clearly demonstrate the need for development of alternative, more efficient processes for the production of HDO.

## SUMMARY

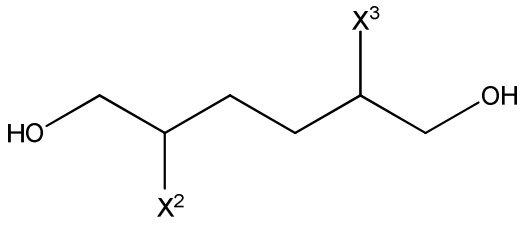
**[0011]** Briefly, therefore, the present ~~invention~~disclosure is directed to processes for preparing hexamethylenediamine from a carbohydrate source by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst to produce 1,6-hexanediol; and, converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. The present ~~invention~~disclosure is also directed to processes for preparing hexamethylenediamine from a carbohydrate source by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce a reaction product comprising 1,2,6-hexanetriol; converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol; and converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. In some ~~embodiment~~examples, the heterogeneous reduction catalyst comprises Pt. In other ~~embodiment~~examples, the heterogeneous reduction catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re. In other ~~embodiment~~examples, the step of converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol is conducted in the presence of hydrogen and a hydrogenation catalyst comprising Pt. In other ~~embodiment~~examples, the yield of 1,6-hexanediol is at least about 40%. In other ~~embodiment~~examples, the yield of 1,6-hexanediol is at least about 50%. In other ~~embodiment~~examples, the yield of 1,6-hexanediol is at least about 60%. In other ~~embodiment~~examples, the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other ~~embodiment~~examples, the furfural substrate is 5-hydroxymethylfurfural. In other ~~embodiment~~examples, the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose. In other ~~embodiment~~examples, the catalyst further comprises a support selected from the group consisting of zirconias, silicas and zeolites. In other ~~embodiment~~examples, the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 100°C and about 180°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other ~~embodiment~~examples, the hydrogenation catalyst comprises Pt and W supported on zirconia. The present ~~invention~~disclosure is also directed to hexamethylenediamine produced by the processes of any of the above ~~embodiment~~examples.

**[0012]** The present ~~invention~~disclosure is also directed to processes for preparing 1,6-hexanediol from a carbohydrate source by converting the carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol. The present ~~invention~~disclosure is also directed to processes for preparing 1,6-hexanediol from a carbohydrate source by converting the carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a Pt containing heterogeneous reduction catalyst to produce a reaction product comprising 1,2,6-hexanetriol; and, converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol. In some ~~embodiment~~examples, the heterogeneous catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re. In other ~~embodiment~~examples, the step of converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol is conducted in the presence of hydrogen and a hydrogenation catalyst comprising Pt. In other ~~embodiment~~examples, the hydrogenation catalyst is a supported heterogeneous catalyst. In other ~~embodiment~~examples, the yield of 1,6-hexanediol from the furfural substrate is at least 40%. In other ~~embodiment~~examples, the yield of 1,6-hexanediol from the furfural substrate is at least 50%. In other ~~embodiment~~examples, the yield of 1,6-hexanediol from the furfural substrate is at least 60%. In other ~~embodiment~~examples, the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other ~~embodiment~~examples, the furfural substrate is 5-hydroxymethylfurfural. In other ~~embodiment~~examples, the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose. In other ~~embodiment~~examples, the catalyst further comprises a support selected from the group consisting of zirconias, silicas and zeolites. In other ~~embodiment~~examples, the reaction of the furfural substrate with hydrogen to produce 1,2,6-hexanetriol is carried out at a temperature in the range of about 100°C and about 140°C and a pressure of hydrogen in the range of about 200 psig to about 1000 psig. In other ~~embodiment~~examples, the catalyst comprises Pt and W supported on zirconia. The present ~~invention~~disclosure is also directed to 1,6-hexanediol produced by the processes of any of the above ~~embodiment~~examples.

