Impact of Pre-extraction on Xylose Recovery from Two Lignocellulosic Agro-wastes

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A dilute acid hydrolysis of rice husk (RH), wheat straw (WS), and their extractive-free residues was investigated with the objective of recovering the highest yield of xylose while keeping at minimum its conversion into furfural. The hydrolysis conditions were determined for different concentrations of sulfuric acid and different reaction times at 121 °C. The pre-extraction with ethanol-water (1:1, v/v) was also examined as a parameter. Using response surface methodology, the optimum conditions for xylose production were identified as 1.8% of acid and 41.4 min of hydrolysis time for RH, while those for its counterpart EF-RH (extractives-free rice husks) were 1.0% acid concentration, for 60 min. The same conditions were also predicted for WS and its EF-WS. Under these conditions, the xylose yield was 79.6%, 82.8%, 94.3%, and 88.6% for RH, EF-RH, WS, and EF-RW, respectively. Under these conditions the minimal furfural yields obtained were 1.2% and 1.3% for RH and EF-RH, and 0.8% and 1.5%, for WS and EF-WS, respectively. These results suggested that the pre-extraction step before the acid hydrolysis affected, at least in part, the xylose recovery from RH, but it was not necessary for a better xylose yield of WS for its bioconversion into valuable bioproducts like xylitol.

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INTRODUCTION

The major concern associated with the use of petroleum and its derivatives to supply energy and raw materials for commodity products is its negative impact on the environment. Likewise, the petroleum source is limited, while its consumption leads to higher greenhouse gas emissions that contribute to global warming. Moreover, since the war in Ukraine, many developing countries have realized that their dependence on fossil fuels is a major geopolitical issue that places them in a week position in presence of petroleum-producing countries. Hence, there is considerable interest to accelerate the energy transition by promoting alternative and sustainable sources of carbon, which can provide chemical compounds and energy needs. Lignocellulosic biomass is the most abundant resource on earth and is mainly composed of cellulose, hemicelluloses, and lignins (Juhasz *et al.* 2005). As a renewable resource, lignocellulosic biomass has the potential to replace most petroleum-based chemicals (Moreira *et al.* 2011). Cellulose and hemicelluloses are polysaccharides, which can be hydrolysed to simple sugars that are fermentable into bioethanol. Lignins are phenolic polymers that can be used to produce, among other applications, biohydrogen and biomethane through gasification (Resende *et al.* 2008; Cao *et al.* 2021). However, the production of a renewable source of energy is not the only available application of lignocellulosic biomass. Cellulose can be extracted and modified to develop biomaterials with biomedical applications because of its biocompatibility (Hickey and Pelling 2019). Hemicelluloses can also be converted into biochemicals and biomaterials, while its monomers, such as xylose, can be recovered through pretreatment or hydrolysis for other applications (Ajao *et al.* 2018). Lignin is also identified as a valuable candidate for the production of hydrocarbons (benzene, toluene, *etc*.), simple phenols (vanillin, eugenol), polymeric macromolecules (carbon fiber and thermosets), nutraceuticals, drugs, and cosmetics (Cao *et al.* 2018; Sugiarto *et al.* 2021).

Lignocellulosic agro-wastes, such as rice husk and wheat straw, have high potentials to be valorized into value-added products. Since they are considered poor quality nutrients, they are either left in the fields, used in bedding, or burned (Li *et al.* 2008). Rice husk is a massive by-product from rice milling and contributes to 20 to 25 wt% of the dry weight of paddy rice (Yu *et al.* 2009). The worldwide production of milled rice in 2021 was about 518 million tonnes (FAO 2022), which generates about 130 to 173 million tonnes of rice husk globally. The chemical composition of rice husks is close to 25% hemicellulose, 22% lignin, 38% cellulose, 20% amorphous silica, and 2% other organic components (Zhang *et al.* 2014, 2015; Abaidea *et al.* 2019). Because of the substantial amount of cellulose and hemicelluloses present, most studies have focused on the comprehensive use of rice husks, primarily in terms of sugars production (Megawati *et al.* 2011; Zhang *et al.* 2015), bioethanol (Banerjee *et al.* 2009) or valorization of silica (Pandey *et al.* 2014).

Wheat straw is a by-product supplied in vast quantities annually from wheat harvest. Depending on the climate and wheat varieties, the straw produced is about 130 wt% of the weight of grain harvested (*i.e.*, 1.3 kg of straw per kg grain) (Ruiz e*t al.* 2011). The worldwide production of wheat in 2021 was about 770 million tonnes (FAO 2022). This implies an approximate annual production of 1000 million tonnes of wheat straw. The chemical composition of wheat straw varies, but it is typically composed of 21% to 28% hemicellulose, 11% to 23% lignin, 33% to 40% cellulose, 4% to 6% silica and silicates, and 7% to 10% ash (Khan and Mubeen 2012; Rajput *et al.* 2018). According to Makhatov *et al*. (2021), the hemicellulose content can reach up to 30 wt%, however the high density of wheat straw makes it difficult to use traditional technologies for its processing into xylose (or glucose) through hydrolysates for bio-alcohols formation. This high hemicellulos content, compared to other agro-residues (sugarcane bagasse, corn cob, corn stover, *etc*.), indicates the potential of this material for production of xylose, which may be used as a raw material for the production of xylitol. However, most studies reported that hemicelluloses are difficult to remove from the straw by hydrolysis. Generally, the residual hemicelluloses co-crystallize with cellulose and tend to remain in cellulose (Yang *et al.* 2011).

