

SYNTHESIS OF SHORTER CHAIN POLYOLS

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TECHNICAL FIELD

[0001] The present invention relates generally to the catalytic synthesis of shorter chain polyols, including sorbitol and 1,2,5,6-hexanetetrol (HTO), from soluble cellulose, in the absence of a homogeneous acid or zeolite.

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BACKGROUND OF THE INVENTION

[0002] Methods of synthesizing sorbitol from cellulose are well known. Fukuoka et al. reported that sugar alcohols could be prepared from cellulose using supported platinum or ruthenium catalysts, which showed high activity for the conversion of cellulose into sugar alcohols with the choice of support material being important. Fukuoka et al., Catalytic Conversion of Cellulose into Sugar Alcohols, 118 Agnew. Chem. 5285-87 (2006). The mechanism involves the hydrolysis of cellulose to glucose followed by the reduction of glucose to sorbitol and mannitol.

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[0003] More recently, Verendel et al. reviewed one-pot conversions of polysaccharides into small organic molecules under a variety of conditions. Verendel et al., Catalytic One-Pot Production of Small Organics from Polysaccharides, 11 Synthesis 1649-77 (2011). Hydrolysis-by-hydrogenation of cellulose under acidic conditions and elevated pressure was disclosed as yielding up to 90% sorbitol, although these processes were categorized as “by no means simple.” The direct hydrolysis-hydrogenation of starch, inulin, and polysaccharide hydrolysates to sugar alcohols by supported metals under hydrogen without the addition of soluble acids was also disclosed. Ruthenium or platinum deposited on aluminas, a variety of metals supported on activated carbon, and zeolites were reported as suitable catalysts for cellulose degradation. The effect of transition-metal nanoclusters on the degradation of cellobiose was also disclosed, with acidic conditions yielding sorbitol. A different study looked at the conversion of cellulose with varying crystallinity into polyols over supported ruthenium catalysts, with ruthenium supported on carbon nanotubes giving the best yield of 73% hexitols.

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[0004] There remains a need for cost-effective methods of producing shorter chain polyols, including sugar alcohols, from cellulose with high selectivity and through alternate pathways.

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SUMMARY OF THE INVENTION

[0005] The present invention relates in one aspect to a method of synthesizing shorter chain polyols comprising reacting a feed solution comprising at least one component with a high degree of polymerization with hydrogen in the presence of at least one catalyst; wherein a homogeneous mineral acid is not added; thus making at least one shorter chain polyol.

[0006] The present invention relates in another aspect to a method of hydrolyzing polysaccharides comprising contacting a feedstock comprising a sugar concentration of about 3% with a catalyst in the presence of hydrogen; wherein the feedstock further comprises at least one component with a degree of polymerization (DP) number above 3; wherein a homogeneous mineral acid is not added; resulting in formation of at least one shorter chain polyol and a decrease in the at least one component with a DP number above 3.

[0007] The present invention relates in yet another aspect to a method of selectively producing sorbitol comprising contacting a feed solution with a catalyst in the presence of hydrogen; wherein the feed solution comprises a compound selected from the group consisting of soluble cellulose, starch, maltodextrin, maltitol, and combinations of any thereof; wherein a homogeneous mineral acid is not added; thus producing a product with a higher proportion of sorbitol as compared to other compounds formed.

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BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 shows a scheme for the synthesis of sorbitol from starch or maltodextrin feed (high degree of polymerization [DP] feed) using a ruthenium-sulfur supported on carbon (Ru-S/C) catalyst and a copper (Cu) catalyst.

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[0009] Figure 2 shows a scheme for DP hydrolysis (hydrolysis of high degree of polymerization compounds, such as maltitol) and sugar hydrogenation (formation of sorbitol and 1,2,5,6-hexanetetrol [HTO]).

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE
INVENTION

[0010] In an illustrative embodiment, a method of the present invention
5 includes synthesizing shorter chain polyols comprising reacting a feed solution
comprising at least one component with a high degree of polymerization with hydrogen
in the presence of at least one catalyst; wherein a homogeneous mineral acid is not
added; thus making at least one shorter chain polyol.