**[0013]** The present ~~invention~~disclosure is also directed to processes for preparing hexamethylenediamine from a carbohydrate source by: (a) converting a carbohydrate source to a furfural substrate; (b) reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to a reaction product comprising 1,2,6-hexanetriol; (c) reacting at least a portion of the 1,2,6-hexanetriol with

hydrogen in the presence of the heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol; and (d) converting at least a portion of the 1,6-hexanediol to hexamethylenediamine, wherein steps b) and c) are conducted in a single reactor. The present ~~invention~~disclosure is also directed to processes for preparing 1,6-hexanediol from a carbohydrate source by: (a) converting a carbohydrate source to a furfural substrate; (b) reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to a reaction product comprising 1,2,6-hexanetriol; and (c) reacting at least a portion of the 1,2,6-hexanetriol with hydrogen in the presence of the heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol, wherein steps b) and c) are conducted in a single reactor. In some ~~embodiment~~examples, the heterogeneous reduction catalyst further comprises W. In other ~~embodiment~~examples, steps (b) and (c) are carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig. In other ~~embodiment~~examples, the Pt containing catalysts of steps b) and c) are different and the temperatures and pressures at which steps b) and c) are conducted are substantially the same. In other ~~embodiment~~examples, the temperatures and pressures at which steps b) and c) are conducted are different. In other ~~embodiment~~examples, step b) is conducted at a temperature in the range of about 100°C to about 140°C and a pressure in the range of about 200 psig to about 1000 psig and step c) is conducted at a temperature in the range of about 120°C to about 180°C and a pressure in the range of about 200 psig to about 2000 psig. In other ~~embodiment~~examples, the yield of 1,6-hexanediol from the furfural substrate is at least about 40%. In other ~~embodiment~~examples, the yield of 1,6-hexanediol from the furfural substrate is at least about 50%. In other ~~embodiment~~examples, the yield of 1,6-hexanediol from the furfural substrate is at least about 60%. In other ~~embodiment~~examples, the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose. In other ~~embodiment~~examples, steps (b) and (c) are carried out in one reaction zone. In other ~~embodiment~~examples, the catalyst comprises Pt and W supported on zirconia. The present ~~invention~~disclosure is also directed to hexamethylenediamine produced by the processes of any of the above ~~embodiment~~examples. The present ~~invention~~disclosure is also directed to 1,6-hexanediol prepared by the process of any of the above ~~embodiment~~examples.

**[0014]** The present ~~invention~~disclosure is also directed to processes for preparing a compound of formula II



(II);

**[0015]** wherein each of $X^2$ and $X^3$ is selected from the group of hydrogen and hydroxyl; by converting a carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce the compound of formula II. In some ~~embodiment~~examples, the catalyst further comprises W. In other ~~embodiment~~examples, the catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re.

**[0015a]** In a first aspect, the present disclosure refers to a process for preparing 1,6-hexanediol comprising reacting 1,2,6-hexanetriol with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt.

**[0015b]** In a second aspect, the present disclosure refers to a process for preparing hexamethylenediamine comprising converting 1,6-hexanediol obtained by the process of the first aspect to hexamethylenediamine.

## DETAILED DESCRIPTION

**[0016]** The following description sets forth exemplary methods, parameters and the like. It should be recognized, however, that such description is not intended as a limitation on the scope of the present invention.

**[0017]** In accordance with the present invention, applicants disclose processes for the chemocatalytic conversion of a furfural substrate, which may be derived from a carbohydrate source (e.g., glucose or fructose) to hexamethylenediamine, and intermediate processes and products along the pathway. In some embodiments, the processes are carried out by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst to produce 1,6-hexanediol; and, converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. In other embodiments, the processes are carried out by converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce a reaction product comprising 1,2,6-hexanetriol; converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol; and converting at least a portion of the 1,6-hexanediol to hexamethylenediamine. In some embodiments, the processes are carried out by converting the carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol. In other embodiments, the processes are carried out by converting

# CLAIMS

We claim:

~~1. A process for preparing hexamethylenediamine from a carbohydrate source, the process comprising: converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst to produce 1,6-hexanediol; and, converting at least a portion of the 1,6-hexanediol to hexamethylenediamine.~~

~~2. A process for preparing hexamethylenediamine from a carbohydrate source, the process comprising: converting a carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce a reaction product comprising 1,2,6-hexanetriol; converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol; and converting at least a portion of the 1,6-hexanediol to hexamethylenediamine.~~

~~3. The process of claim 1, wherein the heterogeneous reduction catalyst comprises Pt.~~

~~4. The process of claim 2 or 3, wherein the heterogeneous reduction catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re.~~

~~5. The process of any of claims 2-4, wherein the step of converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol is conducted in the presence of hydrogen and a hydrogenation catalyst comprising Pt.~~

~~6. The process of any of claims 2-5, wherein the yield of 1,6-hexanediol is at least about 40%.~~

