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OBTAINING XYLITOL BY HYDROLYSIS-HYDROGENATION OF LIQUORS DERIVED FROM SUGARCANE BAGASSE

Article Highlights
- Acid hydrolysis was carried out using an RCT275 sulfonated resin and sulfuric acid as reference
- RCT275 was suitable for hydrolysis, avoiding the presence of sulfur traces in liquors
- The maximum xylose yield was 82% using the RCT275 under mild conditions
- Ni/γ-Al$_2$O$_3$ reached total xylose conversion with selectivity towards xylitol of 100%
- RCT275 and Ni/γ-Al$_2$O$_3$ can be easily separated and reused in several reaction cycles

Abstract

This work presents the study of heterogeneous catalysis of sugarcane bagasse hydrothermal treatment spent liquors using a sulfonated resin. Besides, results were compared with those obtained by a conventional route using sulfuric acid as a homogeneous catalyst. Heterogeneous catalysis is suitable for the hydrolysis of sugarcane bagasse hydrothermal liquors under mild conditions (100 °C and 6 h). The obtained maximum xylose yield was 82% due to furfural formation, which causes a xylose selectivity drop. The hydrogenation of this xylose-rich liquor at 100 °C and 3 MPa of hydrogen pressure employing a supported Ni/γ-Al$_2$O$_3$ produced the total conversion of xylose with a selectivity towards xylitol of 100% by using a catalyst to xylose mass ratio of 0.5. Heterogeneous catalysis in a two-step route (hydrolysis and hydrogenation) constitutes an outstanding alternative to producing xylitol from sugarcane bagasse hydrothermal spent liquors since materials can be easily separated and reused in several reaction cycles.

Keywords: sugarcane bagasse, hydrolysis, hydrogenation, xylose, xylitol.

Lignocellulosic materials constitute one of the most abundant biomass residues, which have recently gained interest. Its use as a raw material in biorefineries would allow obtaining fuels, energy, and high added-value bio-products [1-3]. These materials can come from agricultural residues, such as rice husk, corn stubble, and sugarcane bagasse, and have the advantage of not requiring extra resources such as water, land, or energy to be produced. In 2018, global sugarcane production was approximately 1.9 billion tons. About 40% of the world's sugarcane was produced in South America (about 0.8 billion tons in 2018) [4]. Sugarcane bagasse is a renewable and abundant lignocellulosic waste with a high xylans content, which gives it enormous potential industrial with a wide range of applications. The amount of bagasse obtained from sugarcane depends on the fiber content, the cane variety, the plants' physiological state, and the technology available for harvesting [3,5]. Generally, about 30% of the ground cane is transformed into bagasse, which is composed of cellulose (35–43%), lignin (21–23%), hemicelluloses (25–32%), and soluble organic and inorganic compounds called extractives (2–11%), [3,5].

The structural complexity of lignocellulosic materials requires a pretreatment to fractionate their

major components [3,6,7]. Autohydrolysis in an aqueous medium as pretreatment allows the disaggregation of lignin-carbohydrate complexes, altering the physical properties of the fiber and facilitating the extraction of hemicelluloses [3,6,8]. The protons generated by the autoionization of water catalyze the hydrolysis of hemicelluloses, producing acetic acid as a by-product. Then, the acid medium allows the generation of oligosaccharides and monosaccharides. Lignin is also degraded and causes a sharp increase in hydroxyphenyl compounds [3,9]. Depending on the raw material and used conditions, about two-thirds of lignin and one-quarter of cellulose can be dissolved at this stage [8]. The soluble fraction, rich in hemicelluloses (liquor), is separated from the solid residue composed of cellulose and lignin at the end of the autohydrolysis.

The next stage of liquor treatment is homogeneous hydrolysis, which aims to extract the component sugars from the hemicelluloses. Generally, it is carried out in the presence of acids (H_2SO_4, HCl, H_3PO_4, organic acids) or alkalis (NaOH, Ca(OH)$_2$, KOH, hydrazine, NH_3). Among these options, treatment with H_2SO_4 (0.4–4 wt.%) at high temperatures (120–200°C) is one of the most widely used since it allows recovery of 80–90% of the sugars from hemicelluloses but presents the disadvantage of causing the degradation of sugars to furfural and HMF, phenolic acids and aldehydes, levulinic acid and other aliphatic compounds [8,10,11]. In addition, this treatment requires an acid neutralization step and subsequent concentration by water evaporation [5,6,10,12–14].

Heterogeneous hydrolysis is proposed as a possible alternative to reduce the environmental impact and facilitate the separation and reuse of the catalyst [15–25]. The hydrolysis of hemicelluloses is influenced by their structures, the conformation of their sugar units, and the type of catalyst acid sites, among others [18].

There are numerous studies on the heterogeneous hydrolysis of cellulose, whereas very few have studied the heterogeneous hydrolysis of hemicelluloses. A range of zeolites, resins, carbonaceous acid materials, functionalized silicas, metal oxides, and acidified clays have been used to hydrolyze hardwood and softwood hemicelluloses [15–25].

Xylose obtained from hemicelluloses hydrolysis is of particular interest because their hydrogenation leads to xylitol. Xylitol is a polyalcohol used as a sugar substitute for the consumption of diabetics and has anti-caries and anti-carcinogenic properties, among others [11,26–28]. The production and quality of xylitol depend on xylose purity. Xylitol can be obtained biotechnologically using specific microorganisms.

However, the process is affected by multiple factors, such as the initial concentration of inoculum, type of substrate, temperature, pH, transfer of oxygen, and culture medium composition. When using lignocellulosic hydrolyzates as xylose sources, several purification steps are required to remove all compounds that inhibit the metabolism and growth of the microorganisms [5,8,10].

Xylose hydrogenation has been studied using metallic catalysts based on Pt, Pd, Ru, Ni, and Ni-Raney, in the range of 80–140°C and hydrogen pressures greater than 5 MPa [11, 26,27,29]. Lee *et al.* [29] studied the hydrogenation of xylose in the aqueous phase at 100 °C and 5.5 MPa with Pt, Pd, Ru, Co, and Ni catalysts supported on γ-Al$_2$O$_3$. In all cases, xylitol was the only product obtained, following the activity order Ru> Ni ~ Co> Pt> Rh ~ Pd [29]. The same order was obtained by Wisniak *et al.* [30] using Rh, Ru, and Pd catalysts supported on activated carbon.