[0011] In another illustrative embodiment, a method of the present invention
10 includes hydrolyzing polysaccharides comprising contacting a feedstock comprising a
sugar concentration of about 3% with a catalyst in the presence of hydrogen; wherein
the feedstock further comprises at least one component with a degree of polymerization
(DP) number above 3; wherein a homogeneous mineral acid is not added; resulting in
formation of at least one shorter chain polyol and a decrease in the at least one
15 component with a DP number above 3.

[0012] In yet another illustrative embodiment, a method of the present
invention includes selectively producing sorbitol comprising contacting a feed solution
with a catalyst in the presence of hydrogen; wherein the feed solution comprises a
compound selected from the group consisting of soluble cellulose, starch, maltodextrin,
20 maltitol, and combinations of any thereof; wherein a homogeneous mineral acid is not
added; thus producing a product with a higher proportion of sorbitol as compared to
other compounds formed.

[0013] In a further embodiment, the at least one component with a high degree
of polymerization is selected from the group consisting of cellulose, polysaccharides,
25 starch, maltodextrin, maltitol, and combinations of any thereof. In yet a further
embodiment, the at least one component with a high degree of polymerization is present
in the feed solution in an amount greater than about 0.5%. In still a further embodiment,
the at least one component with a high degree of polymerization has a degree of
polymerization (DP) number above 3.

30 [0014] The present invention contemplates various feed solutions and feed
stocks. In a further embodiment, the feed solution further comprises a sugar
concentration of about 3%. In a further embodiment, the feedstock further comprises a

compound selected from the group consisting of maltodextrin, soluble cellulose, maltitol, and combinations of any thereof. In yet further embodiments, the feed solution or feedstock further comprise a solvent. In still a further embodiment, the solvent comprises water.

5 **[0015]** In a further embodiment, the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen gas in the presence of the at least one catalyst is carried out at a pressure of about 1200 psi. In a further embodiment, the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out at a pressure of
10 about 1200 psi. In a further embodiment, the contacting the feed solution with the catalyst in the presence of hydrogen is carried out at a pressure of about 1200 psi.

[0016] The present invention contemplates different catalysts, including sponge copper, Ru-S/C (sulfide-ruthenium supported on carbon), and combinations of any thereof.

15 **[0017]** In a further embodiment, the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen in the presence of the at least one catalyst further comprises reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen in the presence of a first catalyst at a first temperature, thus forming a first
20 product; and reacting the first product in the presence of a second catalyst at a second temperature, thus making the at least one shorter chain polyol. In yet a further embodiment, the first catalyst consists of Ru-S/C. In still a further embodiment, the first temperature is 120°C. In yet a further embodiment, the second catalyst consists of copper. In still a further embodiment, the second temperature is 200°C.

25 **[0018]** In a further embodiment, the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen gas in the presence of the at least one catalyst is carried out at a temperature of below about 225°C. In yet a further embodiment, the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen gas in the
30 presence of the at least one catalyst is carried out at a temperature of between about 100°C and about 223°C. In a further embodiment, the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of

hydrogen is carried out at a temperature of below about 225°C. In yet a further embodiment, the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out at a temperature of between about 100°C and about 223°C. In a further embodiment, the contacting the feed solution with the catalyst in the presence of hydrogen is carried out at a temperature of below about 225°C. In yet a further embodiment, the contacting the feed solution with the catalyst in the presence of hydrogen is carried out at a temperature of between about 100°C and about 223°C.

[0019] In a further embodiment, the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out by a process selected from the group consisting of a batch process and a continuous process.

[0020] In a further embodiment, the at least one shorter chain polyol comprises a compound selected from the group consisting of sorbitol, mannitol, glucitol, dulcitol, 1,2,5,6-hexanetetrol, and combinations of any thereof.

[0021] In a further embodiment, the product comprises at least 25% sorbitol.

[0022] In a further embodiment, the product comprises less than about 1% C5 polyols.

