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DOI

[10.1021/acs.oprd.6b00169](https://doi.org/10.1021/acs.oprd.6b00169)

Publication date

2017

Document Version

Final published version

Published in

Organic Proces Research & Development

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Citation for published version (APA):

Dietrich, K., Hernandez-Mejia, C., Verschuren, P., Rothenberg, G., & Shiju, N. R. (2017). One-Pot Selective Conversion of Hemicellulose to Xylitol. *Organic Proces Research & Development*, 21(2), 165-170. <https://doi.org/10.1021/acs.oprd.6b00169>

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One-Pot Selective Conversion of Hemicellulose to Xylitol

Work from the Organic Reactions Catalysis Society Meeting 2016

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Supporting Information

ABSTRACT: Converting hemicellulose into valuable platform chemicals is a key step in developing an integrated biorefinery. Traditionally, hemicellulose conversion into xylitol is done in two steps, using mineral acids and enzymes. Here we report a one-pot hydrolysis–hydrogenation of hemicellulose to xylitol. We used a combination of either heteropoly acid or biomass-derived organic acid and Ru on carbon as catalyst. Silicotungstic acid, phosphotungstic acid, and lactic acid can be used efficiently in the hydrolysis part. Phosphomolybdic acid was not very active (<5% yield). The reduction can be done using either hydrogen gas or isopropanol as the reductant. The entire process runs in water, at relatively mild temperatures and pressures (140 °C and 20 bar). Lactic acid or phosphotungstic acid combined with Ru/C gave around 70% xylitol yield in 3 h using H₂ as a reductant. With isopropanol as a reductant, phosphotungstic acid and Ru/C gave a high xylitol yield (82%), while only ~20% xylitol yield was obtained with lactic acid.

■ INTRODUCTION

High-value chemicals from biomass are a financial driving force for the transition to a biobased economy.¹ Current research efforts focus on sustainable conversion routes with nonfood biomass as starting material. Lignocellulosic biomass is the most promising sustainable source, because the worldwide agricultural and forestry waste is higher than 3×10^9 tpa.² Lignocellulose has three main components: cellulose, hemicellulose, and lignin. While cellulose and lignin have been extensively explored,^{3–24} studies on hemicellulose are scant. Unlike cellulose, hemicelluloses vary in their sugar monomer composition of different C5 and C6 sugar units (xylose, arabinose, mannose, glucose, and galactose) depending on the biomass source.²⁵ Here we are interested in the hemicellulose xylan, a polymer of xylose units linked by $\beta(1-4)$ -glycosidic bonds. Xylans are abundant in hardwoods, pulping liquors, and agricultural waste such as sugar cane bagasse, rice straw, wheat straw, vegetable fibers, and cottonseed residual cake.²⁵ Recent reports focus on hemicellulose conversion to monomers and/or furfural using solid acid catalysts.^{26–33} Conversion of hemicellulose to γ -valerolactone using supported metallic catalysts is also reported.^{34–36} Recently, Hu et al. reported a three-step method for the selective conversion of hemicellulose in pubescens to γ -valerolactone with Pt/C catalyst without the addition of external hydrogen.³⁴ Selective hydrolysis and hydrogenation of xylan can give xylitol,^{25,37} an important artificial sweetener which is 20% sweeter yet has 40% less calories than sucrose.³⁸ Xylitol is an approved food additive in many countries (most famously, perhaps, as the sweetener in sugarfree chewing gum). Furthermore, it can be used as a raw material for polyols, lactic acid, and new polymers.³⁹

Industrially, xylitol is produced by a multistep process. The final xylitol yield in this process is 50–60% based on raw xylan.⁴⁰ There are research efforts for developing an economically viable and eco-friendly alternative route to xylitol.

