} \right]} \quad (4)$$

$$t_{opt} = \left[ \frac{\ln(k_2) - \ln(k_1)}{k_2 - k_1} \right] \quad (5)$$

where  $P_o$ ,  $k_1$  and  $k_2$  have the same meaning and units to that mentioned before.

The calculation of thermodynamic parameters is an important tool to understand the energetic changes and molecular behavior of hydrolysis reaction at different operational conditions. Previous studies have shown that hydrolysis rate constants increase as a function of temperature, thus conventional Arrhenius equation can be used to estimate Activation Energy (Ae) and Frequency factor (A) (Gómora-Hernández *et al.*, 2020; Swati *et al.*, 2013; Tizazu & Moholkar, 2018). The linear form of Arrhenius equation is shown in Eq. 6. The enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were determined by the linear form of Eyring equation (Eq. 7) while Free Gibbs Energy ( $\Delta G$ ) was calculated according to Eq. 8.

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

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

$$(8)$$

where  $T$  is the absolute temperature (K),  $R$  the ideal gas constant ( $8.3144 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $k_B$  the Boltzmann

constant ( $1.381 \times 10^{-23} \text{ J K}^{-1}$ ),  $h_v$  the Planck constant ( $6.6261 \times 10^{-34} \text{ J s}$ ) and  $k$  the rate constant in  $\text{min}^{-1}$  for Arrhenius and in  $\text{s}^{-1}$  for Eyring equation. Ae,  $\Delta H$  and  $\Delta G$  are given in  $\text{kJ mol}^{-1}$ ,  $A$  in  $\text{min}^{-1}$  and  $\Delta S$  in  $\text{J mol}^{-1} \text{ K}^{-1}$ .

Sugars production data were fitted to Saeman kinetic model by non-linear regression while rate constants were fitted to the linear form of Arrhenius and Eyring equations. All fittings were performed in Origin 8.6 software.

## 3 Results and discussion

### 3.1 Composition and acid hydrolysis of oat bagasse

The composition of oat bagasse in terms of complex carbohydrates were (g / 100 g raw oat bagasse): holocellulose =  $60.05 \pm 1.22$  and lignin =  $33.25 \pm 2.68$ , like that reported by (Romaní *et al.*, 2016) with oat straw from Spain. While the moisture percentage was of  $3.57 \pm 0.05\%$ , the percentage of TVS and ash was  $69.21 \pm 0.07\%$  and  $30.79 \pm 0.03\%$ .

The production of reducing sugars as a function of reaction time and temperature is shown in Fig. 2. At  $90^\circ \text{C}$  (Fig. 2a) reducing sugars production increased as reaction time rises reaching the maximum yields at 270 minutes, between the three acids used, hydrochloric acid was whose showed sugar decomposition phase at  $90^\circ \text{C}$  and 300 minutes.

From Fig. 2b can be appreciated that sugar decomposition phase was observed for each acid being sulphuric acid the most efficient to produce sugars since its highest sugar yield was  $37.54 \text{ g}$  of sugar /  $100 \text{ g}$  oat bagasse observed at 180 minutes. The lowest sugar yield reached at this hydrolysis temperature was  $20.56 \text{ g}$  /  $100 \text{ g}$  oat bagasse observed after 270 minutes reaction time with phosphoric acid. For hydrochloric acid, the highest sugar yield was  $22.71 \text{ g}$  sugar /  $100 \text{ g}$  oat bagasse observed at 90 minutes, after this time sugars production decreased to a final value of  $16.56 \text{ g}$  sugar /  $100 \text{ g}$  oat bagasse obtained at the end of the experiment, which were lower to observed with phosphoric acid ( $19.57 \text{ g}$  sugar /  $100 \text{ g}$  oat bagasse) and attributed to the strong nature of hydrochloric acid promoting sugar transformation into another compounds.

For all acids, at  $110^\circ \text{C}$  not only the highest sugars yields but also the longest thermo-chemical decomposition phase was observed (Fig. 2c).

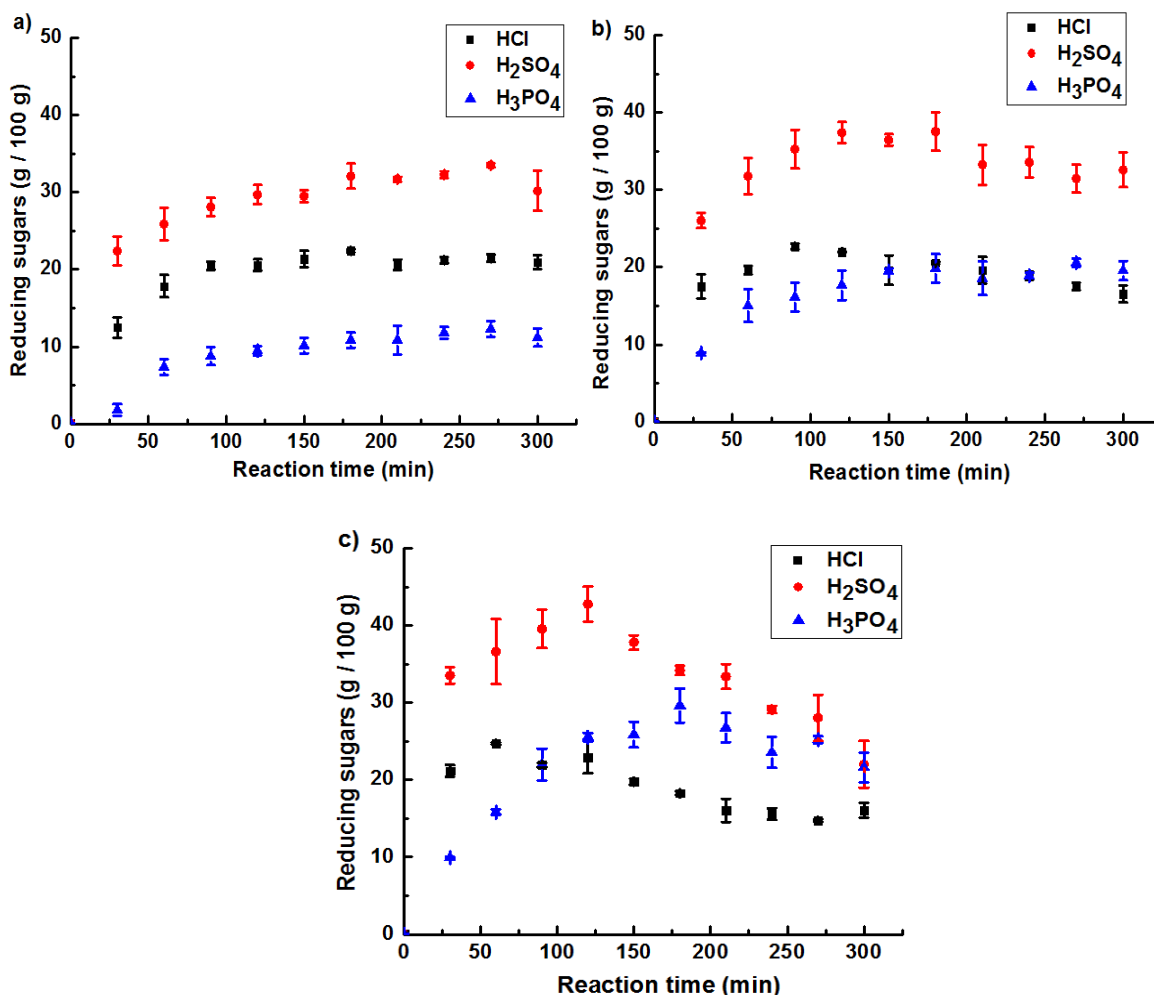


Fig. 2. Reducing sugars yields obtained by acid hydrolysis of oat bagasse with different inorganic acids at a) 90 °C, b) 100 °C and c) 110 °C.