This research aimed to evaluate the hydrolysis of spent liquor from sugarcane bagasse hydrothermal treatment and its subsequent hydrogenation to obtain xylitol. Hydrolysis was studied using a solid acid catalyst (commercial sulfonated resin). The work consisted of producing a liquor rich in xylose, comparing it with one obtained by the homogeneous catalysis path, and determining the conditions of the heterogeneous route that o generates the maximum xylose yield. In the subsequent hydrogenation reaction to obtain xylitol, the hydrogenating activity of a Ni catalyst supported on γ-Al$_2$O$_3$ was studied. The overall yield of xylitol production by heterogeneous catalysis in two stages and the possibility of reusing and (or) regenerating the studied catalysts were analyzed.

MATERIAL AND METHODS

Catalyst

For the hydrolysis reaction, a commercial Purolite CT-275 resin was used, a macroporous strongly acid cation resin called RCT275, with a sulfonic acid as a functional group, and an acid amount of 5.2 mmol g^{-1}. For the hydrogenation of the hydrolyzed liquors, a Ni catalyst supported on γ-Al$_2$O$_3$ was prepared by incipient wetness impregnation, using an aqueous solution containing a metal precursor Ni(NO$_3$)$_2$ x 6H$_2$O to obtain 10 wt.% of Ni in the final solid. The solid was dried at 105 °C for 12 h and activated in H$_2$ flow (50 cm^3 min^{-1}) at 550 °C for 2 h (10 °C min^{-1}). The γ-Al$_2$O$_3$ support was prepared by thermal treatment of Al(OH)$_3$, which was directly calcined (without a heating ramp) at 600 °C for 30 min in the air atmosphere.

Ni-Raney was activated according to the procedure described by Devred *et al.* [31], employing

Ni-Al alloy (50 wt.% Ni) and NaOH (20 wt.%) solution at 80 °C for 3 h was used as a reference of a hydrogenation catalyst. First, the obtained solid was washed with distilled water until neutrality to remove the remaining NaOH.

Catalyst characterization

Adsorption-desorption measurements were performed for textural characterization. Surface area measurements, the Brunauer-Emmett-Teller (BET) multipoint method, and textural analysis were obtained using Micromeritics ASAP 2020 equipment. The samples were pretreated under vacuum in two stages of 1 h each, at 100 °C and 300 °C.

The acid-base properties of the solids were determined by the test of isopropanol decomposition (IPA). This reaction was tested in a continuous-flow fixed-bed reactor between 70 and 350 °C, atmospheric pressure, feed 4.5% IPA in Helium, with a flow of 40 cm^3 min^{-1}.

Potentiometric titrations were performed with 0.05 g of support suspended in acetonitrile (Merck) and stirred for 3 h. Then, the suspension was titrated with 0.05 mol L^{-1} n-butylamine (Carlo Erba) in acetonitrile using a Metrohm 794 Basic Titrino apparatus with a double junction electrode.

The Ni/γ-Al_2O_3 catalyst was characterized by atomic absorption spectrometry (AA), X-ray diffraction (XRD), temperature-programmed reduction (TPR), and transmission electron microscopy (TEM). Experimental details are attached as Supplementary data.

Obtaining and characterizing liquors

The sugarcane bagasse was supplied by the San Javier Mill, located in Misiones province, Argentina. This bagasse was collected, demodulated, and subjected to an autohydrolysis treatment. Autohydrolysis was performed in water at 180 °C for 20 min in a reactor heated with direct steam without stirring using a 7:1 (liquid: solid) ratio. These reaction conditions produce an autohydrolysis liquor with the maximum xylans concentration and the minimum formation of sugar degradation products such as furfural or HMF [9]. The liquors obtained from this treatment were vacuum-concentrated and were called Liquors A.

A subsequent acid hydrolysis step allows obtaining the so-called Liquors B. Heterogeneous acid hydrolysis was performed using the solid catalyst RCT275 resin in a 100 cm^3 reactor (Berghof Instruments BR-100) operated in batch mode, using catalyst/polymers mass ratios of 0.65 to 1.3, corresponding to an acid sites concentration of 0.52

and 1.04 mol L^{-1}, respectively. The obtained liquors were called liquor B1-4 and B1-6.

Homogeneous acid hydrolysis was performed under the optimum conditions using a 1 wt.% H_2SO_4 solution at 120 °C for 1 h (Liquor B2) [14]. Sulfuric acid used in the post-hydrolysis was removed by overliming with Ca(OH)$_2$ at ambient temperature.

The neutralization and purification stages of Liquors B1-4, B1-6, and B2, allow obtaining the Liquors C1-4, C1-6, and C2. For the neutralization, Ca(OH)$_2$ pro-analysis (Cicarelli) was used. Next, the treatment with 3 wt.% of activated carbon (Clarimex, DICA, Argentina) was carried out at 60 °C for 60 min. Finally, Liquors B1-4, B1-6, and B2 were stirred with Amberlite IRA-67 anion exchange resin (Adrem Corporación Industrial S.A., Argentina) to a constant pH for the acetic acid removal.

A diagram of the work stages and the terminology used for the different liquors is shown in Figure 1.
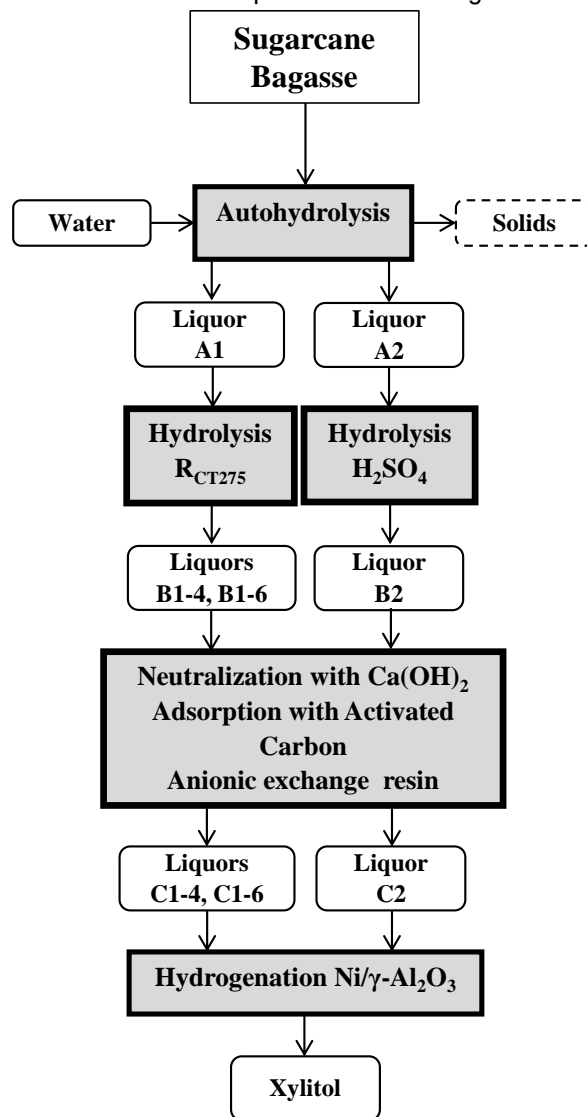

Figure 1. Diagram of the work stages and terminology used for the different liquors.

