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One-Pot Selective Conversion of Hemicellulose (Xylan) to Xylitol under Mild Conditions

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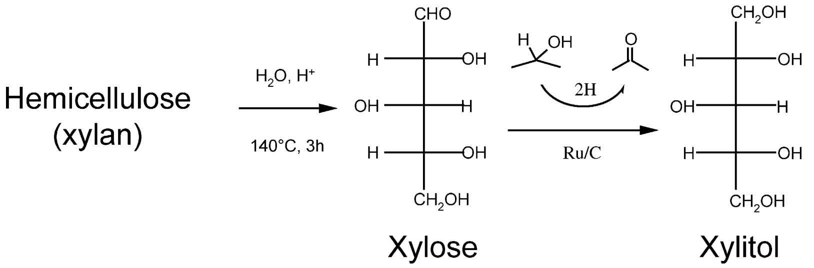
The conversion from biomass to value-added bulky chemicals has attracted increasing attention due to its renewable source and the depletion of fossil-fuel resources.[1,2] Xylitol, a five-carbon sugar alcohol with high sweetening power, was listed in the top 11 high-value chemicals from biomass by the US Department of Energy.[3] Compared to white sugar (sucrose), it is 1.2 times sweeter and contains 40 % less calories.[4] It is safe for diabetics and is approved for use in food by many countries and organizations including the U.S. Food and Drug Administration,[5] the European Union, and the World Health Organization.[6]

Industrially, xylitol is produced by the reduction of pure xylose, obtained from acidic hydrolysis of xylan-containing products such as hardwoods or corn cobs.[7] This process contains multiple steps, including the production of xylose by acid decomposition of xylan-containing natural products, concentrating the hydrolysis solution to remove impurities, catalytic hydrogenation of xylose to xylitol under high-pressure H_2 gas (up to 50 atm) at elevated temperatures, and the consequent purification and isolation. This entire chemical process is laborious, cost- and energy-intensive and environmentally unfriendly. The final yield of xylitol obtained from such a process only corresponds to about 50–60 % of xylan present in the raw materials.[8] All these factors have contributed to the higher cost of xylitol compared to sugar and the consequently smaller share in the huge market.[9]

Intensive research has been initiated for economically viable and eco-friendly alternative strategies for the production of xylitol.[8–10] However, most of the research activities have focused on the bioconversion of xylose that has been obtained by the hydrolysis of xylan-containing products to xylitol by employing specific microbial strains for fermentation. A considerable number of bacteria, fungi and yeasts were found to produce xylitol from xylose.[10d,11] Despite all these efforts, such methods have not yet been able to replace the current chemical process.[9a] Consequently, there is an urgency to develop a cost-efficient and green chemical process for the transformation.

The main challenge for the current industrial process of xylitol production is the multi-step operation and the high-pressure hydrogenation reaction process. In contrast to the less developed hemicellulose hydrolysis/hydrogenation process,[12] the process for cellulose hydrolysis/hydrogenation has been widely studied and well documented.[13] Most of the protocols reported in literature employ the use of acids/transition metal catalysts or bifunctional catalysts for the cellulose hydrolysis/hydrogenation under high pressures of hydrogen gas.[14] Recently, Fukuoka et al.[15] reported an alternative protocol by using alcohol as hydrogen source, with a hydrogen transfer reaction to convert cellulose to sorbitol and mannitol. The reaction conditions included the treatment of cellulose at a temperature of 190 °C for 18 h, generating a maximum yield of sorbitol and mannitol of ~45 %. Inspired by this work, herein, we have developed a one-pot process for the selective catalytic conversion of hemicellulose to xylitol via a hydrogen transfer reaction. Xylitol of high purity was produced with a yield of >80 % under mild conditions (140 °C, 3 h). Instead of using the high-pressure H_2 gas currently utilized by industrial processes,[7,10c,16] isopropanol was used as the hydrogen source in the presence of Ru/C catalyst. This one-pot simple process converts hemicellulose into xylitol in high yields under mild reaction conditions and represents a cost- and energy-efficient method. The reaction is illustrated in Scheme 1.

The reaction conditions were optimized to pursue high catalyst and engineering efficiency. Firstly, it was found that the reaction temperature is crucial to the yield of xylitol production. As shown in Figure 1, the xylitol yield increased almost linearly with the increase in temperature, in the range of 100 °C to 140 °C, in which a higher xylitol yield was obtained with higher temperature. At 140 °C and 150 °C, the xylitol yield reached a plateau, and beyond a reaction temperature of 150 °C, the yield of xylitol decreased. In addition, the conversion of hemicellulose was also increased as the reaction temperature in-



Scheme 1. One-pot transfer hydrogenation of xylan to xylitol in isopropanol.