However, most of the research activities are based on the hydrolysis of xylan-containing materials and the bioconversion of the resultant xylose.⁴¹ These methods cannot replace the current chemical process.⁴² The use of acids combined with transition metal catalysts for hydrolysis/hydrogenation was extensively studied for cellulose.^{9,43–46} Therein, sugar hydrogenation works well with ruthenium and raney-nickel, but efficient and environmentally benign hydrolysis remains a challenge.^{13,47–49} Such studies are rare with hemicelluloses.^{41,45} In line with green chemistry principles, we want to substitute mineral acids with either recyclable or biomass derived alternatives.⁴⁶ Promising alternatives are solid, yet strongly acidic heteropolyacids. Though water-soluble,⁵⁰ they are potentially recyclable by precipitation, extraction or anchoring on a solid support.⁵¹ From biomass-derived acids, we selected lactic acid, one of the top biobased chemicals.³⁹ Lactic acid is already used in the food industry (e.g., as food preservative and production of cheese and yogurt), and it is becoming cheaper due to its large-scale use in several other applications.^{52,53}

Here we report a cost-efficient selective route from xylan to xylitol. We tested Ru/C with different organic/heteropoly acids (Scheme 1). We varied several parameters in this study, such as type of acid, acid concentration, reaction temperature, and time. All of these parameters influence the xylitol yield significantly. We found that lactic/phosphotungstic/silicotungstic acids are efficient for one-pot xylan hydrolysis and hydrogenation under mild conditions together with Ru/C.

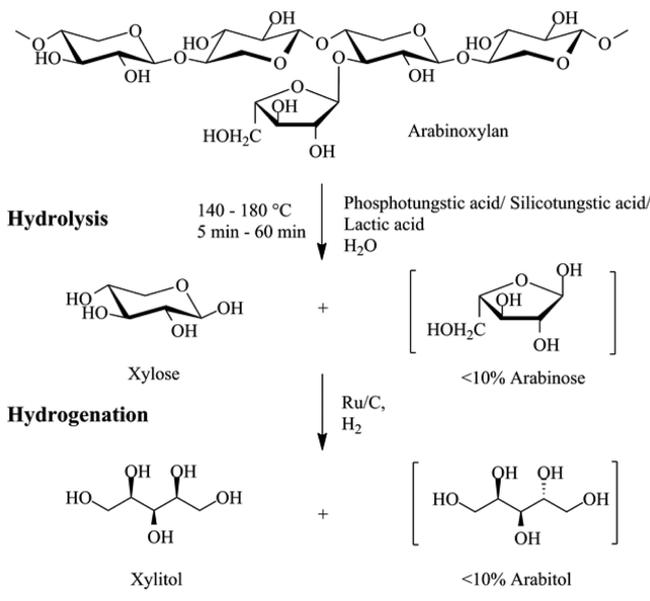
■ EXPERIMENTAL SECTION

Materials and Instrumentation. All experiments were done in a Parr 5000 multiautoclave system. Heating was conducted with a constant heating rate of 7 deg/min. Samples

Received: May 13, 2016

Published: November 29, 2016

Scheme 1. Catalytic Cascade Hydrolysis + Hydrogenation of Xylan Hemicellulose (Arabinoxylan) To Xylitol and Arabitol in the Presence of Heteropolyacids or Organic Acids and Ru/C



were analyzed by HPLC, using a Rezex RPM-monosaccharide Pb²⁺ (8%) column (300 × 7.8 mm) operating at 60 °C together with a guard column containing Carbo-Pb (4 × 3 mm), a refractive index detector (RID-10A, Shimadzu), and ultrapure water (0.6 mL/min) as the mobile phase. Lactic acid samples were analyzed using a Shimadzu HPLC system with a Bio-Rad Aminex HPX-87H H⁺ (8%) column (300 × 7.8 mm) operating at 60 °C and with a refractive index detector (RID-10A, Shimadzu) operating at 40 °C and 5 mM sulfuric acid (0.55 mL/min) as mobile phase. Xylitol yields were determined via peak areas based on the calibration of pure samples with ethylene glycol as external standard. The calibration protocol and graphs are included in the [Supporting Information](#).

X-ray diffraction patterns (XRD) were measured on a Rigaku miniflex diffractometer. Data were recorded in the 2θ range of 5–100° with an angular step size of 0.05° and a counting time of 1 deg/min. Unless stated otherwise, chemicals were purchased from commercial sources and used as received. Beechwood xylan (Sigma-Aldrich, lot no. BCBH7762 V) composed of 90% xylose and 10% arabinose was used as the hemicellulose substrate. Ru/C was purchased from Alfa Aesar; phosphotungstic acid (PTA), phosphomolybdic acid (PMA), and silicotungstic acid hydrate (SWA) were from Sigma-Aldrich; formic acid from Fluka Chemistry; lactic acid (LA) from Acros Organics; isopropanol from VWR International.