After 300 minutes reaction time, phosphoric acid showed the highest sugars production yield; this fact suggested that the acid concentration and the temperature range employed favours reducing sugars production around 60 - 120 minutes with sulphuric and hydrochloric acid while phosphoric acid was more efficient in long-term hydrolysis (210 minutes). Furthermore, sulfuric acid was the best option to produce reducing sugars from oat bagasse since the maximum yield; 42.77 g sugar / 100 g oat bagasse, was obtained at 110 °C and 120 minutes in sulphuric acid solution. This maximum yield was higher than those reported previously in acid hydrolysis of corn stover (Chen *et al.*, 2015; Gomora-Hernandez *et al.*, 2020), sugarcane bagasse (Tizazu & Moholkar, 2018), waste mushroom medium (Na & Lee, 2015), bamboo

(Timung *et al.*, 2015) and wheat straw (Guerra-Rodríguez *et al.*, 2012; Rojas-Rejón & Sánchez, 2014). In addition, it was in the range obtained with different lignocellulosic materials during their direct acid hydrolysis (Sun *et al.*, 2014) and acid pretreatment - enzymatic hydrolysis processes (Pesce *et al.*, 2020; Sahoo *et al.*, 2018).

Fig. 3 shows furfural production during acid hydrolysis of oat bagasse. As can be seen in this figure, the concentration of furfural increased as a function of reaction time and hydrolysis temperature reaching the maximum production at 110 °C and 300 minutes for each acid. Phosphoric acid produced the lowest amount of furfural; 999.9 mg/L, while hydrochloric acid was the most catabolic acid producing a maximum furfural concentration of 1729.3 mg/L.



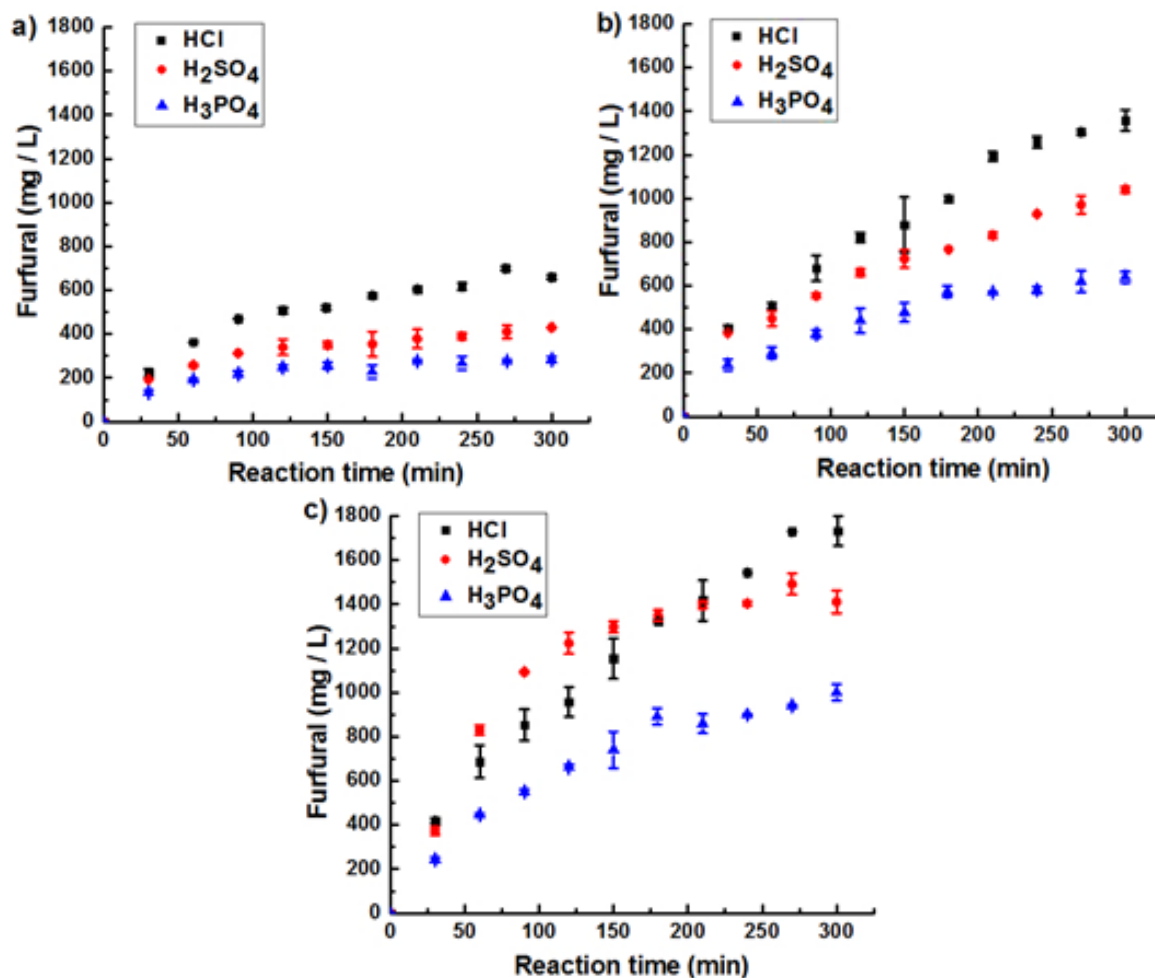


Fig. 3. Furfural production during acid hydrolysis of oat bagasse with different inorganic acids at a) 90 °C, b) 100 °C and c) 110 °C.

At 110 °C, sulfuric and phosphoric acid showed a rapid increase in furfural concentration from 0 to 120 minutes (Fig. 3c), after this time the concentration increased slowly until the end of the experiment, this behaviour suggests a furfural degradation into low molecular weight decomposition products which are promoted in the presence of organic acids such as levulinic and formic from hexoses decomposition (Danon *et al.*, 2014).

The maximum reducing sugars production yield was observed in sulphuric acid solution at 110 °C and 120 minutes, at these conditions the furfural concentration (1223.18 mg / L) was lower than reported in previous works with different lignocellulosic materials (Guerra-Rodríguez *et al.*, 2012; Han *et al.*, 2019; Rafiqul & Mimi Sakinah, 2012) and slightly higher to the 1 g / L reported

before as the concentration limit at which hydrogenic microorganisms activity is inhibit (Akobi *et al.*, 2017; Muñoz-Páez *et al.*, 2019). Detoxification methods have been usually employed to reduce furfural concentration in acid hydrolysates and evaporation is the most economical and feasible method; the subsequent detoxification can improve the fermentability of the obtained sugars and increase their potential for products production in biorefinery concept.