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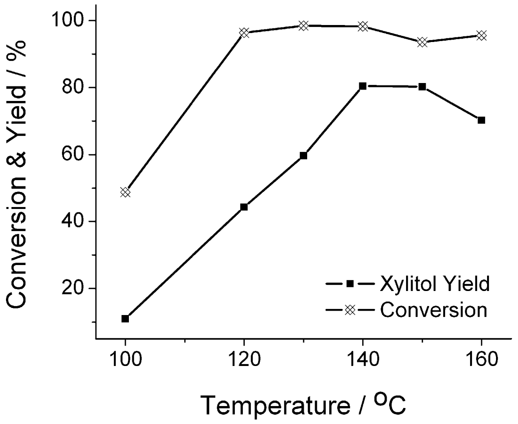


Figure 1. Production yield of xylitol vs. reaction temperature. Reaction conditions: 75 mg hemicellulose (xylan, 0.513 mmol D-xylose units), 25 mg Ru/C (2.4 mol %), 4 mL water, 4 mL isopropanol, 7 μL H_2SO_4 (0.126 mmol, 49.2 mol % H^+), in 10 mL Teflon-lined hydrothermal reactor for 14 h.

creased, but reached a plateau at 120 °C. The reaction temperature was then fixed at 140 °C for the subsequent experiments.

Kinetic studies showed that the reaction was almost complete in 3 h, with a high xylitol yield of 83 % (Figure 2). The xylitol yield remained stable at about the same value for reaction times varying from 3 to 8 h but started to decline slightly as the reaction time was extended beyond 8 h.

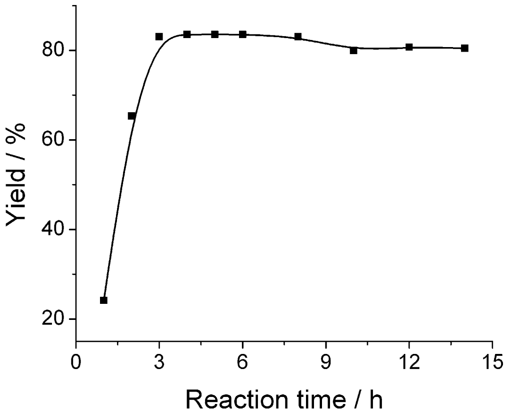


Figure 2. Production yield of xylitol vs. reaction time at 140 °C. Reaction conditions: 75 mg hemicellulose, 25 mg Ru/C, 4 mL water, 4 mL isopropanol, 7 μL H_2SO_4, in 10 mL Teflon-lined hydrothermal reactor.

In our reaction system, a mixture of water and isopropanol was employed as solvent. Water plays an important role in the hydrolysis of hemicellulose to the D-xylose monomer, and the isopropanol provides the hydrogen source for the transfer hydrogenation reduction of xylose to xylitol in the presence of the Ru/C catalyst.[15] In our system, the ratio of water and isopropanol was also optimized, as shown in Table 1. In the case of pure water or pure isopropanol as solvent, only a small amount of xylitol was formed. However, when a water and isopropanol mixture was used as solvent, the yield of xylitol was significantly increased. Table 1 shows that if the ratio of water to isopropanol was in the range from 7:1 to 1:3, no significant change in the xylitol yield was observed. This tolerance to a broad range of solvent composition is important for practical applications, as well as for solvent recycling.[17] In fact, a reaction with a larger scale (375 mg hemicellulose) was carried out under the same conditions in a 50 mL Teflon-lined hydrothermal reactor and 313.3 mg of isolated xylitol (80.3 %) was obtained. Reaction with recycled isopropanol[17] was also carried out with the standard reaction procedure without any detriment to the reaction yield, as 81.8 % yield of xylitol was obtained.

Table 1. Effect of the water-to-isopropanol ratio on the xylitol yield.[a]

Entry	Water [mL]	*Iso*-PrOH [mL]	Xylitol [mg (%)]
1	8	0	8.62 (11.1)
2	7	1	61.4 (78.7)
3	6	2	62.8 (80.5)
4	4	4	64.8 (83.0)
5	2	6	62.8 (80.5)
6	1	7	46.8 (60.0)
7	0	8	9.84 (12.6)

[a] Reaction conditions: 75 mg hemicellulose, 25 mg Ru/C, water, isopropanol, 7 μL H_2SO_4, in 10 mL Teflon-lined hydrothermal reactor, 140 °C for 3 h.