All liquors were characterized by the determinations of sugars (glucose, xylose, and arabinose), oligomers (glucans, xylans, arabinans), formic acid, acetic acid, and degradation products (furfural, 5-hydroxymethylfurfural (HMF)), according to Technical Report NREL / TP-510-42623 (January 2008) "Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples," National Renewable Energy Laboratory.

$$Xylans\ conversion\,(\%) = 100\frac{initial\ moles\ of\ xylose\ in\ xylans - final\ moles\ of\ xylose\ in\ xylans}{initial\ moles\ of\ xylose\ in\ xylans} \quad (1)$$

$$Xylose\ yield\,(\%) = 100\frac{moles\ of\ xylose\ produced}{moles\ of\ xylose\ in\ xylans} \quad (2)$$

Hydrogenation

The hydrogenation reaction of xylose to xylitol in the liquid phase was carried out in the 100 cm^3 reactor (BR-100 from Berghof Instruments), operated in batch mode at 3 MPa, in the range of 80–130 °C, with reaction

The quantification of these compounds and xylitol were carried out by HPLC liquid chromatography (Waters HPLC System) using an Aminex-HPX - 87 H87H column (BIO-RAD) with the following chromatographic conditions: 4 mM H_2SO_4 as eluent, 0.6 mL min^{-1}, 35 °C, with refractive index, and diode array detectors.

Xylans conversion (%) and xylose yield (%) were determined according to:

times between 2 and 4 h and a catalyst/xylose mass ratio between 0.25 and 0.5. As a reference, the hydrogenation of a commercial xylose solution (Biopack, 99%) was accomplished under the same conditions.

Xylose conversion and xylitol selectivity were determined according to:

$$Xylose\ conversion\,(\%) = 100\frac{initial\ moles\ of\ xylose - final\ moles\ of\ xylose}{initial\ moles\ of\ xylose} \quad (3)$$

$$Xylitol\ selectivity\,(\%) = 100\frac{moles\ of\ xylitol\ produced}{initial\ moles\ of\ xylose - final\ moles\ of\ xylose} \quad (4)$$

The yield of xylitol was determined as the ratio of the number of xylitol moles formed to the total initial xylose moles:

$$Xylitol\ yield\,(\%) = 100\frac{moles\ of\ xylitol\ produced}{Total\ moles\ of\ xylose\ in\ liquor\ A} \quad (5)$$

The Nickel content in the post-reaction liquors was determined by atomic absorption spectrometry (AA-6650 Shimadzu Spectrophotometer). The equipment was an IL Model 457 spectrophotometer

with a single channel and double beam.

RESULTS AND DISCUSSION

Catalyst characterization

The textural and acidic properties of the catalysts used for the heterogeneous hydrolysis stage (RCT275 resin) and hydrogenation (Ni/γ-Al$_2$O$_3$) are presented in Table 1.

Table 1. Textural and acid-base properties of catalysts for heterogeneous hydrolysis and hydrogenation

Catalyst	BET		Potentiometric titration	IPA decomposition reaction (X$_{IPA}$ = 15%)		
	SBET[a]	Vp[b]	Ei	S$_{propylene}$[d]	S$_{acetone}$[e]	S$_{DIPE}$[f]
RCT275	30	0.5	718	100	0	0
γ-Al$_2$O$_3$	185	0.50	60	73	0	27
Ni/γ-Al$_2$O$_3$	165	0.43	68	n.d.	n.d.	n.d.

[a] Specific surface area (m^2 g^{-1}), [b] total pore volume (cm^3 g^{-1}), [c] initial potential (mV), [d] selectivity to propylene (%), [e] selectivity to acetone (%), [f] selectivity to di-isopropyl eter (%)

The resin R$_{CT275}$ has only strong macropores according to the specifications available on the manufacturer's website (https://www.purolite.com/product/ct275). The potentiometric titration technique with n-butylamine allows determining the strength of the

acid sites in a given solid. The initial potential of the titration curve (E$_i$) indicates the maximum strength of the acid sites. In this sense, R$_{CT275}$ presented very strong acid sites.

The decomposition reaction of isopropanol (IPA)

is an indirect method that allows for characterizing the acid strength and type of sites on the surface of a solid. They are classified according to their ability to dehydrate and form propylene, di-isopropyl ether (DIPE), and (or) acetone, or to dehydrogenize and form acetone and hydrogen. For an IPA conversion of 15%, the selectivity of the different decomposition products is presented in Table 1. R_{CT275} presents propylene as the only product, indicating that these materials possess strong Lewis acid sites and (or) Brønsted [32]. The sulfonic acid groups (HSO_3^-) in the protonated form (H^+) of the R_{CT275} resin give it Brønsted acidity, which agrees with the obtained results.

Regarding the textural properties, γ-Al_2O_3 presents a type IV isotherms with H1 hysteresis, characteristics of mesoporous materials. The XRD diagram for this support (included in supplementary information) shows peaks at 2θ = 32.5°, 36.9°, 39.1°, 45.3°, 59.6°, and 66.7°, which are characteristics of low crystalline aluminum oxide (JCPDS 04 -0858).

The decomposition reaction of isopropanol (IPA) of γ-Al_2O_3 showed the obtaining of propylene and DIPE that would indicate the presence of Lewis acid sites and basic sites, both with medium or high strength, which corresponds to the acid-base character of the alumina's surface [32]. The oxide anions or the OH^- of the surface provide relatively low basicity, whereas the Al^{+3} ions constitute strong Lewis acid sites [32,33]. The strong acidity of the Al^{+3} ions would explain the higher selectivity to propylene obtained in this reaction [33]. The decomposition reaction of isopropanol by Ni/γ-Al_2O_3 catalyst does not allow evaluation of the acidic properties of the sites, as Ni leads to obtaining dehydrogenation and cracking products. Therefore, it was not carried out.