CSF defined as a measure of acid hydrolysis severity has an important effect on sugars production yield and furfural concentration. Fig. 4 correlates reducing sugars yields and CSF for each acid, as can be seen in Fig. 4 the highest CSF values were observed for hydrochloric acid (3.4), while the lowest values were calculated for phosphoric acid (2.4).

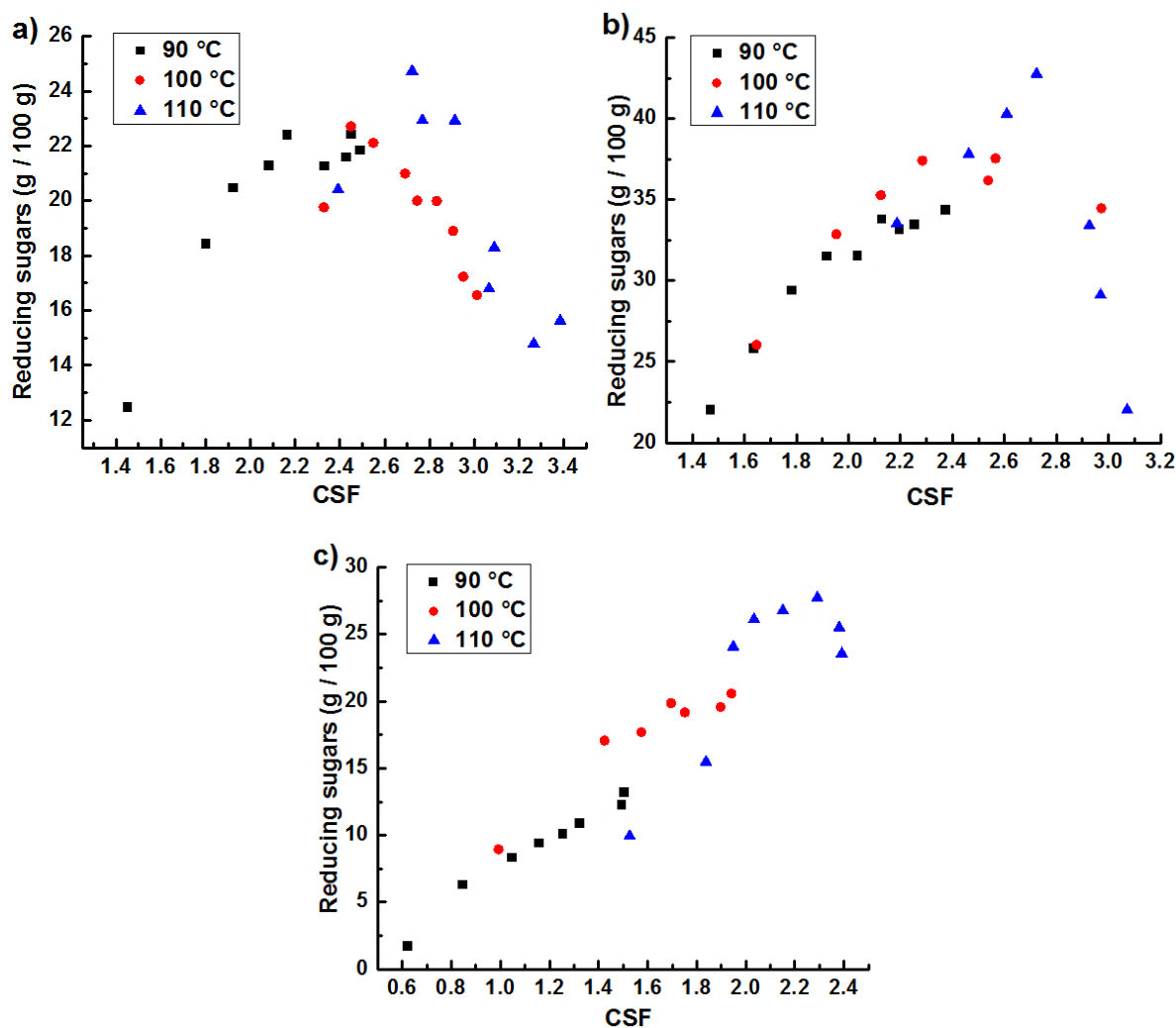


Fig. 4. Behavior of reducing sugars yield as a function of CSF during hydrolysis of oat bagasse with a) hydrochloric, b) sulfuric and c) phosphoric acid.

CSF obtained with sulphuric acid (3.1) were slightly lower to that observed for hydrochloric acid, which agree to the nature of both acids, moreover these acids showed their highest sugars yields in the CSF values range of 2.6 - 2.9 and above these values the decomposition of sugars is favoured. The highest reducing sugars production yield achieved with phosphoric acid was associated to a CSF value of 2.3, which was very close to that obtained by (Sun *et al.*, 2015) during sulphuric acid hydrolysis of corn stalk, the sugars production yield obtained at 2.3 CSF was 32.64 %, this was higher to that determined with phosphoric acid but lower in comparison to observed with sulfuric acid.

Gomora-Hernandez *et al.* (2020) reported a maximum CSF value and sugars production yield of 1.9 and 19 g / 100 g corn stover in hydrochloric acid solution, these values were lower than the obtained in this study. In addition, previous study showed sugars yield ranged from 2.9 to 26.1 g / 100 g *Phalaris aquatica* in CSF range of 0.13 to 1.16 using sulphuric acid as catalyst, two different temperatures (110 and 130 °C) and short reaction times (30 and 60 minute) (Pappas *et al.*, 2014). The difference in both CSF and sugars yields are associated not only to the nature of raw material but also reaction times, temperatures as well as kind and concentration of employed acids.