In the current one-pot system, the detailed process includes a two-step cascade reaction. The first step is acid-catalyzed hemicellulose hydrolysis to xylose, followed by a Ru-catalyzed transfer hydrogenation reaction to convert xylose to xylitol. Although different types of acid additives have been used in biomass hydrolysis,[1,13d,18] we found that a small amount of H_2SO_4 is crucial to convert hemicellulose to xylitol in our system. Without acidic additives the xylitol yield is only 5.7 %, as shown in Figure 3. As a small amount of acid was added, the xylitol yield significantly increased. Moreover, the xylitol yield reached a maximum as 7 μl of 96 % H_2SO_4 (equal to 0.17 % *w/w*, 49.2 mol % H^+) was applied, as shown in Figure 3. An excess amount of acid led to a decrease in the xylitol yield. The optimized conditions with 7 μl of 96 % H_2SO_4 in 8 mL of mixture solvent (pH ~ 2) for the reaction at 140 °C is comparable to the extremely low acid (ELA) conditions (a system with pH 2.2, for reaction at > 200 °C) defined by the National Re-

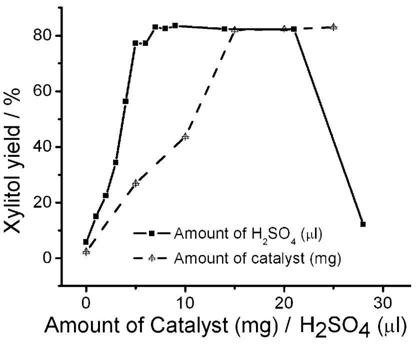


Figure 3. Production yield of xylitol vs. the amount of H_2SO_4 and catalyst added. Reaction conditions: 75 mg hemicellulose, Ru/C, 4 mL water, 4 mL isopropanol, H_2SO_4, in 10 mL Teflon-lined hydrothermal reactor, 140 °C for 3 h.

newable Energy Laboratory (USA).[19] It could be considered as a green technology, since the corrosive characteristics of ELA are close to those of neutral aqueous reactions and the standard-grade stainless steel equipment can be used instead of high-nickel alloys.[19]

Other acids were also screened in this process. An equivalent amount of HCl was used to replace H_2SO_4, and to our surprise, only a negligible amount of xylitol was detected. Instead, a high yield of xylose was observed, indicating that hemicellulose has been hydrolyzed into xylose, but under HCl conditions, xylose was not able to further convert to xylitol. This may be due to the existence of Cl^- ions that quenched the activity of the Ru/C catalyst in the transfer hydrogenation step, as reported by Fukuoka et al.[16a] When H_2SO_4 was used, almost all the xylose was converted to xylitol. We also ran experiments using an equivalent amount of solid acid (Amberlyst-15), and the resulting xylitol yield was 36.1 %. When the amount of Amberlyst-15 was doubled, the yield of xylitol reached 47.9 %. Further increments in the amount of solid acid led to a decrease in xylitol yield, as shown in Table S1 of the Supporting Information.

Ruthenium supported on active carbon (Ru/C, Aldrich, 5 wt %) was selected as catalyst. To test the optimimal catalyst loading, a set of reactions were conducted, as shown in Figure 3. Without the Ru catalyst, negligible xylitol was detected, and xylose was observed instead. When the catalyst loading was increased, the xylitol yield increased steadily and reached a maximum at a catalyst loading of 15 mg. Further increases in the amount of catalyst to 20 mg and 25 mg resulted in small increments in the xylitol yield. As comparison, other heterogeneous catalysts, such as Pd/C and Raney nickel, were also tested in this reaction. However, no catalytic activity was observed for either the Pd/C or Raney nickel catalysts (Supporting Information, Table S2).

To test the durability of the Ru/C catalyst, it was recovered by centrifugation after the first reaction cycle. The recycled catalyst was directly used in the next reaction run. As shown in Figure 4, the Ru/C catalyst demonstrated excellent recyclability in this reaction. There is no significant deactivation observed when the catalyst was reused for five consecutive runs. After five rounds of reaction, the Ru/C catalyst was also characterized by TEM (Supporting Information, Figure S1), and no obvious changes were observed for the morphology and particle size of the Ru nanoparticles when compared to the fresh catalyst. This result indicates that the current reaction conditions are rather mild and that the Ru/C catalyst is stable and recyclable under these process conditions.