As a means to hydrolyze hemicellulose, such as xylan, to get access to xylose, a high amount of energy is required to break the C-O -C bonds (Dhepe 2010). Processes based on acids (Delfín-Ruíz *et al.* 2020), alkali (Khat-udomkiri *et al.* 2018), and enzymes (Hansen *et al.* 2011) do exist, but they often require optimization to effectively extract the hemicellulose Among these processes, acid hydrolysis is one of the oldest, simplest, and most efficient methods of producing xylose from biomass, which can use concentrated or dilute acid solutions. Several researchers have studied the dilute acid hydrolysis of different lignocellulosic wastes, such as corn stover (Lloy, 2005; Qin *et al.* 2012), eucalyptus residue (Canettieri *et al.* 2007), palm waste (Rahman *et al.* 2007), rapeseed straw (Castro *et al.* 2011; Jeong and Oh 2011; Lee and Jeffries 2011), wheat straw (Akpınar *et al.* 2012; Liavoga *et al.* 2007), rice husk (Dagnino *et al.* 2013; Zhang *et al.* 2010), and rice straw (Hsu *et al.* 2010; Kim *et al.* 2012; Lee and Jeffries 2011; Roberto *et al*. 2003). In fact, dilute acid hydrolysis is often useful when lignocellulosic biomass has a significant content of hemicellulose since the hemicellulose fraction is more easily hydrolyzed than cellulose (Lloyd and Wyman 2005). However, there are several disadvantages of the dilute acid hydrolysis of the lignocellulosic biomass, such as the production of inhibitors, including acetic acid, furfural (Panagiotopoulos *et al.* 2012) and phenolics from lignin degradation products (Akpınar *et al.* 2012; Temiz and Akpinar 2017). To this list, it is important to also add the production of extractives (notably free phenolics) released from lignocellulosic biomass during the hydrolysis process. The presence of these compounds is undesirable because they either decrease the purity or the production of xylose or inhibit its further microbial metabolism into different products. (Liu *et al.* 2012).

In the present work, the effect of pre-extraction treatments of rice husks and wheat straw, before the dilute acid hydrolysis, was investigated relative to the recovery of xylose. The pre-extraction consisted of removing extractives (phenolics, *etc.*), using ethanol-water (1:1, v/v) as solvent system, from rice husks and wheat straw. The pre-extraction could increase the porosity of both lignocellulosic agro-wastes and thus, through better penetrability of acid solution, it could improve the dilute acid hydrolysis of xylan into xylose. Moreover, application of the pre-extraction step was also investigated to evaluate the quality of the hydrolysed material for further conversion through the organosolv process applying the same pre-extraction step with ethanol-water (1:1, v/v) (Kasangana *et al.* 2020). In this study, the xylose and furfural yields were systematically determined under the various acid hydrolysis conditions of rice husks and wheat straw. The hydrolysis conditions, such as the concentration of sulfuric acid and the hydrolysis time, were optimized via response surface methodology. The extractive-free residues of rice husks and wheat straw were compared with their non-extracted counterparts. The major goal of this research was to achieve the maximal conversion of xylan hemicellulose, from rice husks and wheat straw, into xylose, while keeping at minimum its further acid conversion into furfural.

EXPERIMENTAL

Materials

The ground rice husks (RH) were obtained as a by-product of another project from the Department of Chemical Engineering. The RH powder was sieved with a sieve shaker (C. E. Tyler Rotap Sieve 3990 in Painesville, OH, USA) to keep only particles between 20- to 60-meshes. The particles were washed with distilled water and then oven-dried at 40 °C for 24 h prior to experiments. Wheat straw (WS) was purchased from a local producer (Saint-Augustin-de-Desmaures, Quebec, Canada). It was dried in an industrial wood dryer and cut into small pieces before storage in plastic bags at room temperature. Prior to the experiments, the wheat straw was grounded by a laboratory mill (Retsch ZM 100, Retsch, USA; Verder Scientific, Inc., Newtown, MA, USA) and sieved with an automatic sieve shaker (to pass through 20- to 60-mesh sieve) to obtain a similar particle size as with RH.

Methods

Chemical composition analysis

Before the acid hydrolysis of xylan in the samples, the chemical composition of RH and WS was determined according to the National Renewable Energy Laboratory (NREL) standard method (Sluiter *et al.* 2008).