Regarding the potentiometric titration results, the initial potential (Ei) for the Ni/γ-Al_2O_3 catalyst indicates the presence of stronger acid sites than in the γ-Al_2O_3 support.

The supplementary information shows the XRD diagram of the Ni/γ-Al_2O_3 catalyst. As mentioned before, it is possible to observe characteristic peaks of low crystalline aluminum oxide (JCPDS 04 -0858) and a peak at 51.7° that corresponds to the metallic phase of Ni (JCPDS 4-850). Due to the low intensity of that peak, it is not possible to calculate an average crystallite size (using the Scherrer equation), but this may indicate that these particles are highly dispersed, which is corroborated by TEM (Figure 2) since the average particle diameter is ~4 nm.

Hydrolysis of liquors from sugarcane bagasse hydrothermal treatment

The average chemical composition of sugarcane bagasse was: 43.1% glucans, 23.8% xylans, 1.7%

arabinans, 1.7% acetyl groups, 21.3% lignin, 4.8% extractives, and 1.5% ash. The raw materials for hydrolysis reactions are obtained from sugarcane bagasse autohydrolysis. They are named liquors A. It is important to note that this type of lignocellulosic raw material has inhomogeneous characteristics. Therefore, there was little difference in the used liquors A compositions.
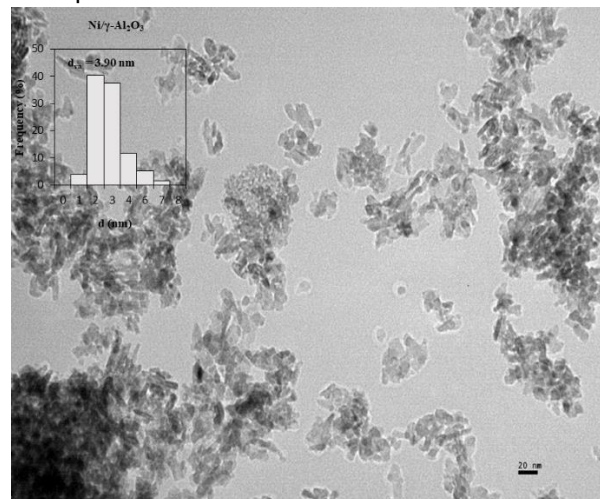

Figure 2. TEM micrograph and particle size distribution of Ni/γ-Al_2O_3 catalyst.

Liquors B1-4, B1-6, and B2 were obtained from liquors A1 and A2 acid hydrolysis. Their ulterior purification led to the xylose-rich liquors denominated Liquors C1-4, C1-6, and C2. Finally, these last liquors were hydrogenated to obtain xylitol. Table 2 summarizes the hydrolysis results employing R_{CT275} as the heterogeneous catalyst and H_2SO_4 as a reference.

The liquors A (raw material) has a xylans concentration (between 300 and 400 mmol L^{-1}) and a concentration of xylose as a monomer (~70 mmol L^{-1}). Acetic acid, which comes from the hydrolysis of acetyl bonds in arabinoxylans, is among the main components. The presence of acetic acid is beneficial for the hydrolysis reactions of polymers [9]. The main organic compounds are reported in Table 2. However, numerous and diverse aromatic compounds are difficult to identify and quantify. It has been reported that phenolic derivatives such as *p*-coumaric acid, ferulic acid, vanillic acid, and vanillin, produced by lignin degradation, are present in a total concentration of approximately 5 g L^{-1} (determined as g equivalent of vanillin L^{-1}) [14].

The Liquor B1-4 is obtained using R_{CT275} as a catalyst and a catalyst/polymers mass ratio of 0.65, corresponding to a concentration of acid sites of 0.52 mol L^{-1}, employing 100 °C and 4 h of reaction time. Liquor B1-4 contains a high content of xylose (392.16 mmol L^{-1}), arabinose (19.85 mmol L^{-1}), glucose (10.13 mmol L^{-1}), cellobiose (6.53 mmol L^{-1}) and acetic acid (115.57 mmol L^{-1}). The reached conversion was

84% after 4 h of reaction, meaning incomplete hydrolysis of the xylans in liquor A. The acetic acid content increased to 115.57 mmol L^{-1} due to the cleavage of the acetylenic bonds favored by the acidity of the medium.

These results are comparable with that reported by Cará *et al.* [24]. These authors employed different sulfonated resins (Amberlyst-35 and Amberlyst-70) for the hydrolysis of commercial Beechwood xylans at 120 °C for 4 h, and they reported a yield of sugar monomers (xylose and arabinose) in the range of 55% to 80% [24].

The variables affecting the hydrolysis yield are temperature, time, and catalyst mass. This study was accomplished at 100 °C because the resin R_{CT275} has a temperature limit of 130 °C. In addition, the effect of reaction time was studied with acid sites concentration of 0.52 mol L^{-1} and 1.04 mol L^{-1} of R_{CT275} as the catalyst, as shown in Figure 3.

Table 2. Composition of the liquors obtained from autohydrolysis, heterogeneous hydrolysis, and purification steps

Treatment		Hydrolysis with R_{CT275}					Hydrolysis with H_2SO_4		
Concentration of products (mmol L^{-1})		A1	B1-4[a]	C1-4	B1-6[b]	C1-6	A2	B2	C2
Monomer	Xylose	66.81	392.16	390.33	408.51	407.65	68.61	353.03	345.70
	Glucose	1.94	10.13	8.33	14.38	13.32	0.94	27.36	und.
	Cellobiose	und.	6.53	6.13	5.84	5.84	und.	3.51	und.
	Arabinose	14.65	19.85	18.65	19.18	18.65	19.78	21.85	und.
	HMF	0.79	0.79	und.	0.87	und.	und.	0.87	und.
	Furfural	5.20	9.26	1.56	56.20	8.43	und.	10.20	7.70
	Acetic acid	73.27	115.57	28.31	107.74	26.64	43.13	128.23	24.98
	Formic acid	und.	18.63	18.47	und.	und.	14.34	9.34	7.39
Polymer	Xylose	418.5	65.78	und.	3.73	und.	304.40	und.	und.
	Glucose	62.39	39.13	und.	45.68	und.	30.47	und.	und.
	Arabinose	8.33	2.33	und.	5.73	und.	4.20	und.	und.
	Acetic acid	31.31	und.	und.	0.50	und.	und.	und.	und.
pH		3.0	1.8	6	1.8	6	3.4	1.3	6
Xylans conversion (%)			84		99			100	
Xylose yield (%)			78		82			95	