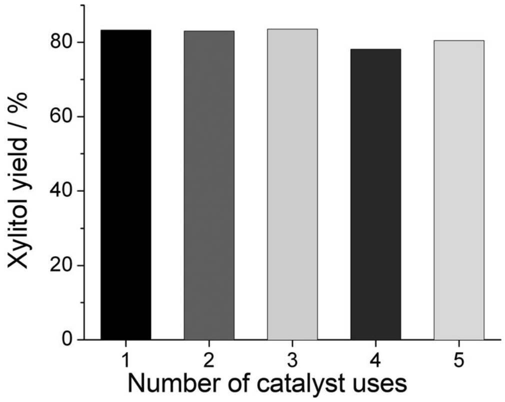
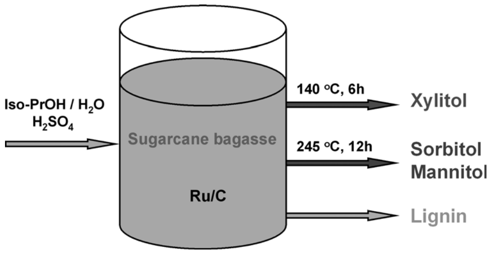


Figure 4. Durability of Ru/C catalyst. Reaction conditions: 75 mg hemicellulose, 25 mg Ru/C, 4 mL water, 4 mL isopropanol, 7 µL H_2SO_4, in 10 mL Teflon-lined hydrothermal reactor, 140 °C for 3 h.

The reaction pathway for this process is rather straightforward. Hemicellulose is first hydrolyzed into xylose under acidic conditions. Following with that, xylose is converted to xylitol by Ru catalyzed hydrogen transfer reaction (Scheme 1). During this hydrogen transfer process, 1.8 % of isopropanol (0.94 mmol) was converted to acetone, which is more than two times the yield of xylitol (64.8 mg, 0.426 mmol). This Figure was much lower than the hydrogen transfer from cellulose to sorbitol and mannitol as reported by Fukuoka et al (22 times),[15] indicating the milder reaction conditions and higher hydrogen transfer efficiency in our reaction.

Hemicellulose is the second-most common polysaccharide in nature and represents about 20–35 % of lignocellulosic biomass, while cellulose and lignin makes up the remaining percentage. It is well known that both hemicellulose and cellulose can be hydrolyzed under different acidic conditions.[19] The mild conditions applied in our one-pot conversion of hemicellulose to xylitol provide an interesting opportunity for the selective conversion of hemicellulose, over cellulose or lignin in raw biomass.[20] To test the selectivity of hemicellulose over cellulose, 75 mg of mixture (37.5 mg hemicellulose and 37.5 mg cellulose) was put into the reactor and kept at 140 °C for 3 h. To our delight, the hemicellulose was efficiently converted to xylitol in more than 80 % yield, while the cellulose remained unreacted (100 % recovered). Cellulose was not hydrolyzed under these conditions, mainly due to its robust crystal structure. Inspired by this result, a one-pot step-by-step selective conversion of hemicellulose and cellulose in raw biomass to polyols process is proposed, as shown in Scheme 2.

Sugarcane bagasse is abundant waste biomass and has balanced components of both hemicellulose and cellulose (~25 % hemicellulose, ~42 % cellulose with lignin in the remaining percentage.).[21] It was selected as an example of a raw-material feedstock to demonstrate the one-pot selective conversion process proposed in Scheme 2. In the initial test, 75 mg of sugarcane bagasse was treated in a reactor, under standard conditions for 3 h. Trace amounts of xylitol was detected in the reac-



Scheme 2. One-pot step-by-step selective conversion of sugarcane bagasse to different products.