[0023] Referring now to the drawings, various schema are provided for methods of synthesizing shorter chain polyols according to the present invention, for hydrolyzing polysaccharides according to another aspect, and for selectively synthesizing sorbitol according to yet another aspect. Thus, in Figure 1, a scheme for the synthesis of sorbitol from starch, or at least one component with a high degree of polymerization [DP], feed using a Ru-S/C catalyst and a copper (Cu) catalyst is shown. The starch or at least one component with a high DP feed is reacted in the presence of hydrogen and the Ru-S/C catalyst at 120°C, forming a first product. The first product is then reacted in the presence of the copper catalyst at 200°C, thus producing sorbitol.

[0024] In Figure 2, a scheme for DP hydrolysis (hydrolysis of at least one component with a high degree of polymerization, such as maltitol) and sugar hydrogenation (formation of 1,2,5,6-hexanetetrol [HTO]) is shown. Maltitol is reacted with hydrogen in the presence of a copper catalyst. Because the catalyst is bi-functional,

it can be used for both the hydrolysis and the hydrogenation, resulting in sorbitol and HTO.

[0025] The present invention is more particularly illustrated by the following non-limiting examples:

- 5 **[0026]** Example 1: Aliquots of a feed stock solution containing 3% sugars and 1% compounds with a high DP number (greater than 3) in a solvent (preferably water), H₂ at 1200 psi, and a sponge copper catalyst were combined for reaction in a 1 liter (L) batch reactor at a number of reaction temperatures. The effects that temperature had on the hydrolysis/hydrogenation were tested.

- 10 **[0027]** Table 1: Temperature Effects on Hydrolysis/Hydrogenation

Temp (°C)	Sugar conc. (%)	C5 polyols (%)	Sorbitol(%)	DP (%)
0	2.88	0.44	25.1	0.8
223	0	0.72	21.7	0
205	0	0.56	25.9	0

- [0028]** Table 2: Temperature Effects on Hydrolysis/Hydrogenation

Temp (°C)	Sugar conc. (%)	C5 polyols (%)	Sorbitol(%)	DP (%)
0	2.88	0.42	23.7	0.69
150	0.01	0.47	28.2	0.51
100	2.2	0.43	25.5	0.59

- 15 **[0029]** It was thus determined that sponge copper catalysts can catalyze the hydrolysis of compounds with a high DP number and can reduce sugars to sugar alcohols under a range of temperatures, with good selectivity for producing sorbitol.

- 20 **[0030]** Example 2: Starch (290 g, J.T. Baker), Ru-S/C catalyst (10.0 g), and water (325.0 g) were introduced into a 1 liter (L) stainless steel autoclave reactor, and the reactor was purged with hydrogen gas (800 psi) three times. The reactor was heated to 225°C with stirring at 1200 rpm. After the reaction, the product was filtered. The filtered water-soluble products were analyzed by high-performance liquid chromatography (HPLC). HTO was produced with high selectivity.

[0031] The present invention has been described with reference to certain examples. However, it will be recognized by those of ordinary skill in the art that various substitutions, modifications, or combinations of any of the examples may be made without departing from the spirit and scope of the invention. Thus, the invention is
5 not limited by the description of the examples, but rather by the appended claims as originally filed.

CLAIMS

What is claimed is:

1. A method of synthesizing shorter chain polyols comprising:

reacting a feed solution comprising at least one component with a high degree
5 of polymerization with hydrogen in the presence of at least one catalyst;

wherein a homogeneous mineral acid is not added;

thus making at least one shorter chain poloyol.
2. The method of claim 1, wherein the at least one component with a high
degree of polymerization is selected from the group consisting of cellulose,
10 polysaccharides, starch, maltodextrin, maltitol, and combinations of any thereof.
3. The method of any of claims 1-2, wherein the feed solution further
comprises a sugar concentration of about 3%.
4. The method of any of claims 1-3, wherein the feed solution further
comprises a solvent.
- 15 5. The method of claim 4, wherein the solvent comprises water.
6. The method of any of claims 1-5, wherein the at least one component
with a high degree of polymerization is present in the feed solution in an amount
greater than about 0.5%.
7. The method of any of claims 1-6, wherein the reacting the feed solution
20 comprising the at least one component with a high degree of polymerization with
hydrogen gas in the presence of the at least one catalyst is carried out at a pressure of
about 1200 psi.
8. The method of any of claims 1-7, wherein the at least one catalyst is
selected from the group consisting of sponge copper, ruthenium-sulfur supported on
25 carbon, and combinations of any thereof.