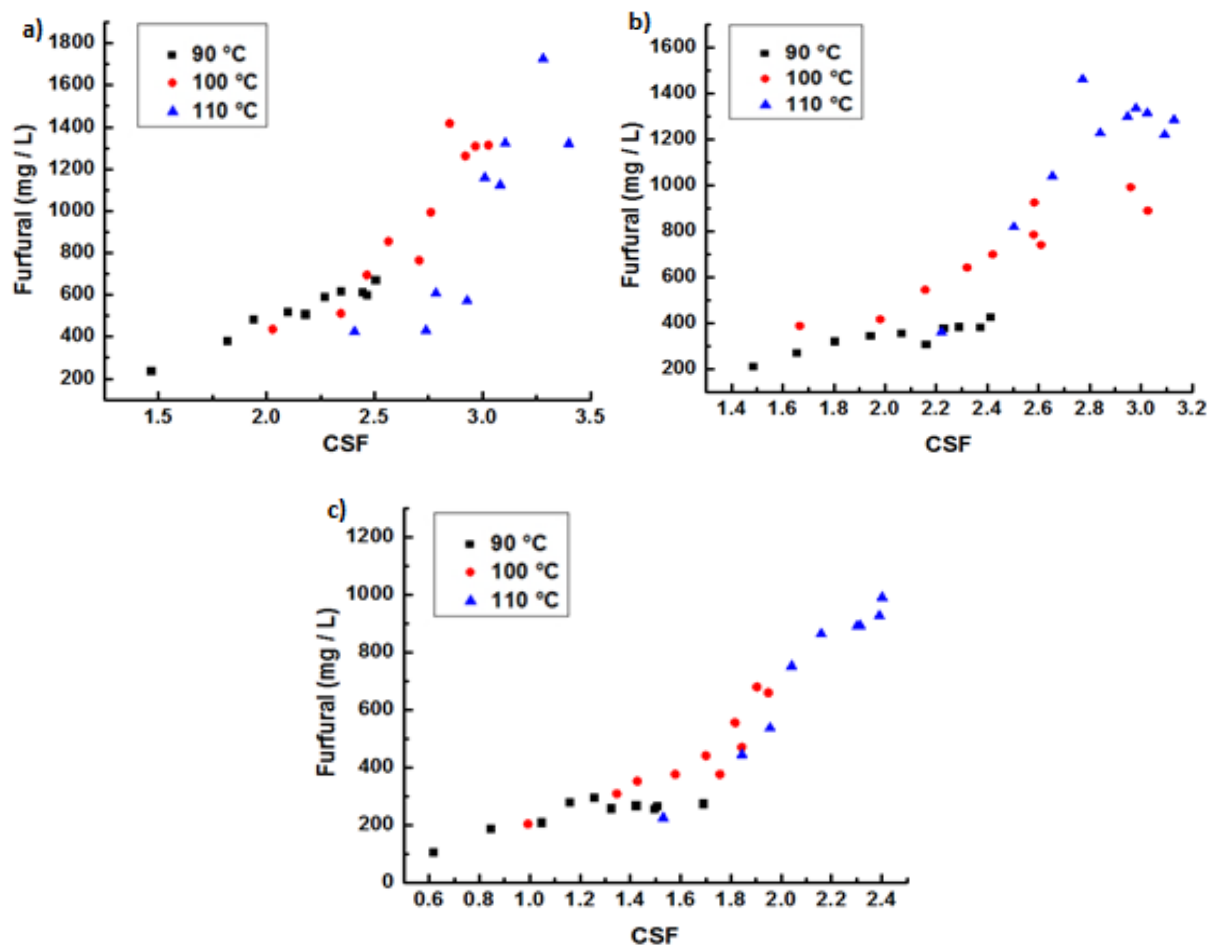


Fig. 5. Behavior of furfural production as a function of CSF during hydrolysis of oat bagasse with a) hydrochloric, b) sulphuric and c) phosphoric acid.

For each acid, an increase in CSF promotes a raise in furfural production reaching the highest concentrations at CSF values of 3.4, 3.1 and 2.4 for hydrochloric, sulphuric and phosphoric acid respectively (Fig. 5), this trend suggests that increasing reaction temperature and hydrolysis time furfural production will be favoured. For each acid, highest furfural production yields were related to the highest CSF; being hydrochloric acid the best option to produce this aldehyde. In order to increase furfural production, more severe hydrolysis conditions are needed.

CSF can be used as starting point to improve the acid hydrolysis performance and to increase either reducing sugars or aldehydes concentration. If furfural is the desirable product CSF values higher than 2.6 are required, on the other hand if hydrolysis of oat

bagasse is focused on sugars production the most beneficial CSF are in the range between 2.4 - 2.8, these values could be obtained maintaining reaction temperatures and diminishing acid concentration in longer processes.

### 3.2 Kinetic and thermodynamic study of oat bagasse acid hydrolysis

The kinetic study was carried out assuming no influence of mass transfer in the overall process and a solubilisation phase of oligosaccharides prior chemical reaction. According to (Girisuta *et al.*, 2007) and (Saeman, 1945) acid hydrolysis can be considered as homogeneous process when particle size is less than 840  $\mu\text{m}$ , in present study the particle size employed for hydrolysis tests were lower than 250  $\mu\text{m}$ .



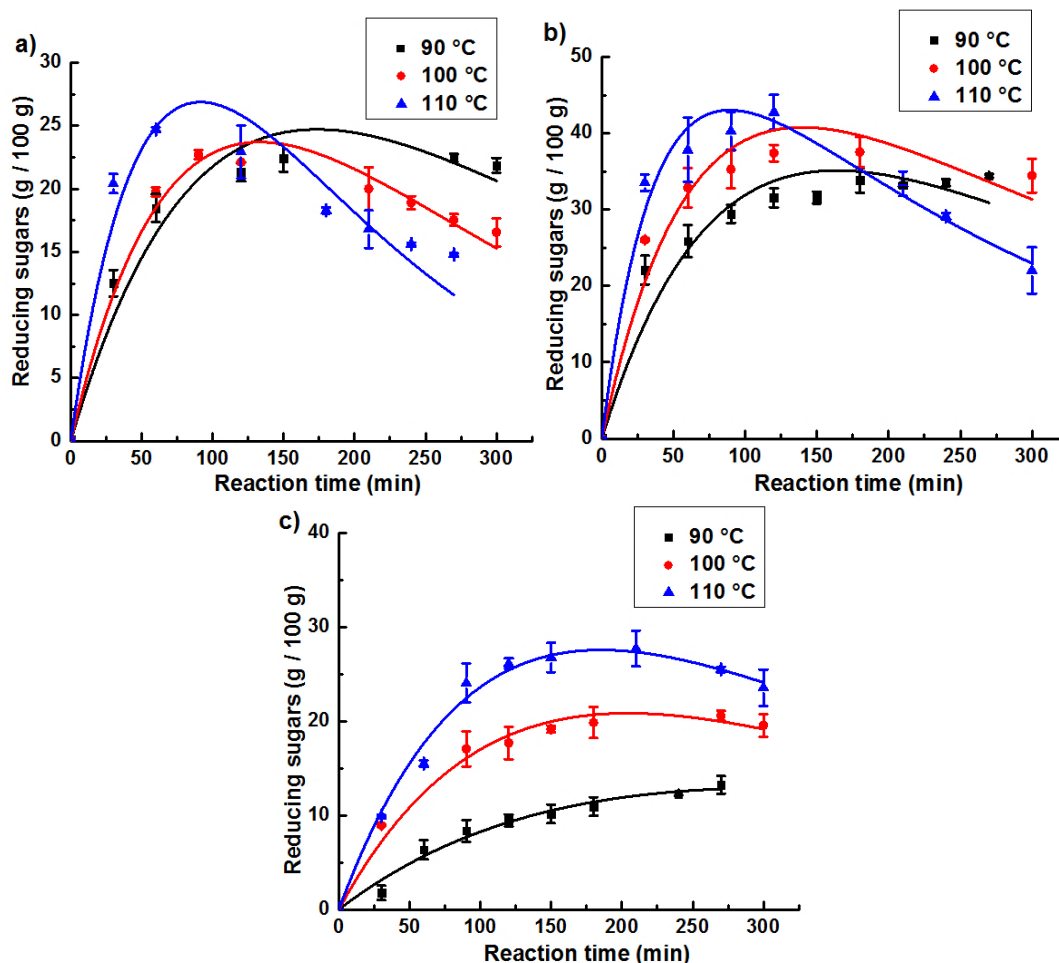


Fig. 6. Experimental data of reducing sugars produced by hydrolysis with a) hydrochloric, b) sulphuric and c) phosphoric acid fitted to Saeman kinetic model.

Table 1. Kinetic and statistical parameters of oat bagasse hydrolysis with different inorganic acids.