Pre-extraction process

Pre-extraction was performed to remove the extractives from RH and WS materials and to evaluate its effect on the final xylan hydrolysis. A total of 100 g for each sample (RH and WS) was extracted with 1.0 L of an ethanol-water mixture (1:1, v/v) in a Soxhlet extractor at 80 °C for 6 h. After filtration, the extractive-free samples were dried in an oven at 40 °C for 48 h prior to analysis. Before the hydrolysis process, the moisture content of each sample was measured as reported by NREL standard method. The pre-extraction procedure is an integral step of the organosolv process, and it will be applied to the agro-wastes residues after hydrolysis (Kasangana *et al.* 2020).

Hydrolysis process

The hydrolysis of RH, WS, and their extractive-free counterparts (EF-RH and EF-WS) was performed in an autoclave at 121 °C and at constant pressure (15 psi). The solid-to-acid ratios were set at 1:10 for rice husk and at 1:20 for wheat straw because of its higher capacity to absorb water. The reaction was carried out under various sulfuric acid concentrations (1%, 2%, and 3%) and hydrolysis times (20, 40, and 60 min), according to the conditions reported in the central composite design matrix (Table 1). After a specified time, the resulting hydrolysate was cooled to room temperature, neutralized by the addition of $CaCO_3$, filtered through a syringe filter (0.45 μm), and stored at 4 °C prior to high performance liquid chromatography (HPLC) analysis.

Table 1. Range and Levels of Independent Process Variables Used in the Experimental Design

Variables	Symbol	Range and Levels		
		-1	0	1
Sulfuric acid concentration (%)	X_1	1	2	3
Hydrolysis time (min)	X_2	20	40	60

Analytical methods

Xylose in the acid hydrolysate was analyzed using an Agilent 1200 Series HPLC system (Agilent Technologies, Santa Clara, CA, USA), equipped with a Rezex RHM-Monosaccharide H+ 8% column (300 mm × 7.8 mm) and RI detector. Nanopure water was used as the mobile phase with a flow rate of 0.5 mL/min and the oven temperature was fixed at 75 °C. Furfural was analyzed by an Agilent 1100 Series HPLC system (Agilent Technologies, Santa Clara, CA, USA) using Zorbax SB-C18 column (250 mm × 4.6 mm, 5 μm) and its detection was done by diode-array detector (DAD) at 277 nm using a standard furfural solution. Furfural was eluted with a gradient of nanopure water and acetonitrile (95:5) mixture at a flow rate of 0.7 mL/min (Kasangana *et al.* 2020). All the experiments and analyses were conducted in duplicate. The mass yields of xylose and furfural were calculated based on the weight of xylan in each sample.

Statistical analysis and response surface methodology

Statistical analysis and the response surface regression were performed using Minitab 21.0 (Minitab, State College, PA, USA) software. The response surface methodology (RSM) was used for statistical data treatment and optimization of the hydrolysis conditions. A two-factor, three-level central composite design (Table 1) was selected to optimize the maximum xylose yield and minimum furfural yield in each hydrolysate by deriving a second-order polynomial equation (Eq. 1) and building response surface plots to predict result outcomes,

$$Y_{1,2} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{1,2} X_1 X_2 + \beta_{1,1} X_1^2 + \beta_{2,2} X_2^2 \qquad (1)$$

where β, Y, and X represent the regression coefficients, dependent, and independent variables, respectively. As mentioned above, the parameters investigated were sulfuric acid concentration (X_1), hydrolysis time (X_2), and the response variables were xylose (Y_1) and furfural (Y_2) concentrations, obtained through eighteen combinations. The matrix studied for the hydrolysis is shown in Table 3. The statistical significance of regression coefficients and effects was checked by analysis of variance (ANOVA).

RESULTS AND DISCUSSION

Compositional Analysis

The initial chemical compositional (cellulose, hemicellulose (pentosans), lignin, extractives, ashes contents) analysis of RH and WS were carried out before pre-extraction and acid-hydrolysis of each sample.

Table 2. Compositional Analyses of RS and WS

Chemical Composition	Rice Husk (RS)			Wheat Straw (WS)		
	This Study (%)	Ref. Study (%)	Reference	This Study (%)	Ref. Study (%)	References
Extractives	2	3	Al-Rubaia'ay and Shakir 2018; Sherif *et al.* 2021	7	4	Kabel *et al.* 2007; Nabarlatz *et al.* 2007; Carvalheiro *et al.* 2009
Cellulose	40	36-40	Sarkar and Aikat 2013; Al-Rubaia'ay and Shakir 2018	41	37 to 48	Al-Rubaia'ay and Shakir 2018; Saha et al. 2005; Ruiz *et al*. 2011
Lignin	25	17-24	Zhang *et al.* 2015; Sherif *et al.* 2021	24	14 to 25	Ruiz *et al.* 2011; Michelin and Teixeira 2016; Al-Rubaia'ay and Shakir 2018
Xylan	18	17-20	Megawati *et al.* 2011; Zhang *et al.* 2020	25	18 to 24	Saha *et al.* 2005; Kabel *et al.* 2007; Nabarlatz *et al.* 2007; Carvalheiro *et al.* 2009; Ruiz *et al.* 2011
Ash	16	12	Chen *et al.* 2013; Al-Rubaia'ay and Shakir 2018	2	1.6 to 10	Carvalheiro *et al.* 2005; Al-Rubaia'ay and Shakir 2018

Table 2 shows that the extractive content of RH (2%) was lower than that of WS (7%), while its ash content (16%) was substantially higher than that of WS (2%). RH is well known as being rich in amorphous silica, the contents of which range between 15 and 25 wt% (Chen *et al.* 2013; Temiz and Akpinar 2017). According to Carvalheiro *et al.* (2009), the high content of extractives in WS might be partially explained by the presence of proteins that can constitute approximately 5 wt% of the material.