~~7. The process of any of claims 2-5, wherein the yield of 1,6-hexanediol is at least about 50%.~~

~~8. The process of any of claims 2-6, wherein the yield of 1,6-hexanediol is at least about 60%.~~

~~9. The process of any of claims 1-8, wherein the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig.~~

~~10. The process of any of claims 1-9, wherein the furfural substrate is 5-hydroxymethylfurfural.~~

~~11. The process of any of claims 1-10, wherein the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose.~~

~~12. The process of any of claims 2-11, wherein the catalyst further comprises a support selected from the group consisting of zirconias, silicas, and zeolites.~~

~~13. The process of any of claims 1-12, wherein the reaction of the furfural substrate with hydrogen is carried out at a temperature in the range of about 100°C and about 180°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig.~~

~~14. The process of any of claims 2, 5 or 13, wherein the hydrogenation catalyst comprises Pt and W supported on zirconia.~~

~~15. Hexamethylenediamine produced by the process of any of claims 1-14.~~

~~16.~~1. A process for preparing 1,6-hexanediol ~~from a carbohydrate source, the process~~ comprising~~: converting the carbohydrate source to a furfural substrate; and,~~ reacting 1,2,6-hexanetriol~~at least a portion of the furfural substrate~~ with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt ~~to produce 1,6-hexanediol~~.

~~17. A process for preparing 1,6-hexanediol from a carbohydrate source, the process comprising: converting the carbohydrate source to a furfural substrate; reacting at least a portion of the furfural substrate with hydrogen in the presence of a Pt containing~~

~~heterogeneous reduction catalyst to produce a reaction product comprising 1,2,6-hexanetriol; and, converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol.~~

~~18.~~2. The process of ~~either of claims 16 or 17~~claim 1, wherein the heterogeneous reduction catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re.

~~19.~~3. The process of ~~any of claims 16~~claim 2, wherein the molar ratio of Pt to the at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re is from about 20:1 to about 1:10~~the step of converting at least a portion of the 1,2,6-hexanetriol to 1,6-hexanediol is conducted in the presence of hydrogen and a hydrogenation catalyst comprising Pt~~.

~~20.~~4. The process of ~~any of claims 16-19~~claim 1 or 2, wherein the heterogeneous reduction ~~hydrogenation~~ catalyst is a supported heterogeneous reduction catalyst.

~~21.~~5. The process of ~~any of claims 16-20~~claim 4, wherein the heterogeneous reduction catalyst is on the surface of the support~~the yield of 1,6-hexanediol from the furfural substrate is at least 40%~~.

~~22.~~6. The process of ~~any of claims 16-20~~claim 4, wherein the supported heterogeneous reduction catalyst comprises a support selected from the group consisting of acidic ion-exchange resin, gamma alumina, fluorinated alumina, sulfate or tungsten promoted zirconia, titania, silica, silica promoted alumina, aluminum phosphate, tungsten oxide supported on silica-alumina, acidic clay, supported mineral acid and zeolites~~the yield of 1,6-hexanediol from the furfural substrate is at least 50%~~.

~~23.~~7. The process of ~~any of claims 16-20~~claim 4, wherein the supported heterogeneous reduction catalyst comprises a support selected from the group consisting of metal-doped titania, metal-doped zirconia, metal-doped ceria and metal-modified niobia~~the yield of 1,6-hexanediol from the furfural substrate is at least 60%~~.

8. The process of claim 4, wherein the supported heterogeneous reduction catalyst comprises a zirconia, silica or zeolite support.

~~24.~~9. The process of ~~any of claims 16-21~~claim 1, wherein 1,2,6-hexanetriol is reacted with hydrogen in the presence of the heterogeneous reduction catalyst ~~the reaction of the furfural substrate with hydrogen is carried out~~ at a temperature in the range of about ~~60~~80°C ~~and~~ to about 200°C and at a pressure ~~of hydrogen~~ in the range of about 200 psig to about 2000 psig.

~~25.~~10. The process of ~~any of claims 16-24~~claim 1, wherein the process is conducted in the presence of a solvent selected from the group consisting of water, alcohols, esters, ethers, ketones, and mixtures thereof~~the furfural substrate is 5-hydroxymethylfurfural~~.

~~26.~~11. The process of ~~any of claims 16-25~~claim 10, wherein the solvent is water~~the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose~~.