Acid	°C	$k_1$ ( $\text{min}^{-1}$ )	$k_2$ ( $\text{min}^{-1}$ )	$R^2$	Sug <sub>max</sub> (g / 100 g)	$t_{opt}$ (min)
HCl	90 °C	$6.08 \times 10^{-3}$	$4.90 \times 10^{-3}$	0.966	24.51	182.86
	100 °C	$8.06 \times 10^{-3}$	$6.98 \times 10^{-3}$	0.978	23.69	133.21
	110 °C	$1.34 \times 10^{-2}$	$8.78 \times 10^{-3}$	0.900	26.88	91.55
H <sub>2</sub> SO <sub>4</sub>	90 °C	$7.42 \times 10^{-3}$	$2.55 \times 10^{-3}$	0.997	34.32	219.32
	100 °C	$1.47 \times 10^{-2}$	$2.77 \times 10^{-3}$	0.931	40.76	139.84
	110 °C	$2.91 \times 10^{-2}$	$3.55 \times 10^{-3}$	0.998	44.82	82.38
H <sub>3</sub> PO <sub>4</sub>	90 °C	$1.92 \times 10^{-3}$	$4.86 \times 10^{-3}$	0.976	12.94	315.89
	100 °C	$4.90 \times 10^{-3}$	$5.41 \times 10^{-3}$	0.962	21.01	194.14
	110 °C	$6.80 \times 10^{-3}$	$4.2 \times 10^{-3}$	0.987	27.57	185.32

Reducing sugars experimental data were well fitted to Saeman kinetic model as shown in Fig. 6. All acids showed the sugar decomposition phase at 100 and 110 °C, however, hydrochloric acid was the only that showed this decomposition at 90 °C, behaviour that

can be associated to the strong nature of this acid and its monoprotic character (Fig. 6a). Sulphuric acid acts also as strong acid, however is a diprotic acid and its proton dissociation is not complete, thus, its potential to hydrolyse lignocelluloses is lower than

the hydrochloric acid. This fact is appreciated in Fig. 6b where no decomposition of sugars is observed at 90 °C and the amount of sugars obtained after 300 minutes were similar at 90 and 100 °C. Phosphoric acid showed the lowest decomposition phase of sugars for both experimental and predicted values.

All fittings were performed greatly and the  $R^2$  coefficients were higher than 0.90. Table 1 summarizes the kinetic and statistical parameters for oat bagasse hydrolysis with different inorganic acids, from this table can be observed that an increase in reaction temperature promotes an increase in  $k_1$  rate constants; with exception of phosphoric acid similar behaviour was observed for  $k_2$ , this trend has been reported previously with different kinetic models and lignocellulosic materials (Ajala *et al.*, 2020; Arslan *et al.*, 2012; Na & Lee, 2015; Sun *et al.*, 2014).

From chemical kinetic approach, hydrolysis performed with phosphoric acid at 90 and 100 °C was more efficient to produce aldehydes, since at these conditions  $k_2$  rate constants were higher than  $k_1$  constants. Opposite behaviour was observed for the rest of the experiments suggesting that reducing sugars production is the most favourable reaction during hydrolysis of oat bagasse with hydrochloric and sulfuric acid 2.2 M.

The  $k_1$  and  $k_2$  rate constants are usually employed to estimate the maximum sugars production expected (Eq. 4) and the time at which this concentration is achieved (Eq. 5). As can be seen in Table 1 the highest sugars production (44.82 g / 100 g) was observed with sulphuric acid and 110 °C at an optimum time of 82.38 minutes which were very similar to that determined experimentally. On the other hand, the lowest sugars production expected was 12.94 g / 100 g oat bagasse determined in phosphoric acid solution at 90 °C and 315.89 minutes as optimum time. The maximum sugars production expected yield calculated for sulphuric and phosphoric acid increased as a function of reaction temperature, opposite behaviour was observed for the optimum times where an increase in reaction temperature is associated to a lower time reaching the longest values with phosphoric acid. With

exception of the test performed at 110 °C, the shortest optimum times were achieved with hydrochloric acid. Curiously, oat bagasse hydrolysis with sulphuric acid shows the highest sugars production yields and the maximum expected yield was determined at the minimum optimal time. Moreover, both maximum sugars expected yield and optimum time agree to the experimental data shown in Fig. 6.

For thermodynamic study, both  $k_1$  and  $k_2$  rate constants were fitted to the linear form of Arrhenius (Eq. 6) and Eyring (Eq. 7) equations. After that an average Free Gibbs energy change was calculated using Eq. 8. Table 2 summarizes the thermodynamic and statistical parameters for hydrolysis of oat bagasse with different acids, is important to mention that  $k_2$  rate constants calculated for phosphoric acid does not follow Arrhenius law, thereby they were not considered for thermodynamic parameters calculation. The values of  $A_e$  determined for sulphuric and hydrochloric acid suggest that sugars production from holocellulose fraction required more energy than their transformation into aldehydes, since  $A_e$  for  $k_1$  are higher than those calculated for  $k_2$ . Similar trend was reported previously during acid hydrolysis of hazelnut shells (Arslan *et al.*, 2012), corn stover (Gómora-Hernández *et al.*, 2020; Jin *et al.*, 2011) and empty fruit bunches (Girisuta *et al.*, 2007). The lowest  $A_e$  determined for  $k_1$  rate constants was observed with hydrochloric acid which confirms the rapid increase in sugars production in the time range of 0 to 90 minutes. The  $A_e$  calculated for sulphuric (78.99 kJ mol<sup>-1</sup>) and phosphoric (73.45 kJ mol<sup>-1</sup>) acid employing  $k_1$  constants were close to each other, and they were like that reported by (Chen *et al.*, 2015), (Lavarack *et al.*, 2002) and (Jensen *et al.*, 2008) who respectively studied acid catalysed hydrolysis of corn stover, sugarcane bagasse and balsam using sulphuric acid. Moreover,  $A_e$  values were lower than 100.85 kJ mol<sup>-1</sup> calculated by (Murillo-Luke *et al.*, 2022) during sulphuric acid hydrolysis of wood biomass (*Ipomoea arborescens*). This is attributed to the differences in composition and structure of the agricultural and wood biomass.

Table 2. Thermodynamic and statistical parameters of oat bagasse hydrolysis with different inorganic acids.

Acid	Constant	$A_e$ (kJ mol <sup>-1</sup> )	$A$ (min <sup>-1</sup> )	$R^2$	$\Delta H$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$R^2$	$\Delta G$ (kJ mol <sup>-1</sup> )
HCl	$k_1$	45.54	$2.1 \times 10^4$	0.968	42.44	-206.49	0.964	119.49
	$k_2$	33.79	$3.6 \times 10^2$	0.989	30.69	-240.16	0.986	120.31
H <sub>2</sub> SO <sub>4</sub>	$k_1$	78.99	$1.7 \times 10^9$	0.999	75.89	-112.44	0.999	117.85
	$k_2$	19.05	$1.4 \times 10^1$	0.915	15.95	-286.57	0.883	122.88
H <sub>3</sub> PO <sub>4</sub>	$k_1$	73.45	$7.7 \times 10^7$	0.936	70.35	-138.13	0.930	121.89

The frequency factor ( $A$ ) showed the same behaviour than  $A_e$ , the highest values of  $A$  corresponded to sugars production reaction, this trend agrees to the energy required to perform this reaction which increased the molecular dynamic and collisions. Moreover, lowest  $A$  values are associated to the smallest  $A_e$  as can be seen in Table 2 for sulphuric and hydrochloric acid.