[a] 100 °C, 4 h, mass ratio catalyst/polymer = 0.65, 0.52 mol acid sites L^{-1}. [b] 100 °C, 6 h, mass ratio catalyst/polymer = 1.3, 1.04 mol acid sites L^{-1}. und.- undetected.
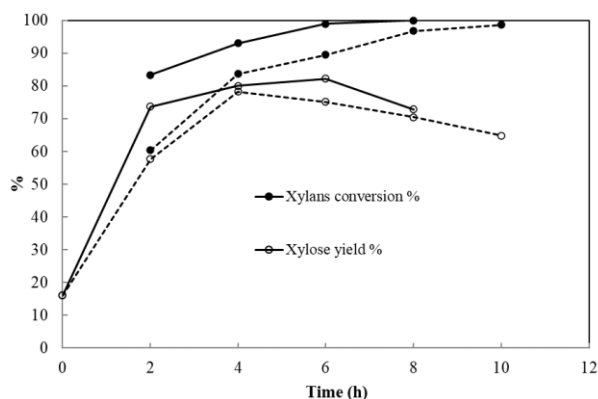

Figure 3. Xylans conversion and xylose yield as a time function. Dotted lines: 0.52 mol L^{-1} acid sites. Full lines: 1.04 mol L^{-1} acid sites.

A xylans conversion of 98.7% was achieved at 10 h, while the maximum xylose yield (78%) was obtained at 4 h of reaction time (liquor B1-4) using an acid concentration of 0.52 mol L^{-1}. With a higher concentration of acid sites (1.04 mol L^{-1}), the total conversion of xylans was achieved at 6 hours, with a maximum xylose yield of 82% (Figure 3 and Table 2).

Figure 4 shows the concentration of the products obtained from the hydrolysis of xylans as a function of time. When using an acid sites concentration of 0.52 mol L^{-1}, due to the dehydration of xylose to furfural, after 4 h of reaction, the decrease in the xylose

concentration and the increase in the furfural concentration were observed. The same behavior was observed with an acid site concentration of 1.04 mol L^{-1} after 6 h of reaction, which explains the decrease in the yield to xylose shown in Figure 3. Ormsby *et al.* [25] reported that when using Amberlyst-15 to hydrolyze birchwood xylans, xylose concentration decreased after 5 h at 120 °C, suggesting a sequential reaction and formation of a dehydrated product, as furfural.
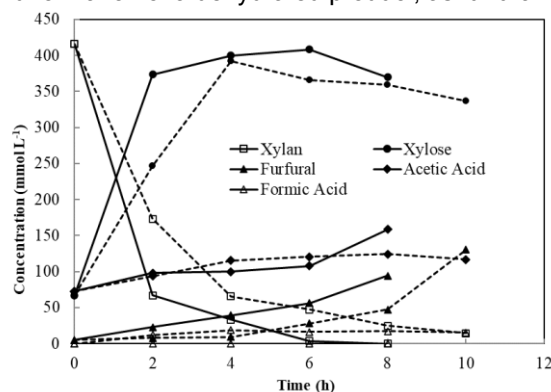

Figure 4. The concentration of xylans hydrolysis products. Dotted lines: 0.52 mol L^{-1} acid sites. Full lines: 1.04 mol L^{-1} acid sites.

The homogeneous hydrolysis of liquor A2 was carried out using H_2SO_4 1 wt.% at 120 °C and 1 h of reaction time. The liquor obtained was named

Liquor B2. In this case, the xylans conversion was 100%, and the xylose yield was 95%. Based on preliminary post-hydrolysis assays, the maximal xylose concentration in spent liquors was achieved using 1 wt.% of H_2SO_4. Higher acid concentrations produce a decrease in xylose concentration and an increase in furfural concentration [14].

The next step for obtaining xylitol by hydrogenation of the xylose-rich liquors B1-4, B1-6, and B2 is a subsequent neutralization (with $Ca(OH)_2$) followed by a purification (with activated carbon Clarimex and Amberlite IRA-67 resin). Details from the previous work of Vallejos *et al.* [14] are in the experimental section. The treatment using activated carbon reduced the phenolic compounds content, furfural, HMF, and polymers, without affecting the concentration of sugars and organic acids. Removal of 80-85% acetic acid was possible using Amberlite IRA-67 resin. This treatment allowed obtaining liquors C1-4, C1-6, and C2 rich in xylose, with a low acetic acid content (Table 2).

Hydrogenation of xylose-rich liquors to obtain xylitol

The first step in studying xylitol production from xylose-rich liquors is to find the most suitable operating condition for the Ni/γ-Al_2O_3 catalyst in the hydrogenation reaction of pure xylose (Biopack, 99%) using the same concentration of xylose that has a liquor C (400 mmol L^{-1}).

Conditions varied between 80 °C and 130 °C of temperature, 2 MPa and 3 MPa of hydrogen pressure, and 2 h and 4 h of reaction time (Table 3). Only xylitol was observed at 100 °C, whereas the selectivity towards xylitol decreased at 130 °C to 74% due to the generation of xylose degradation products. At temperatures above 150 °C other authors have obtained by-products such as D-arabinitol, D-xylulose, acid D-xylonic, furfural, and even others from C-C bond break reactions [27,30].

Table 3. Hydrogenation of commercial xylose

Catalyst	mc/mx[a]	Temperature (°C)	Hydrogen Pressure (MPa)	Time (h)	Xylose conversion (%)	Selectivity towards xylitol (%)
	0.25	80	2	2	36	100
	0.25	100	2	2	58	100
Ni/γ-Al_2O_3	0.25	130	2	2	80	74
	0.25	100	2	4	81	100
	0.25	100	3	2	85	100
Ni-Raney	0.25	100	3	2	70	100
Ni/γ-Al_2O_3	0.50	100	3	2	100	100

[a] mc/mx: mass ratio catalyst to xylose.