~~27. The process of any of claims 16-26, wherein the catalyst further comprises a support selected from the group consisting of zirconias, silicas, and zeolites.~~

~~28. The process of any of claims 16-27, wherein the reaction of the furfural substrate with hydrogen to produce 1,2,6-hexanetriol is carried out at a temperature in the range of about 100°C and about 140°C and a pressure of hydrogen in the range of about 200 psig to about 1000 psig.~~

~~29. The process of any of claims 16-28, wherein the catalyst comprises Pt and W supported on zirconia.~~

~~30. 1,6-hexanediol produced by the process of any of claims 16-29.~~

~~31.~~12. A process for preparing hexamethylenediamine comprising converting 1,6-hexanediol obtained by the process of claim 1 to hexamethylenediamine. ~~from a carbohydrate source, the process comprising:~~

~~(a) converting a carbohydrate source to a furfural substrate;~~

(b) reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to a reaction product comprising 1,2,6-hexanetriol;

(c) reacting at least a portion of the 1,2,6-hexanetriol with hydrogen in the presence of the heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol; and

(d) converting at least a portion of the 1,6-hexanediol to hexamethylenediamine, wherein steps b) and c) are conducted in a single reactor.

32. A process for preparing 1,6-hexanediol from a carbohydrate source, the process comprising:

(a) converting a carbohydrate source to a furfural substrate;

(b) reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to a reaction product comprising 1,2,6-hexanetriol; and

(c) reacting at least a portion of the 1,2,6-hexanetriol with hydrogen in the presence of the heterogeneous reduction catalyst comprising Pt to produce 1,6-hexanediol, wherein steps b) and c) are conducted in a single reactor.

33. The process of claim 31 or 32, wherein the heterogeneous reduction catalyst further comprises W.

34. The process of any of claims 31-33, wherein steps (b) and (c) are carried out at a temperature in the range of about 60°C and about 200°C and a pressure of hydrogen in the range of about 200 psig to about 2000 psig.

35. The process of any of claims 31-34, wherein the Pt containing catalysts of steps b) and c) are different and the temperatures and pressures at which steps b) and c) are conducted are substantially the same.

36. The process of any of claims 31-34, wherein the temperatures and pressures at which steps b) and c) are conducted are different.

37. The process of claim 31 or 32 wherein step b) is conducted at a temperature in the range of about 100°C to about 140°C and a pressure in the range of about 200 psig to about 1000 psig and step c) is conducted at a temperature in the range of about 120°C to about 180°C and a pressure in the range of about 200 psig to about 2000 psig.

38. The process of any of claims 31-37 wherein the yield of 1,6-hexanediol from the furfural substrate is at least about 40%.

39. The process of any of claims 31-37 wherein the yield of 1,6-hexanediol from the furfural substrate is at least about 50%.

40. The process of any of claims 31-37 wherein the yield of 1,6-hexanediol from the furfural substrate is at least about 60%.

41. The process of any of claims 31-40, wherein the carbohydrate source is glucose, fructose, or a mixture comprising glucose and fructose.

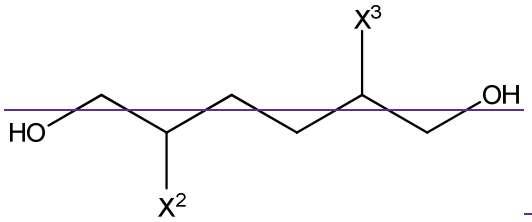
42. The process of any of claims 31-41, wherein steps (b) and (c) are carried out in one reaction zone.

43. The process of any of claims 31-42, wherein the catalyst comprises Pt and W supported on zirconia.

44. Hexamethylenediamine prepared by the process of any of claims 31 and 33-43.

45. 1,6-Hexanediol prepared by the process of any of claims 32 and 33-43.

46. A process for preparing a compound of formula II




(II);

~~wherein each of $X^2$ and $X^3$ is selected from the group of hydrogen and hydroxyl;~~

~~the process comprising: converting a carbohydrate source to a furfural substrate; and, reacting at least a portion of the furfural substrate with hydrogen in the presence of a heterogeneous reduction catalyst comprising Pt to produce the compound of formula II.~~

~~47. The process of any of claims 46, wherein the catalyst further comprises W.~~

~~48. The process of claim 46, wherein the catalyst further comprises at least one metal selected from the group consisting of Mo, La, Sm, Y, W, and Re.~~