The non-spontaneous and endothermic nature of the hydrolysis reaction was confirmed from positive values of  $\Delta G$  and  $\Delta H$  respectively (Gómora-Hernández *et al.*, 2020; Tizazu & Moholkar, 2018). The values of  $\Delta G$  calculated for  $k_1$  rate constants were slightly lower in comparison to that determined for  $k_2$  constants, while for  $\Delta H$  and  $\Delta S$  the highest values were observed for  $k_1$ . As  $A_e$ , the major values of activation enthalpy ( $\Delta H$ ) were calculated for sulphuric and phosphoric acid, this fact means that both acids required more energy to reach the activated complex in comparison with hydrochloric acid which can be due to the incomplete deprotonation associated with their dissociation constants. According to (Gurgel *et al.*, 2012) and the activated complex theory,  $\Delta S$  is a measure of the degree of organization resulting from the formation of activated complex, moreover,  $\Delta S$  indicates where the maximum amount of energy come from; complex or products, positive values are associated with the maximum amount of energy in the chemical complex while negative values correspond to the reactants side and implies that the activated complex is more ordered than the reactants (Ajala *et al.*, 2020); this last one was observed for oat bagasse hydrolysis with hydrochloric, sulphuric and phosphoric acid. In addition, from the thermodynamic principles any process with negative entropy is designed as stable. As shown in Table 2, sugars decomposition was the most favoured reaction during acid hydrolysis of oat bagasse and furfural was the most stable product.

Some studies have focused to determine  $A_e$  and  $A$  values for acid hydrolysis of different lignocellulosic materials, however, only a few of them have reported the complementary thermodynamic parameters;  $\Delta H$ ,  $\Delta S$  and  $\Delta G$ . (Ajala *et al.*, 2020; Gómora-Hernández *et al.*, 2020; Gomora-Hernandez *et al.*, 2020; Gurgel *et al.*, 2012) and (Tizazu & Moholkar, 2018) calculated not only positive values for  $\Delta H$  and  $\Delta G$  but also negative entropies ( $-\Delta S$ ) which are in agree to the trend observed in this paper.

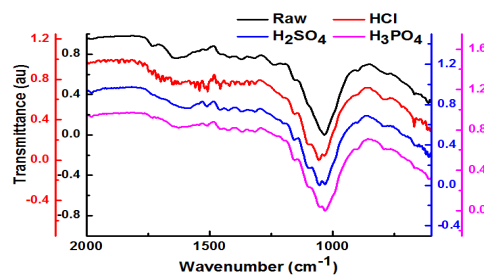


Fig. 7. FTIR spectra of raw and hydrolysed oat bagasse at 110 °C and 300 minutes reaction time.

### 3.3 Characterization of hydrolysed oat bagasse

#### 3.3.1 FTIR analysis

All FTIR spectra were normalized to a unit basis. Fig. 7 shows FTIR spectra of raw and hydrolysed oat bagasse with different inorganic acids at 110 °C and 300 minutes. The main vibrational bands of cellulose are located in the range of 1200 to 950  $\text{cm}^{-1}$  and correspond to C-C, C-C-O and C-O-C bonds. Raw oat bagasse showed only one vibrational band at 1032  $\text{cm}^{-1}$  which split into two bands at 1031 and 1052  $\text{cm}^{-1}$  after hydrolysis, this last band has been related to the C-C bond of cellulose (Jensen *et al.*, 2008), however Hsu *et al.*, (2010) associated it to O-H bonds of primary and secondary lignin alcohols which did not observed in raw oat bagasse since it was overlapped by predominant vibrational bands of cellulose.

The characteristic bands of hemicellulose observed at 1735  $\text{cm}^{-1}$  (C=O of acetyl groups) and 1240  $\text{cm}^{-1}$  (C-O) decreased their intensity after acid hydrolysis suggesting a dissolution and transformation of hemicellulose into monomeric sugars. The vibrational band located at 899  $\text{cm}^{-1}$  was observed in all spectra and is characteristic of the  $\beta$ -1-4 glycosidic linkage of cellulose (Sahoo *et al.*, 2018). For lignin, the wavenumbers at 1510 and 1590  $\text{cm}^{-1}$  correspond to aromatic skeletal ring while the aliphatic C-O and C-H bonds are located at 1320, 1425 and 1425  $\text{cm}^{-1}$  (Hsu *et al.*, 2010; Sahoo *et al.*, 2018), the intensity of these bands increased slightly after acid hydrolysis and can be attributed to an increase in lignin concentration caused by the degradation of polysaccharides (Li *et al.*, 2018). Similar behaviour to that observed in our spectra was reported previously for acid hydrolysis of *Phalaris aquatica* (Pappas *et al.*, 2014), water hyacinth (Boontum *et al.*, 2019) and rice straw (Li *et al.*, 2018).