Ni/γ-Al_2O_3 was more active than the commercial Ni-Raney catalyst (Table 3). The explanation could be the smaller metal particle size in Ni/γ-Al_2O_3 compared to the Ni-Raney catalyst. Besides, in the aqueous phase, the xylose forms a cyclic hemiacetal due to the reaction between its aldehyde and hydroxyl groups [10]. Thus, the presence of the acid sites of the γ-Al_2O_3 support would favor the cleavage of the C-O bond of hemiacetal. The best results were obtained at 100 °C, 3 MPa of hydrogen pressure, and 2 h, with a mass relation of catalyst to xylose of 0.5, reaching a xylose conversion of 100% with a xylitol selectivity of 100%.

The main components in the liquors susceptible to hydrogenation are xylose, arabinose, glucose, and cellobiose. Xylose is present in percentages between 82% and 90%. Mannose and galactose are minor components in bagasse hemicelluloses. Then, other polyols, such as sorbitol, arabitol, and mannitol, can indeed be produced during the hydrogenation of these liquors but have not been detected. Therefore, it was determined that xylitol is the only hydrogenation product of the liquor (Table 4).

The hydrogenation results of Liquor C1-6 (shown in Table 4) allows obtaining xylose conversions close to 82% and 95% for mc/mx of 0.25 and 0.5, respectively. In addition, the xylitol selectivity was 100% in 2 h in both cases.

By atomic absorption analysis of the post-reaction Liquors C1-6, the presence of nickel was undetected (<1 ppm), which evidenced that its leaching did not occur when the pH of the reaction medium was 6. The acetic acid content in these liquors (~30 mmol L^{-1}) did not affect the hydrogenation step. Additional tests, adding acetic acid to the liquor, allowed the determination of 1000 ppm of Nickel loss by leaching when 116 mmol L^{-1} of acetic acid is reached. The above evidenced the importance of its presence in xylose-rich liquors.

In the hydrogenation experiments of the C2 liquor (from hydrolysis with H_2SO_4), a xylose conversion of 16% was achieved. This low level could be associated with sulfur traces (1–5 ppm) in the liquor, a known poison of the metallic function for any supported metallic catalyst [34,35]. However, this low sulfur content is not detrimental to the biotechnological production of xylitol [14].

Table 4. Hydrogenation of xylose-rich liquors

Concentration of products (mmol L^{-1})	Liquor C1-6 mc/mx^a = 0.25	Liquor C1-6 mc/mx^a = 0.50	Liquor C2 mc/mx^a = 0.50
Xylose	75.27	4.00	335.71
Xylitol	326.65	390.40	63.10
Glucose	5.05	4.72	und.
Cellobiose	6.13	5.84	und.
Arabinose	14.99	15.32	und.
HMF	und.	und.	7.70
Furfural	und.	und.	15.61
Acetic acid	28.31	28.31	5.66
Xylose conversion (%)	81	99	16
Xylitol selectivity (%)	100	100	100
Xylitol yield (%)	67	83	15

^{a} mc/mx: mass ratio catalyst to xylose. Reaction conditions: 100 °C, 3 MPa of H_2 and 2 h. und.- undetected.

The higher xylitol yield (83%) was obtained in the hydrolysis with R_{CT275} and subsequent hydrogenation with Ni/γ-Al_2O_3 (Table 4). Yamaguchi *et al.* [36] achieved a xylitol yield of 60% in a single pot using a RuPt/C bimetallic catalyst in the direct conversion of Japanese cedar bagasse at 190 °C, 5 MPa of H_2, and 16 h. Ribeiro *et al.* [37] achieved a xylitol yield of 46% in a single pot with a Ru/C catalyst in the direct conversion of corncob xylans at 205 °C, 5 MPa of H_2, and 5 h.

In this way, the xylitol yields obtained in this work in two stages (heterogeneous hydrolysis followed by hydrogenation) are higher than the yields obtained in single pot processes using noble metal-based catalysts like Ru and Pt and more severe reaction conditions.

Finally, to determine the possibility of reusing these solids for other reaction stages, experiments were carried out without removing the R_{CT275} catalyst from the reactor and renewing the reaction mixture to evaluate 4 hydrolysis cycles. On the other hand, in each evaluation of the hydrogenation cycle, the Ni/γ-Al_2O_3 catalyst is pre-reduced in the H_2 atmosphere to ensure the presence of metallic Ni after contact with air.

Figure 5 shows that the activity loss between one cycle and another is very low, so it is possible to reuse both catalysts.

Biological methods for xylose saccharification and fermentation to xylitol have recently been reported but are not implemented at an industrial scale. The saccharification of hemicellulosic xylans into xylose is expensive and requests different xylanase enzymes for its complete hydrolysis. For example, endo-1, 4-β-xylanases produce random hydrolysis, and 1,4-β-d-xylosidases generate oligosaccharides. Besides, to achieve high enzymatic saccharification with low xylitol production cost, xylanases require severe conditions, high activity, substrate specificity, stability, and tolerance to inhibitors [38]. It has recently been reported that accessory enzymes from hypercellulolytic *Penicillium funiculosum facilitate* the complete saccharification of sugarcane bagasse [39].
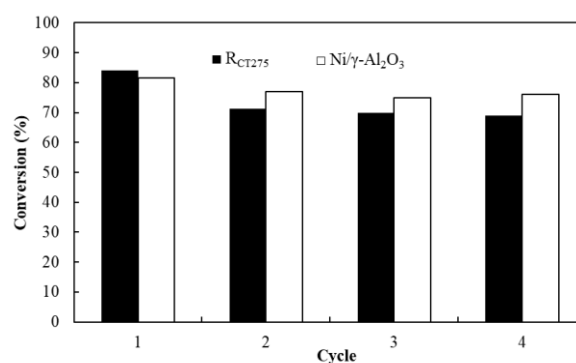

Figure 4. Hydrolysis and hydrogenation catalyst reuses. Reactions conditions: Hydrolysis: 100 °C, 4 h, mass ratio catalyst/polymer = 0.65, (0.52 mol acid sites L^{-1}). Hydrogenation: 100 °C, 2 h, 3 MPa of H_2, mass ratio catalyst/xylose = 0.25.