The contents of cellulose and Klason lignin were similar in both lignocellulosic agro-wastes. The lignin content in WS seemed somewhat higher in comparison with values generally reported in the literature, but close to those reported by Kabel *et al.* (2007) and by Michelin and Teixeira (2016). In terms of hemicellulose, its content in WS was found to be higher than that of RH, but it was in general agreement with those reported in the literature (Megawati *et al.* 2011; Al-Rubaia'ay and Shakir 2018). It is important to highlight that the chemical composition of RH and WS can be expected to vary depending on their variety, climate, and the geographic location (Carvalheiro *et al.* 2009; Ji *et al.* 2017).

Limit Values of Xylose and Furfural

The efficiency of hemicelluloses hydrolysis of various lignocellulosic biomass for recovering the maximum sugar yield or sugar degradation products depends on the type of material and the processing conditions (Rahman *et al.* 2007). In this work, under the range of conditions selected, *i.e.*, sulfuric acid concentration (1%, 2%, and 3%) and hydrolysis time (20 min, 40 min, and 60 min), a series of hydrolysis experiments were conducted on RH and WS, as well as using their extractive-free residues (EF-RS and EF-WS, respectively) at constant temperature (121 °C). The yields of xylose and furfural under the different conditions are also reported in Table 3.

Table 3. Hydrolysis Conditions, Experimental Design, and Results Obtained by Dilute Acid Hydrolysis of RH and WS and their Extractive-Free Residues

Run Number	Acid (wt%)	Time (min)	RH		EF-RH		WS		EF-WS	
			Xylose (%)	Furfural (%)	Xylose (%)	Furfural (%)	Xylose (%)	Furfural (%)	Xylose (%)	Furfural (%)
1	1	20	63.5	0.8	61.2	0.2	60.7	0.4	70.6	0.4
2	3	20	72.4	1.5	73.0	1.4	80.7	1.7	79.5	1.7
3	1	60	78.8	1.7	83.3	1.3	91.2	0.9	89.0	1.7
4	3	60	77.1	2.9	78.4	3.3	84.1	3.7	83.7	3.9
5	1	40	72.6	1.0	74.9	0.8	81.6	0.8	81.9	1.0
6	3	40	75.3	2.3	77.5	2.6	84.3	2.9	83.6	3.2
7	2	20	71.1	0.6	73.3	0.9	52.7	0.5	80.2	1.1
8	2	60	87.8	2.2	87.3	2.4	91.1	1.6	91.1	2.9
9	2	40	79.9	1.4	81.9	1.9	83.3	1.2	86.7	2.3
10	1	20	63.4	0.6	60.8	0.2	59.3	0.2	69.2	0.4
11	3	20	72.2	1.4	72.8	1.4	79.7	1.6	79.5	1.7
12	1	60	78.4	1.7	81.9	1.3	91.1	0.9	88.4	1.3
13	3	60	76.7	2.9	77.4	3.2	84.1	3.7	82.7	3.8
14	1	40	71.8	1.0	74.5	0.8	80.0	0.8	81.3	1.0
15	3	40	74.9	2.3	76.9	2.6	84.3	2.9	83.5	3.2
16	2	20	70.9	0.6	72.9	0.9	52.1	0.3	80.0	1.1
17	2	60	87.4	2.2	85.5	2.4	90.7	1.4	89.9	2.9
18	2	40	79.1	1.2	81.5	1.9	82.3	1.1	86.5	2.3

For all the conditions studied, the xylose yield increased with the acid concentration in the initial stages of hydrolysis, and then it declined after the xylose yield reached its maximum value. For RH, the maximum xylose concentration 87.8% was reached when 2% of acid was used for 60 min of hydrolysis time. For the same duration, the maximum furfural yield reached 2.9% with 77.1% of xylose yield for 3% of acid solution. This behavior indicates that the furfural concentration increased with process severity (*i.e.*, increase in acid concentration or hydrolysis time), which eventually reduced the xylose yield. In contrast, the maximum xylose yield for EF-RH (87.3%) was close to that of RH (87.8%) under the same conditions. However, a difference was observed in terms of furfural production, which was somewhat lower for RH (2.2%) than for ER-RH (2.4%).

Table 3 also reports the same trend for WS and ER-WS. Nevertheless, it was observed that under the same processing conditions (1% acid for 60 min), the same xylose yield (91.1%) was obtained from both samples. Nevertheless, the furfural yield under the same conditions was completely different between both samples. This indicates that the hydrolysis of WS might not be completed under these conditions and some xylose remained in WS, which would need more time to be extracted due to the presence of extractives delaying the hydrolysis reaction.