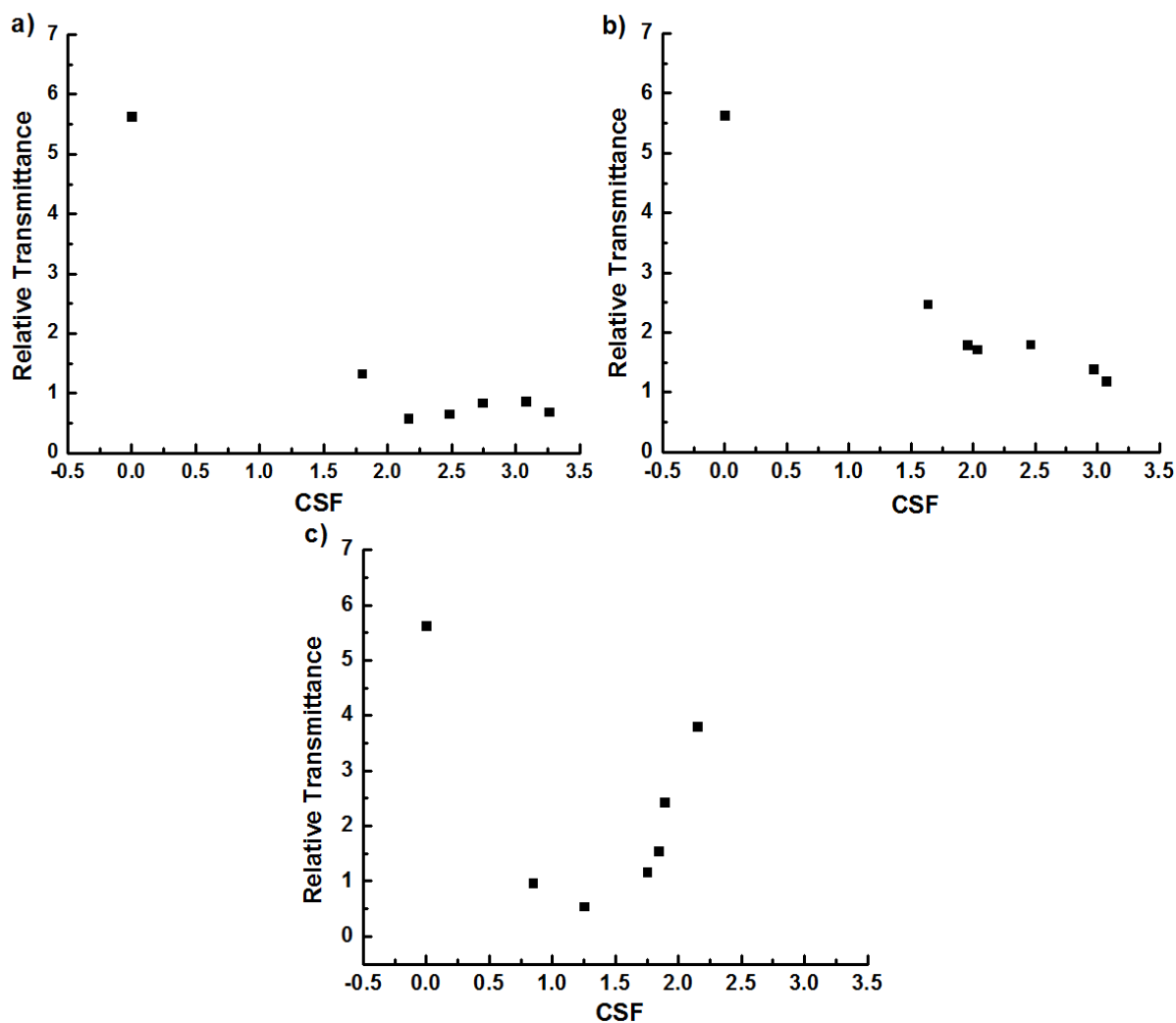


Fig. 8. Relationship between relative transmittance and CSF observe during hydrolysis of oat bagasse with a) hydrochloric, b) sulphuric and c) phosphoric acid.

As can be seen in Fig. 7, the main difference between FTIR spectra of oat bagasse hydrolysed with different inorganic acids was appreciated in the band located at  $1052\text{ cm}^{-1}$ , the highest and the lowest intensities of this band were observed in the samples of oat bagasse hydrolysed with hydrochloric and phosphoric acid respectively, this fact is related with the dissociation capacity and the catabolic power of the acids. Among all studied acids, hydrochloric acid was the most efficient option to hydrolyse polysaccharides and to degrade the obtained monomeric sugars into toxic compounds; however this acid resulted inefficient to remove lignin. On the other hand, FTIR spectra of oat bagasse hydrolysed with phosphoric acid suggested that this acid was capable

to solubilize both polysaccharides and lignin since the intensity of all vibrational bands associated to lignin diminished after acid hydrolysis. The relative absorbance term defined by (Pappas *et al.*, 2014) was adapted in this paper as relative transmittance and used to correlate the effect of different hydrolysis conditions in the form of CSF on the structural changes of oat bagasse. The relative transmittance was calculated as the ratio between the intensity of the characteristic vibration of hemicellulose at  $1735\text{ cm}^{-1}$  and the skeletal aromatic ring band of lignin at  $1510\text{ cm}^{-1}$ . From Fig. 8a can be appreciated that CSFs higher than 2 are associated to relative transmittance values lower than the unit, this is due to the rapid solubilization of hemicellulose caused by hydrochloric

acid maintaining lignin almost unaltered; in most of the analysed spectra of oat bagasse hydrolysed with hydrochloric acid the intensity of the lignin band was higher than the hemicellulose vibration.

Different behaviour was observed for sulphuric acid (Fig. 8b), where negative linear trend of relative transmittance as function of CSF was obtained, in this case the lowest relative transmittance values are around 1.20, thus sulphuric acid was efficient to solubilize hemicellulose but it was not able to decompose monomeric sugars and to remove lignin in high yields, which supports the sugars production observed in Fig. 2. Finally, Fig. 8c shows the behaviour of relative transmittance values as function of CSF obtained with phosphoric acid, the relative transmittances were near to the unit when CSF was in the range of 0.75 and 1.75, values greater than these generated a raise in relative transmittances which is mainly caused by the diminishing in the lignin band intensity. This fact suggests that phosphoric acid was efficient to hydrolysed hemicellulose at CSFs lower than 0.75 and to remove lignin at CSF higher than 1.75.

### 3.3.2 SEM analysis

The morphological changes in oat bagasse caused by acid hydrolysis were observed employing SEM technique. Raw oat bagasse showed a homogeneous, rigid and organized structure with low amount of

porous, moreover some microfibrils seems to be broken as a consequence of the mechanical milling (Fig. 9a). Microfibrils are organized in many layers, after acid hydrolysis these layers were disrupted and some microfibrils were broken increasing the porosity of the oat bagasse, behaviour that is related to the solubilisation of hemicellulose and extractives (Li *et al.*, 2018; Sahoo *et al.*, 2018). The highest amount of porous and holes were observed in the micrograph of oat bagasse hydrolysed with hydrochloric acid (Fig. 9b) which is attributed to its high catabolic power capable to disrupt lignocellulosic matrix and to remove hemicellulose increasing the surface area of the bagasse. Hydrolysis with sulphuric acid was the most efficient to produce reducing sugars, despite this the amount of porous observed in the surface of oat bagasse treated with this acid was lower to that observed with hydrochloric acid (Fig. 9c). In agreement to (Boontum *et al.*, 2019), sulphuric acid generated porous by the compression of carbohydrates which collapsed cellulose fibres and induced hemicellulose solubilization. Fig. 9d shows the SEM image of oat bagasse hydrolysed with phosphoric acid, the lowest amount of porous was observed in this micrograph. The small white particles detected in all micrographs can be related to the presence of chemical elements such as silicon ( $\text{SiO}_2$ ), aluminium and calcium (Gómora-Hernandez *et al.*, 2020).