The xylose fermentation to xylitol by microbial strain has been investigated to improve yield and economic feasibility. In addition, modern genetic engineering and adaptive methods of microbial strains have been widely studied. For example, Hernández-Pérez *et al.* [40] achieved 26.19 g L^{-1} of xylitol from a sugarcane bagasse and straw hemicellulosic hydrolysate *Candida guilliermondii* FTI 20037 with a xylitol volumetric productivity of 0.55 g L^{-1} h^{-1}. Recent studies showed that recombined *Saccharomyces cerevisiae* produces high xylitol yields and ethanol from sugarcane bagasse [41,42]. In previous work, Vallejos *et al.* [14] reported maximal xylitol concentration (32.0 g L^{-1}) from hemicellulosic liquors obtained from sugarcane bagasse autohydrolysis using *Candida tropicalis* (104.1 g L^{-1} xylose, 0.46 g g^{-1} yield, 0.27 g L^{-1} h^{-1} productivity). They also determined technological parameters to obtain a detoxified spent liquor rich in xylose and its bioconversion to xylitol. In this work, using heterogeneous hydrolysis and hydrogenation, xylitol yield was 83% and approximately 59 g L^{-1} concentration, indicating that biological procedures require much development.

CONCLUSION

Heterogeneous catalysis in two-step routs (hydrolysis and hydrogenation) constitutes an outstanding alternative to producing xylitol from sugarcane bagasse hydrothermal spent liquors since materials can be easily separated and reused in several reaction cycles.

In the first step, xylose-rich liquors are obtained by heterogeneous hydrolysis. Then, they can be hydrogenated to xylitol using the Ni/γ-Al$_2$O$_3$ catalyst with good yields.

Acid hydrolysis was carried out using an R$_{CT275}$ sulfonated resin and sulfuric acid as reference. The heterogeneous catalyst R$_{CT275}$ was suitable for hydrolysis, avoiding the presence of sulfur traces in liquors. Although the liquor obtained by homogeneous hydrolysis with sulfuric acid is a usual raw material to produce xylitol by biotechnological processes, it cannot be used for hydrogenation with supported metal catalysts because of the poisoning of the metal phase and the catalyst deactivation. Nevertheless, xylitol yields of about 83%, obtained using R$_{CT275}$ and Ni/γ-Al$_2$O$_3$ catalysts, were higher than those from other studies in the literature.

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REFERENCES

[1]   M. FitzPatrick, P. Champagne, M. F. Cunningham, R. A. Whitney, Bioresour. Technol. 101 (2010) 8915–8922. https://doi.org/10.1016/j.biortech.2010.06.125

[2]   W.E. Mabee, P.N. McFarlane, J.N. Saddler, Biomass Bioenergy 35 (2011) 4519–4529. https://doi.org/10.1016/j.biombioe.2011.06.026

[3]   M.E. Vallejos, F.E. Felissia, M. C. Area, Bioresources 12 (2017) 2058–2080. https://bioresources.cnr.ncsu.edu/wp-content/uploads/2017/02/BioRes_12_1_2058_REVIEW_Vallejos_FA_Hydrothermal_Treatm_Agro_Forest_Indust_Waste_Value_10459.pdf

[4]   Food and Agriculture Organization (FAO). Statistics Division of the FAO (FAOSTAT). http://www.fao.org/faostat/en/#data/QC, [accessed 19 February 2022].

[5]   N. Clauser, S. Gutiérrez, M.C. Area, F.E. Felissia, M.E. Vallejos. J. Renew. Mater. 6 (2018) 139–151. http://dx.doi.org/10.7569/JRM.2017.634145

[6]   H. Boussarsar, B. Rogé, M. Mathlouthi, Bioresour. Technol. 100 (2009) 6537–6542. https://doi.org/10.1016/j.biortech.2009.07.019

[7]   M. Fatih Demirbas, Appl. Energy 86 (2009) 151–161. https://doi.org/10.1016/j.biortech.2009.07.019

[8]   D.J. Hayes, Catal. Today 145 (2009) 138–151. https://doi.org/10.1016/j.cattod.2008.04.017

[9]   M.E. Vallejos, F.E. Felissia, J. Kruyeniski, M.C. Area, Ind. Crops Prod. 67 (2015) 1–6. https://doi.org/10.1016/j.indcrop.2014.12.058

[10]   L. da Costa Sousa, S. Chundawat, V. Balan, B. E. Dale, Curr. Opin. Biotechnol. 20 (2009) 339–347. https://doi.org/10.1016/j.copbio.2009.05.003

[11]   Y. Delgado Arcaño, O.D. Valmaña Garcia, D. Mandelli, W.A. Carvalho, L.A. Magalhães Pontes, Catal. Today 344 (2020) 2–14. https://doi.org/10.1016/j.cattod.2018.07.060

[12]   K. Nakajima, M. Hará, ACS Catal. 2 (2012) 1296–1304. https://doi.org/10.1021/cs300103k

[13]   S. Suganuma, K. Nakajima, M. Kitano, D. Yamaguchi, H. Kato, S. Hayashi, M. Hara, J. Am. Chem. Soc. 130 (2008) 12787–12793. https://doi.org/10.1021/ja803983h

[14]   M.E. Vallejos, M. Chade, E. Beda Mereles, D.I. Bengoechea, J.G. Brizuela, F.E. Felissia, M.C. Area, Ind. Crops Prod. 91 (2016) 161–169. https://doi.org/10.1016/j.indcrop.2016.07.007

[15]   P.L. Dhepe, R. Sahu, Green Chem. 12 (2010) 2153–2156. https://doi.org/10.1039/C004128A

[16]   Y. Jiang, X. Li, X. Wang, L. Meng, H. Wang, G. Peng, X. Wang, X. Mu, Green Chem. 14 (2012) 2162–2167. https://doi.org/10.1039/C2GC35306G

[17]   M. Kitano, D. Yamaguchi, S. Suganuma, K. Nakajima, H. Kato, S. Hayashi, M. Hara, Langmuir 25 (2009) 5068–5075. https://doi.org/10.1021/la8040506

[18]   B.T. Kusema, G. Hilmann, P. Mäki-Arvela, S. Willför, B. Holmbom, T. Salmi, D.Y. Murzin, Catal. Lett. 141 (2011) 408–412. https://doi.org/10.1007/s10562-010-0530-x

[19]   Y. Ogaki, Y. Shinozuka, T. Hara, N. Ichikuni, S. Shimazu, Catal. Today 164 (2011) 415–418. https://doi.org/10.1016/j.cattod.2010.11.002

[20]   M. Okamura, A. Takagaki, M. Toda, J.N. Kondo, K. Domen, T. Tatsumi, M. Hara, S. Hayashi, Chem. Mater. 18 (2006) 3039–3045. https://doi.org/10.1021/cm0605623