Statistical Modelling and Validation

The effect of sulfuric acid concentration and hydrolysis time on the yields of xylose and furfural were evaluated using regression analysis. The equations (Supporting data, Eqs. 2 through 9) were generated based on the outcomes of the regression analysis.

Table 4 reports that the Model F-values for xylose yield (Y_1, Y_3) and furfural yield (Y_2, Y_4) from RH and its EF-RH were significant at the 95% confidence level. Although not perfect, the determination coefficients (R^2) for Y_1 and Y_2 were in the 0.90 to 0.99 range, implying that 90% to 99% of the variability in the response could be well explained by the model. The Adj. R^2 values of both were also higher or equal to 90%, which illustrates that the model fit well. The significance of each variable and their interaction was evaluated using the *P*-value. In both cases, the individual variables (X_1 and X_2), their interaction ($X_1 X_2$), and quadratic effect (X_1^2 and X_2^2) were all significant, but the quadratic effect (X_2^2) of RH was not significant because the P-values of both models (Y_1 and Y_2) were greater than 0.05. This suggests that the effectiveness of xylan conversion into xylose and its degradation into furfural were mainly affected by the acid concentration and reaction time as an individual factor. For RH, this indicates that xylose and furfural yields did not always substantially increase with the hydrolysis time.

Table 4 presents the results of the ANOVA analysis for xylose (Y_5, Y_7) and furfural (Y_6, Y_8) yields for WS and EF-WS. In all cases, the model was statistically significant, as shown by the higher F value and lower P-value (< 0.0001). The goodness of fit of each model was also examined by the determination coefficient (R^2 between 0.90 and 0.99), which implied that the sample variation of 90% to 99% was attributable to the variables, thus confirming the significance of each model. In terms of the significance of each variable and their interaction, X_1, X_2, $X_1 X_2$, X_1^2, and X_2^2 were significant of all models except for Y_5 for which X_1 and X_1X_1 were not significant. This indicates that the acid concentration (X_1) did not strongly affect the hydrolysis of xylan to xylose. Meanwhile, the increased yield of xylose was attributed to the interactive effect of variables X_1X_2 (acid concentration and hydrolysis time) because this interaction had an important effect ($P < 0.004$).

Table 4. Analysis of Variance of Xylose Yield and Furfural Yield for RH, WS, and their Extractive-Free Residues (EF-RH and EF-WS)

	RH				EF-RH				WS				EF-WS			
Source[a]	F value		ProbF		F value		Prob > F		F value		Prob > F		F value		Prob > F	
	Y1	Y2	Y1	Y2	Y3	Y4	Y3	Y4	Y5	Y6	Y5	Y6	Y7	Y8	Y7	Y8
Model	52.5	101.2	0	0	453.9	746.4	0	0	17.1	598.9	0	0	367.4	280.6	0	0
X_1	12.9	184.9	0.004	0	82.4	1997.8	0	0	3.2	1888.0	0.101	0	38.4	764.5	0	0
X_2	167.5	293.6	0	0	1393.8	1622.3	0	0	61.5	659.6	0	0	1123.9	575.5	0	0
X_1	59.9	22	0	0.001	380.3	13.6	0	0.003	3.0	261.5	0.106	0	270.7	6.8	0	0.023
X_2 X_2	0.6	0.4	0.45	0.555	51.6	35.1	0	0	5.2	30.6	0.041	0	46.0	21.2	0	0.001
X_1 X_2	21.3	5.2	0.001	0.043	361.9	63.2	0	0	12.6	155.1	0.004	0	357.9	34.8	0	0
Lack-of-Fit	91.4	13.3	0	0.001	0.8	60.8	0.531	0	296.7	2.3	0	0.151	1.43	2.8	0.297	0.1
R^2 (%)	95.6	97.7			99.5	99.6			87.7	99.6			99.4	99.1		
AdjR2 (%)	93.8	96.7			99.5	99.5			82.6	99.6			99.1	98.8		

[a] where Y_1, Y_3, Y_5, and Y_7 represent the xylose yields and Y_2, Y_4, Y_6, and Y_8 represent the furfural yields as a function of acid concentration (X_1) and reaction time (X_2)

Pre-Extraction Effect Based on Response Surface Methodology

RSM was used to find the optimal conditions for the maximum release of xylose from RH, WS, and their extractive-free counterparts using sulfuric acid with minimal furfural formation (Figs. 1 and 2). The high furfural yield indicates that the xylose produced from xylan was highly dehydrated during the hydrolysis process. Additionally, the presence of furfural (an aromatic compound) in hydrolysate causes problems related to the inhibition of further fermentation of sugars (xylose or glucose) into different products such as xylitol (Karimi *et al.* 2006; Temiz and Akpinar 2017). However, the furfural alone is not a potential inhibitor of the microbial mechanism during xylitol production. Several studies have shown that the glucose level in the xylose-based fermentation of hydrolysate is another important parameter that should be examined because of its adverse effect on the bioconversion of xylose into other chemicals such as xylitol and bioethanol (Roberto *et al.* 2003; Zhang *et al.* 2015; Delfín-Ruíz *et al.* 2020). It is also the main cause of the reduced selectivity in the liquid hydrolysate. The present study did not determine the selectivity factor (xylose/glucose ratio) of each hydrolysate, but examined the optimal conditions to minimize the furfural yield in the hydrolysate, which can also provide more information about the efficiency of xylan hydrolysis (Temiz and Akpinar 2017).