General Procedure for Catalytic One-Pot Hydrolysis–Hydrogenation of Xylan. Beechwood xylan (0.075 g, 0.57 mmol) and 5 wt % Ru/C (0.025 g, corresponding to 5 mg, 0.05 mmol ruthenium) and acid (heteropoly acids: 0.100 g, 0.0347 mmol; lactic acid: 8.00 mmol) were added to 8.0 mL of deionized water. This mixture was placed in a Teflon-lined stainless steel autoclave. It was then heated, under stirring, to the required temperature and pressurized with hydrogen or argon. For experiments with isopropanol as the hydrogen source, 0.052 mol was used, and the autoclave was pressurized with Ar instead of H₂. Xylitol concentrations were quantified by ion exchange-HPLC analysis. The xylitol yield was calculated

based on the maximum theoretical molar xylitol yield from xylan. Consisting of condensed xylose and arabinose units with both the molar mass of 152.13 g/L, the molar mass of xylan is the molar mass of xylose minus water (132.11 g/L). This corresponds to a monomer content of 0.57 mmol for 0.075 g of xylan. At 100% yield, the xylitol content is equal to the monomer content, which corresponds to a maximum xylitol weight of 0.0864 g. The xylitol yield was calculated as the ratio of xylitol mass measured per maximum theoretical xylitol mass.

$$Y_{\text{xylitol}} = \frac{n(\text{xylitol})_{\text{exp}}}{n(\text{xylitol})_{\text{max}}} \times 100 = \frac{m(\text{xylitol})}{M(\text{xylitol}) \times \frac{m(\text{xylan})}{M(\text{xylan})}} \times 100$$

Besides xylitol, xylose, arabinose, arabitol, and carbon were observed in the product mixture. The overall carbon balance was more than 95%. For recycling, the catalyst was recovered by centrifugation, washed with 10 mL of water, and dried for 12 h at 120 °C. During this operation, a small amount of catalyst was lost. This was compensated by adding corresponding amount of used catalyst from previous experiments. For all reactions, time recording started when the desired temperature was reached ($t = 0$ min).

RESULTS AND DISCUSSION

One challenge in working with biomass is that samples vary from batch to batch in their composition, molecular weight distribution, particle size, and crystallinity. These parameters influence the reactivity of the starting material.³⁴ Unlike the highly crystalline cellulose, hemicelluloses are amorphous. [Figure 1](#) shows the X-ray diffraction pattern of our beechwood xylan. The broad peak at 19° indicates a short-range order which can affect hydrolysis rates.

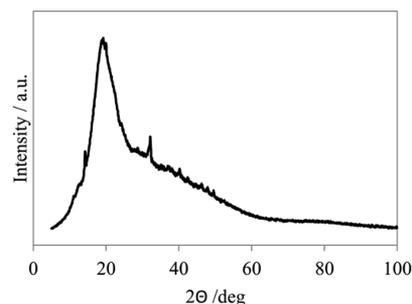


Figure 1. X-ray diffraction pattern of xylan from beechwood.

We investigated several variables that influence hemicellulose hydrolysis–hydrogenation. [Figure 2](#) illustrates the effect of acid and hydrogen source on the xylitol yield. Interestingly, phosphotungstic acid, silicotungstic acid, and lactic acid all gave high xylitol yields with Ru/C as a catalyst and H₂ as a reductant, but the amount of xylitol formed with phosphomolybdic acid was very low. Previous studies indicate that the reaction rate of cellulose hydrolysis depends strongly on acid strength.^{13,50} This should also be the case for hemicellulose. PTA and SWA are strong acids, which leads to their high catalytic activity.⁵⁴ The required acid concentrations are lower than that of lactic acid (see also [Figure 4](#)). Conversely, PMA is a weaker acid and is less stable than PTA and SWA.⁵⁴ This can explain its lower activity.