[21]   A. Onda, T. Ochi, K. Yanagisawa, Green Chem. 10 (2008) 1033–1037. https://doi.org/10.1039/B808471H

[22]   R. Sahu, P.L. Dhepe, ChemSusChem 5 (2012) 751–761. https://doi.org/10.1002/cssc.201100448

[23]   L. Zhou, M. Shi, Q. Cai, L. Wu, X. Hu, X. Yang, C. Chen, J. Xu, Microporous Mesoporous Mater. 169 (2013) 54–59. https://doi.org/10.1016/j.micromeso.2012.10.003

[24]   P.D. Cará, M. Pagliaro, A. Elmekawy, D.R. Brown, P. Verschuren, N.R. Shiju, G. Rothenberg, Catal. Sci. Technol. 3 (2013) 2057–2061. https://doi.org/10.1039/C3CY20838A

[25]   R. Ormsby, J. R. Kastner, J. Miller, Catal. Today 190 (2012) 89–97. https://doi.org/10.1016/j.cattod.2012.02.050

[26]   J.P. Mikkola, R. Sjöholm, T. Salmi, P. Mäki-Arvela, Catal. Today 48 (1999) 73–81. https://doi.org/10.1016/S0920-5861(98)00360-5

[27]   J. Wisniak, M. Hershkowitz, R. Leibowitz, S. Stein, Ind. Eng. Chem. Prod. Res. Dev. 13 (1974) 75–79. https://doi.org/10.1021/i360049a015

[28]   M. Yadav, D.K. Mishra, J. Hwang, Appl. Catal., A 425 (2012) 110–116. https://doi.org/10.1016/j.apcata.2012.03.007

[29]   J. Lee, Y. Xub, G.W. Huber, Appl. Catal., B 140 (2013) 98–107. https://doi.org/10.1016/j.apcatb.2013.03.031

[30]   J. Wisniak, M. Hershkowitz, S. Stein, Ind. Eng. Chem. Prod. Res. Dev. 13 (1974) 232–236. https://doi.org/10.1021/i360052a004

[31]   F. Devred, A.H. Gieskea, N. Adkins, U. Dahlborg, C.M. Bao, M. Calvo-Dahlborg, J.W. Bakker, B.E. Nieuwenhuys, Appl. Catal., A 356 (2009) 154–161. https://doi.org/10.1016/j.apcata.2008.12.039

[32]   A. Gervasini, J. Fenyvesi, A. Auroux, Catal. Lett. 43 (1997) 219–228. https://doi.org/10.1023/A:1018979731407

[33]   G. Busca, Catal. Today 226 (2014) 2–13. https://doi.org/10.1016/j.cattod.2013.08.003

[34]   D.S. Brands, U.A. Sai, E.K. Poels, A. Bliek, J. Catal. 186 (1999) 169–180. https://doi.org/10.1006/jcat.1999.2553

[35]   L.S. Carvalho, C.L. Pieck, M.L. Rangel, N.S. Figoli, C.R. Vera, J.M. Parera, Appl. Catal., A 269 (2004) 105–116. https://doi.org/10.1016/j.apcata.2004.04.006

[36]   A. Yamaguchi, O. Sato, N. Mimura, M. Shirai, Catal. Today 265 (2016) 199–202. https://doi.org/10.1016/j.cattod.2015.08.026

[37]   L.S. Ribeiro, J.J. Delgado, J.J. de Melo Órfão, M.F.R. Pereira, RSC Adv. 6 (2016) 95320–95327. https://doi.org/10.1039/C6RA19666G

[38]   L. Venkateswar Rao, J.K. Goli, J. Gentela, S. Koti, Bioresour. Technol. 213 (2016), 299–310. https://doi.org/10.1016/j.biortech.2016.04.092

[39]   O.A. Ogunyewo, P. Upadhyay, G.H. Rajacharya, O. E. Okereke, L. Faas, L.D. Gómez, S. J. McQueen-Mason, S. S. Yazdani, Biotechnol. Biofuels. 14 (2021), 1–17. https://doaj.org/article/aeeb042f69924f6787414bdcf3e672ab

[40]   A.F. Hernández-Pérez, A.C. Chaves-Villamil, P.V. de Arruda, J.C. dos Santos, M. das G. de A. Felipe, Waste Biomass Valorization 11 (2020), 4215–4224. https://doi.org/10.1007/s12649-019-00742-6

[41]   M.S.S, Reshamwala, A.M. Lali, Biotechnol. Prog. 36 (2020), e2972. https://doi.org/10.1002/btpr.2972

[42]   G. Guirimand, K. Inokuma, T. Bamba, M. Matsuda, K. Morita, K. Sasaki, C. Ogino, J.-G. Berrin, T. Hasunuma, A. Kondo, Green Chem. 21 (2019), 1795–1808. https://doi.org/10.1039/C8GC03864C

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NAUČNI RAD

DOBIJANJE KSILITOLA HIDROLIZOM-HIDROGENACIJOM OTPADNOG LUGA IZ OBRADE BAGAZE ŠEĆERNE TRSKE

Ovaj rad predstavlja proučavanje heterogene katalize otpadnog luga iz hidrotermičke obrade bagaze šećerne trske korišćenjem sulfonovane smole. Pored toga, rezultati su upoređeni sa onima dobijenim konvencionalnim putem korišćenjem sumporne kiseline kao homogenog katalizatora. Heterogena kataliza je pogodna za hidrolizu otpadnog luga iz hidrotermičke obrade bagaze šećerne trske pod blagim uslovima (100 °C i 6 h). Dobijeni maksimalni prinos ksiloze iznosio je 82% zbog formiranja furfurala, što uzrokuje pad selektivnosti ksiloze. Hidrogenizacijom ovog luga bogatog ksilozom na 100 °C i pritisku vodonika od 3 MPa korišćenjem katalizatora Ni/γ-Al$_2$O$_3$ u masenom odnosu prema ksilozi od 0,5 postignuta je ukupnu konverzija ksiloze sa selektivnošću prema ksilitolu od 100%. Heterogena kataliza u dvostepenom putu (hidroliza i hidrogenacija) predstavlja izvanrednu alternativu proizvodnji ksilitola iz hidrotermičkog otpadnog luga šećerne trske, pošto se materijali mogu lako odvojiti i ponovo upotrebiti u nekoliko reakcionih ciklusa.

Ključne reči: bagasa šećerne trske, hidroliza, hidrogenacija, ksiloza, ksilitol.