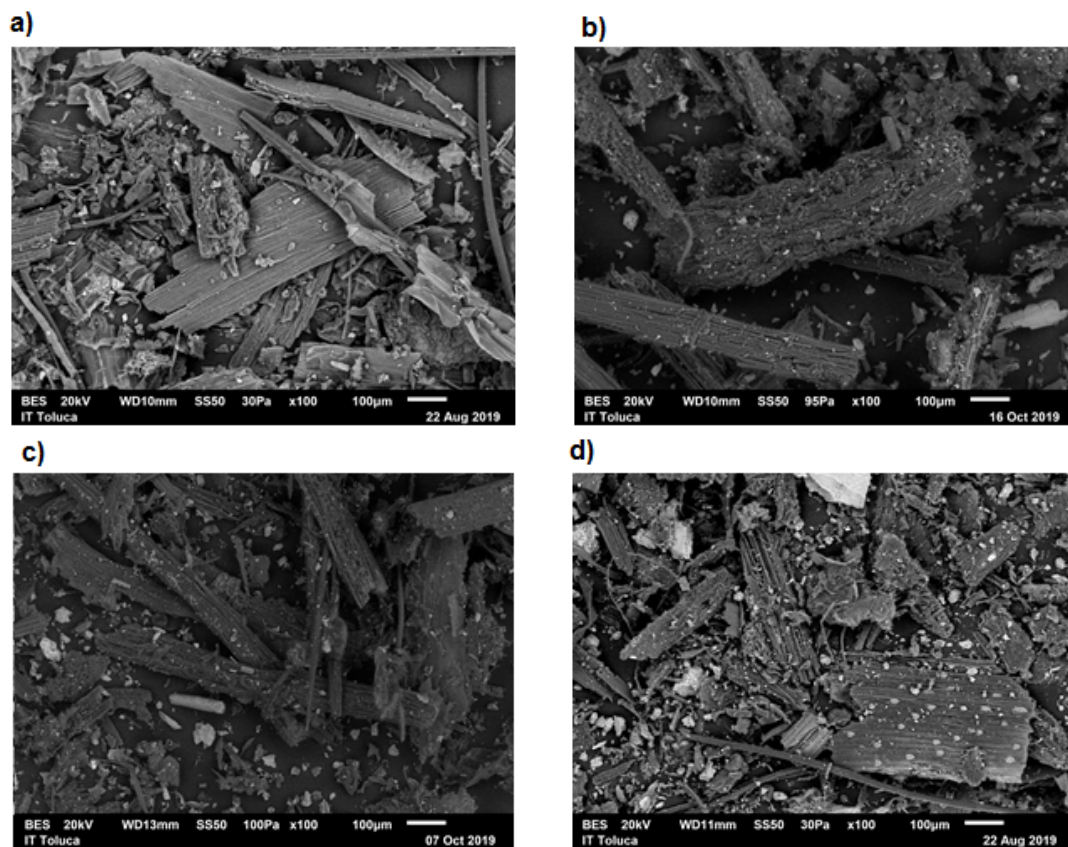


Fig. 9. Micrographs of a) raw oat bagasse and hydrolysed with b) hydrochloric, c) sulphuric and d) phosphoric acid at 110 °C and after 300 minutes reaction time.

### 3.4 Acid hydrolysis in biorefinery and potential uses of the obtained products

After acid hydrolysis different products were obtained; monomeric sugars, aldehydes and low molecular weight organic acids in liquid phase, and the remained solid comprised mainly by cellulose and non-solubilized compounds. Both liquid and solid phases have been used for producing a wide range of bio-based products of commercial and industrial interest such as biofuels, chemicals, enzymes, cellulose derivatives, adsorbent materials, among others. As seen in previous sections, the major component in hydrolysates was monomeric sugar. In the literature, there are some papers on the potential use of these sugars for either bioethanol (Nnaemeka *et al.*, 2021; Shokrkar *et al.*, 2017) or biohydrogen (Akobi *et al.*, 2017; Gómora-Hernández *et al.*, 2016) production, however, to improve energetic yield detoxification processes are usually needed before sugars fermentation. Gómora-Hernández *et al.*

(2016), achieved hydrogen yields of 0.52 and 0.33 mole hydrogen per mole hexose during mesophilic fermentation of corn cob and stem of faba bean hydrolysates. Considering the maximum sugar yield obtained in this work (42.77 g / 100 g oat bagasse) and a hydrogen yield of 0.52 mole hydrogen per mole hexose, a maximum hydrogen production of 2.8 L per 100 g oat bagasse could be expected. Another interesting fact; is the low furfural concentration in oat bagasse hydrolysate (1.22 g / L) which is close to the range reported by Muñoz-Páez *et al.* (2019) as non-inhibitory for hydrogen-producing microorganisms, thus oat bagasse acid hydrolysates could be fermented after neutralization process avoiding detoxification.

On the other hand; remained oat bagasse can be used as raw material for cellulose derivatives production by alkaline, oxidative, mechanical or combined processes. Microcrystalline cellulose is one of the most studied cellulose derivative, this material has interesting characteristics and has been used in the last decades for several sectors:



pharmaceutical, energy, textile, agro-industrial and food industry (Ventura-Cruz & Tecante, 2021). The common route employed to produce microcrystalline cellulose involves acid hydrolysis. Shao *et al.* (2020), showed the importance of acid hydrolysis during microcrystalline cellulose production from corn cob, the results obtained by them suggest that acid hydrolyzed material is a proper precursor to obtain crystalline and porous cellulose derivative with potential applications in environmental sector. In addition, due to the functional groups of cellulose and non-solubilized lignin some pollutants such as heavy metal cations can be removed from aqueous phase (Asencios *et al.*, 2022). Adsorption capacity can be improved by increasing material porosity, thus, remained oat bagasse could act as an efficient adsorbent material since SEM images previously described showed the formation of high amount of porous after hydrolysis.

The products obtained after hydrolysis have a wide range of possible applications from textile and food industries to biofuels production at large scale. One of the most important aims of acid hydrolysis is to serve as either direct or pretreatment method to produce monomeric sugars which are subsequently used for biofuels production. From this perspective, acid hydrolysis technology is a crucial step in biorefinery processes. Biorefinery is a novel term associated to a complete transformation of organic natural sources into several products of high economic value by using one or more of the following stages: mechanical milling, pretreatment, hydrolysis, saccharification, fermentation, separation and purification. Biorefinery is an analogy of the conventional refinery, where different products are synthesized from only one raw material (Pinales-Márquez *et al.*, 2021). The use of lignocellulosic biomass in biorefinery has become common, due to its abundance, low cost and the chemical structure which involves the presence of different macromolecules with peculiar features, however, despite the above mentioned, taking advantage of the complete structure of lignocelluloses is difficult due to its natural recalcitrance. In order to achieve green efficient processes for bio-based products production and to diminish the environmental impact and the global cost of the productive process, biorefinery adopts circular bioeconomy premises. Connection between biorefinery and circular bioeconomy implies the integration of technological, economic, social and environmental strategies focused in the maximum use of natural waste sources and their optimum

transformation into chemical products (Qin *et al.*, 2021).

The main products obtained during oat bagasse acid hydrolysis are monomeric sugars in hydrolysates and porous oat bagasse. In addition to these products, other compounds such as furfural and inorganic salts can be obtained. Furfural in hydrolysates is usually recovered by adsorption process employing activated carbon, while inorganic salts obtained after neutralization are recovered by precipitation. Magnesium phosphate and calcium sulfate are produced during phosphoric and sulfuric acid neutralization, both can be used as either nutritional supplement for the subsequent fermentation or as by-product of commercial interest (Gómora-Hernández *et al.*, 2016).

## Conclusions

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Oat bagasse was a suitable material for monomeric sugars production by long term acid hydrolysis. Sulphuric acid was the most efficient to produce reducing sugars diminishing the amount of furfural came from decomposition of pentoses, however, hydrochloric acid generated the major concentration of furfural and impacted considerably on the morphology of oat bagasse disrupting its structure and increasing the porosity. Sugars production data were well fitted to Saeman kinetic model and the obtained thermodynamic parameters revealed the non-spontaneous, endothermic and stable activated complex nature of the hydrolysis process being the sugar decomposition phase the most favoured reaction and furfural the most stable product. From FTIR analysis, most of the reducing sugars came mainly from hemicellulose however, cellulose and lignin fractions were also solubilized during acid hydrolysis. Phosphoric acid not only depolymerized carbohydrates but also showed potential to remove lignin at CSF values higher than 1.75.

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