9. The method of any of claims 1-8, wherein the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen in the presence of the at least one catalyst further comprises:

5 reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen in the presence of a first catalyst at a first temperature, thus forming a first product; and

reacting the first product in the presence of a second catalyst at a second temperature, thus making the at least one shorter chain polyol.

10. The method of claim 9, wherein the first catalyst consists of Ru-S/C.

10 11. The method of any of claims 9-10, wherein the first temperature is 120°C.

12. The method of any of claims 9-11, wherein the second catalyst consists of copper.

15 13. The method of any of claims 9-12, wherein the second temperature is 200°C.

14. The method of any of claims 1-8, wherein the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen gas in the presence of the at least one catalyst is carried out at a temperature of below about 225°C.

20 15. The method of any of claims 1-8, wherein the reacting the feed solution comprising the at least one component with a high degree of polymerization with hydrogen gas in the presence of the at least one catalyst is carried out at a temperature of between about 100°C and about 223°C.

25 16. The method of any of claims 1-15, wherein the at least one shorter chain polyol comprises a compound selected from the group consisting of sorbitol, mannitol, glucitol, dulcitol, 1,2,5,6-hexanetetrol, and combinations of any thereof.

17. The method of any of claims 1-16, wherein the at least one component with a high degree of polymerization has a degree of polymerization (DP) number above 3.

18. A method of hydrolyzing polysaccharides, comprising:

5 contacting a feedstock comprising a sugar concentration of about 3% with a catalyst in the presence of hydrogen;

 wherein the feedstock further comprises at least one component with a degree of polymerization (DP) number above 3;

 wherein a homogeneous mineral acid is not added;

10 resulting in formation of at least one shorter chain polyol and a decrease in the at least one component with a DP number above 3.

19. The method of claim 18, wherein the feedstock further comprises a compound selected from the group consisting of maltodextrin, soluble cellulose, maltitol, and combinations of any thereof.

15 20. The method of any of claims 18-19, wherein the feedstock further comprises a solvent.

21. The method of claim 20, wherein the solvent comprises water.

22. The method of any of claims 18-21, wherein the catalyst is selected from the group consisting of sponge copper, ruthenium-sulfur supported on carbon, and
20 combinations of any thereof.

23. The method of any of claims 18-22, wherein the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out at a pressure of about 1200 psi.

24. The method of any of claims 18-23, wherein the contacting the feedstock
25 comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out at a temperature of below about 225°C.

25. The method of any of claims 18-24, wherein the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out at a temperature of between about 100°C and about 223°C.

5 26. The method of any of claims 18-25, wherein the contacting the feedstock comprising a sugar concentration of about 3% with the catalyst in the presence of hydrogen is carried out by a process selected from the group consisting of a batch process and a continuous process.

10 27. The method of any of claims 18-26, wherein the at least one shorter chain polyol is selected from the group consisting of sorbitol, dulcitol, mannitol, glucitol, 1,2,5,6-hexanetetrol, and combinations of any thereof.

28. A method of selectively synthesizing sorbitol, comprising:

contacting a feed solution with a catalyst in the presence of hydrogen;

15 wherein the feed solution comprises a compound selected from the group consisting of soluble cellulose, starch, maltodextrin, maltitol, and combinations of any thereof;

wherein a homogeneous mineral acid is not added;

thus producing a product with a higher proportion of sorbitol as compared to other compounds formed.

20 29. The method of claim 28, wherein the contacting the feed solution with the catalyst in the presence of hydrogen is carried out at a pressure of about 1200 psi.

30. The method of any of claims 28-29, wherein the contacting the feed solution with the catalyst in the presence of hydrogen is carried out at a temperature of below about 225°C.

31. The method of any of claims 28-30, wherein the contacting the feed solution with the catalyst in the presence of hydrogen is carried out at a temperature of between about 100°C and about 223°C.

5 32. The method of any of claims 28-31, wherein the product comprises at least 25% sorbitol.

33. The method of any of claims 28-32, wherein the product comprises less than about 1% C5 polyols.