Alcohols can act as transfer hydrogenation agents in the presence of Ru/C. So, we used isopropanol as the hydrogen source (4 mL was added to 4 mL of water and the reactor

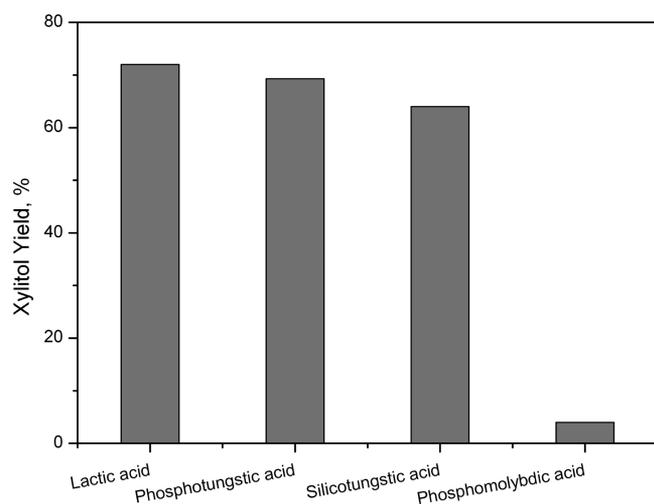


Figure 2. Yield of xylitol with Ru/C and different acids. Reaction conditions: beechwood xylan (0.075 g); Ru/C (0.025 g); water (8.0 mL); 140 °C, 3 h; heteropolyacid (4.34 mmol/L); lactic acid (1000 mmol/L), H₂ (20 bar).

pressurized with 20 bar argon). A high xylitol yield (82%) was obtained in this case using phosphotungstic acid as the acid catalyst. In contrast, the performance of lactic acid depends on the hydrogen source. Lactic acid combined with isopropanol gave merely ~20% xylitol, while H₂ gave ~70% xylitol. This may be explained by the fact that lactic acid can undergo esterification with isopropanol, losing its catalytic activity.

Elsewhere, using alcohols as hydrogen sources for converting cellulose gave a maximum yield of sorbitol and mannitol of ~45% after 18 h at 190 °C.⁵⁵ The higher yields under milder conditions in our experiments show that hemicellulose undergoes hydrolysis–hydrogenation more easily.

We also tested formic acid as a potential hydrogen source. However, no xylitol was formed (these reactions were run using an excess of formic acid equivalent to the amount of hydrogen at 20 bar, phosphotungstic acid as acid catalyst, and 10 bar argon, *T* = 140 °C).

Subsequently, we ran further tests to check the influence of the reaction time and temperature. These tests were conducted under H₂ pressure. The reaction temperature influences the xylitol production (Figure 3). At 140 °C, the reaction was completed after 1 h. Yield remained stable at longer reaction times. Increasing the temperature to 160 and 180 °C lead to faster xylitol formation (~70% yield in merely 5 min). Both lactic and phosphotungstic acid gave similar reaction profiles at 140 °C. We therefore assume that the temperature influence is similar for both acids.

Qualitatively, this reaction has different stages: First, the xylan polymer is hydrolyzed into oligomers. Second, the oligomers are hydrolyzed into xylose. Then xylose is hydrogenated to xylitol. Xylose and xylitol can undergo degradation, which is more likely with the former. The xylitol yield reaches a maximum with full oligomer and xylose conversion. Faster xylitol formation at higher temperatures is likely to be due to improved xylan hydrolysis. Xylitol forms very fast as soon as xylose is present. Sugar hydrogenation is known to be very fast even in milder conditions and mostly dependent on sugar concentration. Indeed, in a control experiment with pure xylose we obtained 100% xylitol at 140 °C after 5 min. This indicates that hydrolysis is the rate-limiting step. Experiments at lower temperatures showed that xylan conversion starts between 100

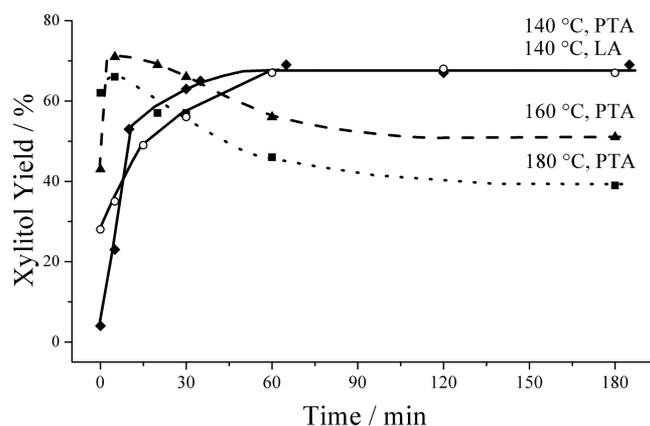


Figure 3. Xylitol yield versus reaction time using phosphotungstic acid (squares) and lactic acid (circles) at 140 °C, 160 °C, 180 °C. Reaction conditions: xylan (0.075 g); Ru/C (0.025 g); water (8.0 mL); phosphotungstic acid (0.100 g) or lactic acid (600 μL), 140 °C, 20 bar H₂.