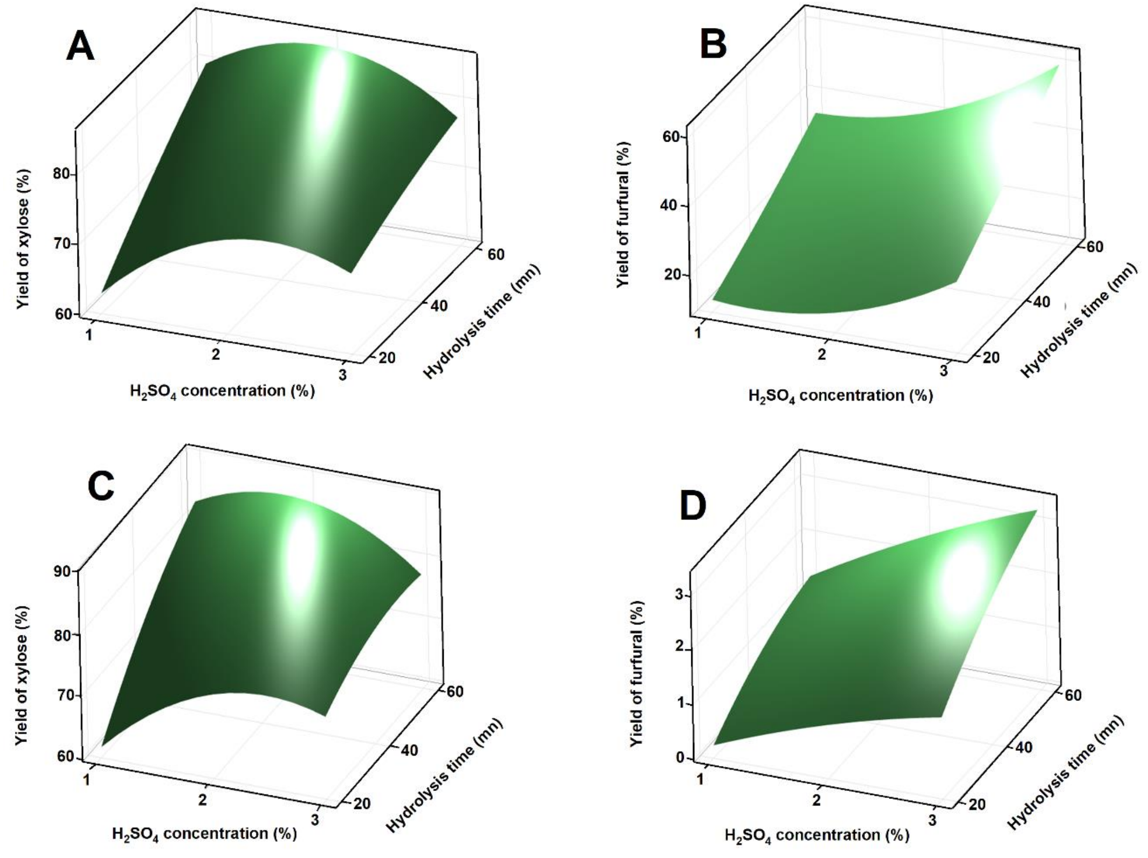

Fig. 1. Response surface obtained from the optimization of hydrolysis of lignocellulosic agro-wastes, where A and C correspond to the optimization of the maximum xylose concentration in RH and EF-RH, respectively; B and D correspond to the optimization of minimum furfural concentration in RH and EF-RH, respectively