tion system and xylose was detected as the major product. A possible reason for the minimal conversion to xylitol includes the buffering capacity of the extraneous lignin in the lignocellulosic biomass for acids, which would hinder the hydrolysis process.[19] We subsequently doubled the reaction time to 6 h. At this stage, 15.4 mg (80.4 %) xylitol (containing a small amount of arabinitol)[10c] was obtained and almost no xylose remained. Most importantly, there was only a negligible amount ($<$1 %) of sorbitol/mannitol products observed in the first step of the reaction (Supporting Information, Table S3), indicating the high selectivity of the first step of the reaction towards hemicellulose. Lignin was also extracted into the isopropanol/water phase and it was precipitated as the isopropanol was removed in vacuo.[22] 4 mL water, 4 mL isopropanol, 7 µl H_2SO_4 were then added to the residual solids (57.7 mg, including cellulose and solid Ru/C catalyst) and the mixture was heated to 245 °C for 12 h,[23] resulting in sorbitol and mannitol yields of 21.1 % (Supporting Information, Table S3). Although this system is less efficient for the transformation of cellulose to the corresponding polyols, it demonstrated the excellent possibility for the one-step separation of the three main components of plant biomass by the selective conversion of hemicellulose to xylitol, with the conversion of the remaining cellulose to related polyols in one pot under mild conditions.

In summary, a one-pot catalytic conversion of hemicellulose (xylan) to xylitol via a hydrogen transfer reaction was developed. Xylitol of high purity was produced with a yield of $>$80 % under mild conditions (140 °C, 3 h). Instead of using high-pressure H_2 gas similar to current industry processes, isopropanol was used as the hydrogen source in the presence of a Ru/C catalyst. Furthermore, a selective step-by-step conversion of hemicellulose and cellulose to different polyols in a one-pot process was also developed. With this process, sugarcane bagasse was converted into xylitol, sorbitol and mannitol, and lignin. This method not only improves on the current industry process for xylitol synthesis, with a simple, one-pot process with mild conditions and higher resultant yields, it also provides new insight in the conversion of biomass in a more efficient and complete way.

Experimental Section

Materials

Hemicellulose (Beechwood xylan) was purchased from Sigma–Aldrich (96.6 % purity, containing 6.5 wt % physisorbed water). The hemicellulose was used directly without any pre-treatment. Sugarcane bagasse was ball-milled for 1 h. D-Xylose ($\geq$99 %), xylitol ($\geq$99 %), Ru/C (5 wt % metal), Amberlyst-15 resin, and cellulose were purchased from Sigma–Aldrich. Isopropanol (HPLC grade) was from J. T. Baker. Sulfuric acid (95–97 %), hydrochloric acid (37 %), Pd/C, and Raney nickel were purchased from Merck and used as received.

General reaction procedure

The conversion of hemicellulose was conducted in a 10 mL Teflon-lined hydrothermal reactor. The reactor was charged with 75 mg hemicellulose, 25 mg Ru/C catalyst, 4 mL water, 4 mL isopropanol, and 7 µL of H_2SO_4, and the reactor was purged with N_2 before sealing. The reactor was heated to 140 °C in a silicon-oil bath and was maintained at this temperature for 3 h with magnetic stirring (600 rpm). After the reaction, the reactor was left to cool on its own.

Product analysis

After reaction, the reaction mixture was separated by filtration. The remaining solid (Ru/C catalyst and the unreacted hemicellulose) were dried and weighed after washing with water. The xylitol yield was analyzed by using a sugar analyzer (DKK-TOA Corporation, Japan. Model: SU-300) and was further confirmed with isolated yield (Supporting Information). The sugar analyzer was operated in sugar alcohol mode, with a xylitol standard solution for calibration. Testing conditions: mobile phase: 200 mM NaOH, 0.5 mL min^{-1}, 39.9 °C.

Characterization

The xylitol product was characterized by ^{1}H and ^{13}C NMR (Bruker AV-400). The Ru/C catalyst was characterized by TEM (FEI Tecnai F20). NMR and TEM spectra are in the Supporting Information (Figures S1 and S2).

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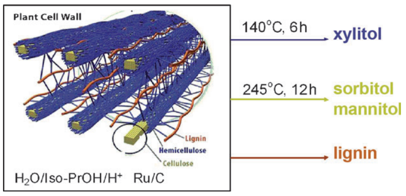
One-Pot Selective Conversion of Hemicellulose (Xylan) to Xylitol under Mild Conditions



Something from nothing: Hemicellulose is selectively converted into valuable xylitol via a mild hydrogen transfer reaction, with a xylitol yield above 80%. Instead of using high-pressure H_2, isopropanol is used as hydrogen source in the presence of a Ru/C catalyst. Furthermore, a selective step-by-step conversion of hemicellulose and cellulose to different polyols in a one-pot process is described.

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