and 120 °C. At 120 °C, the xylitol yield was 20% (see graph S1 in Supporting Information). As soon as the temperature reaches 160 °C, xylan is already fully converted giving maximum xylitol yields. Considering the heating rate of 7 deg/min, xylitol reaches a maximum after 30 min total heating time. These results show that operating at low temperatures is desirable for stable xylitol yields. They also suggest that hydrolysis routes requiring high temperatures, such as reversible acid formation in water above 200 °C, may be unsuitable for selective xylitol production.

Besides the temperature, the concentration of hydronium ions may influence xylan hydrolysis. We therefore tested different concentrations of phosphotungstic acid (50–100 mg corresponding to 2.17–4.34 mmol/L) and lactic acid (50–600 μL corresponding to 84–930 mmol/L). We measured the pH of the reaction mixture, at ambient temperature and pressure, before commencing the reaction. Figure 4 shows the influence of the acid concentration and the related pH on xylitol formation. Interestingly, the minimal acid loading of lactic acid and phosphotungstic acid corresponded to the same pH range of 2.1–2.2. A further decrease leads to a drop of xylitol yield. Indeed, hemicellulose hydrolysis strongly depends on the H⁺ concentration. As phosphotungstic acid is a super acid (−13.6 Hammett acidity⁴³), a concentration of only 3.04 mM gives a proton concentration of 6.6 mM. Without acid, only negligible xylose was detected.

We also did the reactions at lower lactic acid concentrations. Figure 5 shows the yield of xylitol at 1, 3, and 5 h at 160 °C. The highest yield (92%) was obtained at a concentration of 6 g/L (66.6 mmol/L) for 5 h. Hemicellulose was completely converted at this time. Importantly, up to 77% yield was obtained with concentration as low as 2 g/L (22.2 mmol/L). At longer reaction times xylitol yield decreased, and degradation products increased. When we used a lower xylan/Ru ratio (75 mg xylan, 10 mg Ru/C), we observed a 15% drop in xylitol yield.

To test the stability of the Ru/C catalyst when using lactic acid, it was recovered by centrifugation after the first reaction cycle, washed with 10 mL water, and dried for 12 h at 120 °C. The Ru/C catalyst demonstrated excellent recyclability in this reaction (Figure S6 in Supporting Information). After five consecutive runs, we could not detect any deactivation. We also