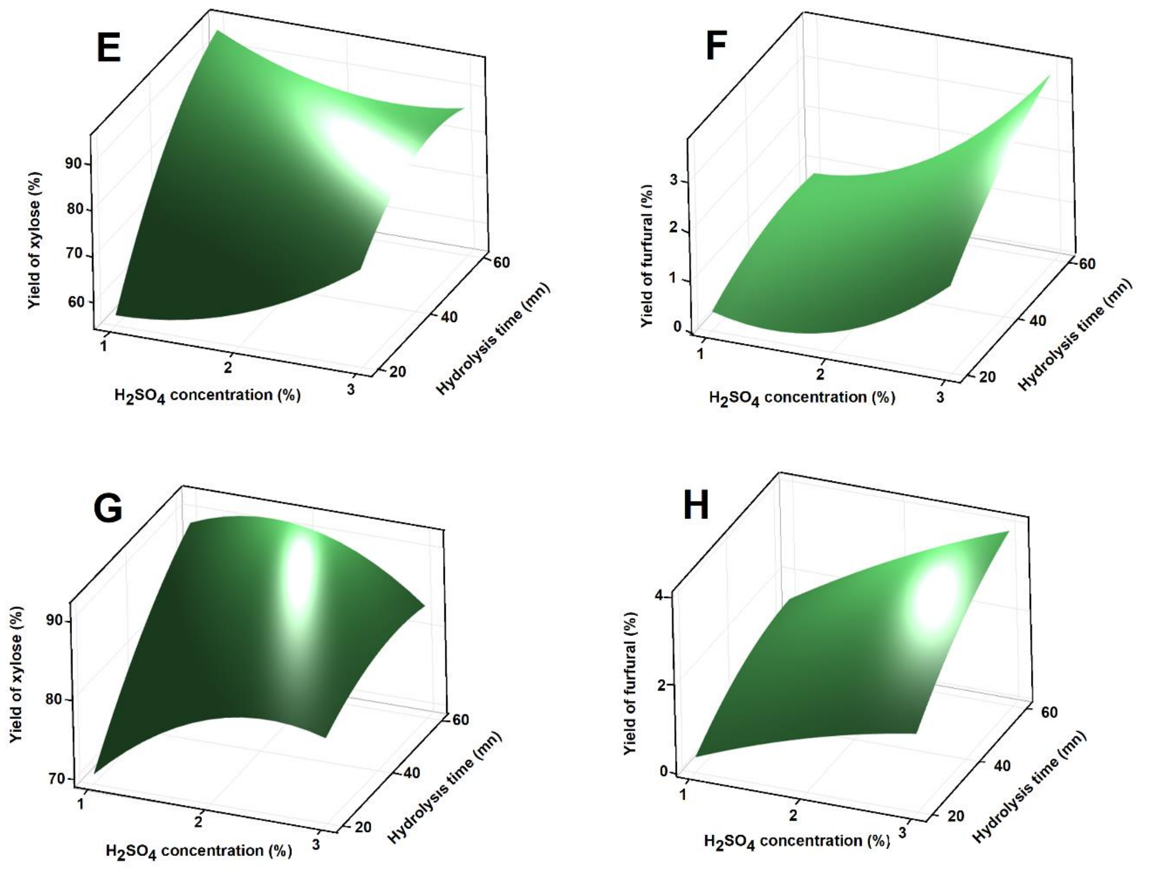

Fig. 2. Response surface obtained from the optimization of hydrolysis of lignocellulosic agro-wastes, where E and F correspond to the optimization of the maximum xylose concentration in WS and EF-WS, respectively; G and H correspond to the optimization of minimum furfural concentration in WS and EF-WS, respectively

Table 5. Results of Hydrolysis Done at Optimum Conditions

	RH	EF-RH	WS	EF-RH
Optimum hydrolysis conditions	1.8% acid, 41.4 min	1% acid, 60 min	1% acid, 60 min	1% acid, 60 min
Xylose yield (predicted, %)	79.6	73	80.7	79.5
Xylose (actual, %)	78.8	83.3	91.2	89
Furfural (predicted, %)	77.1	78.4	84.1	83.7
Furfural (actual, %)	72.6	74.9	81.6	81.9

As illustrated in Table 5, the optimum conditions for the xylose yield of RH at 121 °C were predicted based on the regression equations (Supporting Data, Eqs. 2 to 9) as 1.8% of acid concentration and 41.4 min as hydrolysis time. Under these conditions, the xylose and furfural yields were 79.6% and 1.3%, respectively. To validate these predicted values of the model, an experiment was performed on RH under the established optimal conditions. The obtained xylose yield (80.8 ± 2.9%) was in good agreement with the predicted model value (79.6%), while the furfural yield exhibited a lower value (0.20 ±

0.06% *vs.* 1.3%), which corresponded to a minimum yield of furfural desired for this study. Furthermore, the xylose yield obtained from RH was similar to that reported by Karimi *et al.* (2006), but lower than what was reported by Temiz and Akpinar (2017), who treated RH at 127 °C with 2.6% H_2SO_4 for 60 min and achieved a xylose yield and furfural yield of 87.7% and 0.5%, respectively.

In contrast, the xylose yield of RH was slightly lower than that of EF-HS, which produced 82% of xylose yield and 1.3% of furfural yield, under the optimal conditions of 1% acid for 60 min. Although the yield difference (79.6% *vs.* 82.0%) was not important, it reveals the effect of extractives on xylose yield during the hydrolysis of xylan. One of the extractive groups mentioned in various studies is the phenolic group (sometimes originating from lignin degradation), acting as an inhibitor of the xylan acid hydrolysis. Besides these extractives, it is well known that RH contains a high concentration of silica. The study of Khaleghian *et al.* (2017) revealed that removing the silica from rice straw improved the xylan hydrolysis and ethanol production. In contrast, the yields of furfural were almost the same in RH and EF-RH, which confirms that the hydrolysis of RH was more affected by the acid concentration than by the hydrolysis time, while EF-RH was significantly affected by both variables, which is consistent with the ANOVA analysis presented in Table 4.

Regarding the results of WS and EF-WS reported in Table 5, RSM predicted the same optimal reaction conditions for the recovery of xylose at 121 °C as 1% acid for 60 min. Under these conditions, the WS presented a xylose yield of 94.3% with 0.8% for furfural, while EF-WS gave 88.7% of xylose yield with 1.5% for furfural. This predicted yield of xylose and furfural was in good agreement with that experimentally obtained under the same conditions and is reported in Table 3 (run number 12). Furthermore, in both cases, the xylose yield was higher than that reported by others such as Makhatov *et al.* (2021), who achieved a xylose yield of 75% to 77% at a H_2SO_4 concentration of 2 to 3 wt% for 5 h. However, Ji *et al.* (2017) and Ranganathan *et al.* (1985) found that autoclaving WS at 140 to 210 °C with 0.5% to 1.5% acid produced 80% to 95% xylose. In contrast with RH and EF-RH, these results showed that the presence of extractives in WS improved the xylose yield, while its absence had a negative effect. In this case, the explanation is easier to provide because both yields were achieved under the same optimal conditions. These results can be justified when referring to studies on the chemical composition of the WS hydrolysate in terms of phenolic compound amounts released extractives or by lignin degradation. It is well known that acid hydrolysis process not only breaks down the hemicellulose to monosaccharides, but it also cleaves some of the β-0-4 alkyl-aryl linkages in lignin and lignin-hemicellulose linkages to form soluble phenolic compounds (Akpinar *et al.* 2012; Garrote *et al.* 2004; Nabarlatz *et al.* 2007). Lignin is either covalently linked to polysaccharides via sugar residues, or phenolic acids esterify to polysaccharides. Although most of the lignin is acid-insoluble (Klason lignin), a part of it can be solubilized in acidic media (acid-soluble lignin). Therefore, while hot water can extract the free phenolic acids, acid hydrolysis can release simple esterified phenolic acids. Apkima *et al.* 2012 reported that under various conditions (for instance, 120 °C, 45 min and 4.7% acid concentration), the esterified ferulic acids yield in WS hydrolysate was higher than free ferulic acids yield, which confirmed the highest antioxidant characteristics of esterified ferulic acids (Akpinar *et al.* 2012). Moreover, the yield in phenolic compounds, including free and esterified ferulic acid, was not affected significantly by the sulfuric acid concentration and the reaction time used in the acid hydrolysis stage, but was strongly affected by the temperature. When the overall xylose yield and phenolic content of the acid hydrolysate of wheat straw were compared with those obtained from previous studies carried out for the production of xylose (Akpınar *et al.* 2012; Roberto *et al.* 2003) and phenolic compounds (Moure *et al.* 2008) from lignocellulosic materials with acid hydrolysis, it was found that the xylose yield and the phenolic contents were similar. Therefore, the results of this study could also suggest that phenolic compounds originated from lignin degradation in EF-WS negatively impacted its xylose production. In terms of furfural formation, the absence of extractives promoted the reaction of xylose degradation into furfural, while their presence delayed it. Similarly, both Al-Rubaia'ay and Shakir (2018) and Torget *et al*. (1991) reported that xylose is typically more sensitive to degradation to furfural, especially at acid concentrations over 1% and reaction temperature above 120 °C. Moreover, the difference in furfural content showed that the hydrolysis of EF-WS was more affected by the acid concentration, which promoted xylose degradation and therefore decreased its yield, while WS was mainly affected by the hydrolysis time to achieve higher xylose yield.

CONCLUSIONS

1. For a constant temperature of 121 °C, the optimal processing conditions to achieve maximum xylose yield and minimum furfural yield were 1.8% of sulphuric acid and 41.4 min of hydrolysis time, respectively for rice husk (RH), while the conditions for the pre-extracted wheat straw (EF-WS) were 1% of acid for 60 min. The same conditions were obtained for WS and its EF-WS counterpart.
2. The validation experiments were performed on RH, WS, and their extractive-free counterparts under optimal conditions. The experimental yields were in agreement with the predicted model values, except for the furfural yield of RH, which showed a lower value (0.20 ± 0.06% *vs.* 1.3%), but corresponded to a minimum yield of furfural desired for this study.
3. The parameters affecting the xylose yield from the acid hydrolysis of RH, WS, and their extractive-free counterparts were mainly the reaction time followed by acid concentration.
4. The pre-extraction of RH was favorable to optimal yield of xylose with the lowest yield of furfural during the acid-hydrolysis of rice husks, which was not the case for the hydrolysis of WS, from which a higher xylose yield was achieved than from its extractive-free counterpart under the same hydrolysis conditions.

5. From all the results obtained, the pre-extraction step differently affected two lignocellulosic agro-wastes and, therefore, this effect depends on the type of biomass. In this study, the pre-extraction step was favorable to the better penetration of acid solution into the compact structure of RH, which enhanced the hydrolysis and thus contributed to the high xylose yield that is available for the further conversion processes. In contrast, the result from WS and EF-WS indicates that under the same optimal conditions, the presence of extractives was not harmful, and the pre- extraction was not favorable as was the case for rice husks.

Conflicts of Interest

There are no conflicts to declare.

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