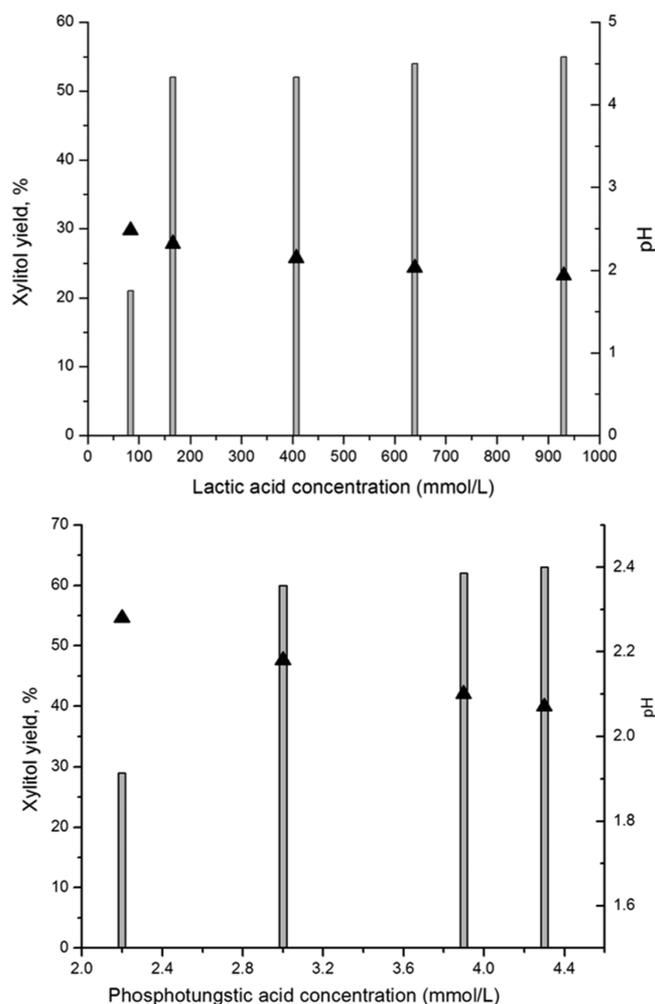


Figure 4. Yield of xylitol depending on pH at different loadings of lactic and phosphotungstic acid. The pH (represented by the filled triangle) was measured for the different acid loadings at standard conditions. Reaction conditions: xylan (0.075 g); Ru/C (0.025 g); water (8.0 mL); phosphotungstic acid (0.050 g, 0.070 g, 0.090 g, 0.100 g)/lactic acid (50 μ L, 100 μ L, 250 μ L, 400 μ L, 600 μ L), 160 °C, 20 bar H₂, 3 min.

tested for ruthenium leaching using ICP after reaction. The aqueous reaction solution of each cycle contained ppm levels of ruthenium; however, this was also present in an independent analysis of raw xylan (Supporting Information). This indicates that the recycled Ru/C remains active which is in good agreement with literature reports.^{41,56} Moreover, X-ray diffraction patterns of the fresh and the used catalyst did not show any major difference (Supporting Information). We also studied the recyclability test with PTA, which confirmed the catalyst stability. The catalyst needs to be washed and dried at 120 °C for 10 h before reuse. The ICP measurements did not show any leaching of Ru for PTA either.

CONCLUSIONS

We showed that one-pot hydrolysis and hydrogenation of hemicellulose using a combination of heteropoly or organic acid and Ru on carbon is an efficient approach for converting beechwood xylan into xylitol. The type of acid, concentration of the acid, reaction temperature, and reaction time influence the xylan conversion significantly. Among heteropoly acids, both silicotungstic and phosphotungstic acids were active. Lactic

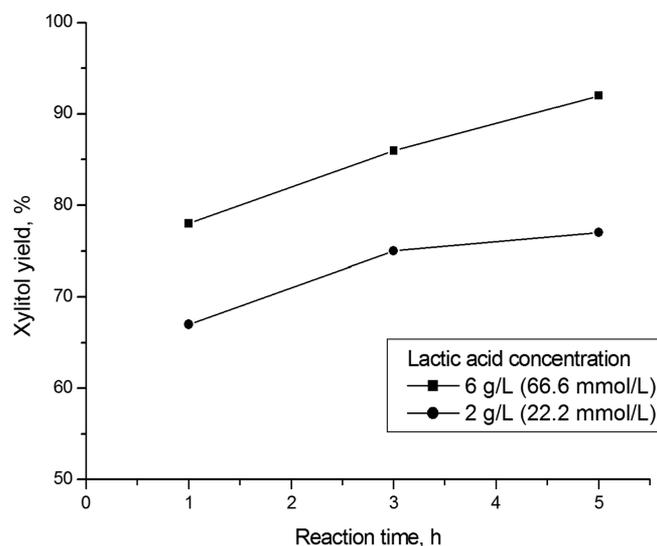


Figure 5. Xylitol yield as a function of reaction time using 6 and 2 g/L of lactic acid for the hydrogenolysis reaction. Reaction conditions: xylan (0.075 g); Ru/C (0.025 g); water (8.0 mL); 160 °C; 20 bar H₂.

acid, which can be produced from biomass, was also active for this conversion. Efficient hydrogenation can be achieved either with H₂ or isopropanol as the reductant when heteropoly acids were used as acid catalysts. However, lactic acid was not very active as catalyst when isopropanol is used as reductant, probably due to the esterification side reaction. Our approach gives high yields of xylitol in short times using water as a solvent and eco-friendly reagents. This makes it a viable alternative for converting hemicellulose directly into valuable platform chemicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.6b00169.

Xylitol yield at different temperatures for phosphotungstic acid, calibrations, overview of products, X-ray diffraction patterns of fresh and spent Ru/C catalysts, and ICP analysis of reaction solution (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the National Council of Science and Technology, Mexico (Consejo Nacional de Ciencia y Tecnología CON-ACyT) for financial support (Scholarship 216968) for C.H.M.

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