New Catalytic Pathways for Production of α,ω-diols from Biomass

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Abstract: In this presentation we outline new catalytic strategies for the synthesis of 1,5-pentanediol (PDO) from hemicellulose and synthesis of 1,6-hexanediol (HDO) from cellulose. Biomass (white birch wood chips) is fractionated in gamma-valerolactone (GVL)/H_2O to generate a pure cellulose solid and liquid stream containing hemicellulose and lignin, which is further dehydrated to furfural. Furfural is converted to PDO by sequential dehydration/hydration, ring-opening tautomerization, and hydrogenation reactions. Acid-catalyzed cellulose dehydration in tetrahydrofuran (THF)/H_2O produces a mixture of levoglucosenone (LGO) and 5-hydroxymethylfurfural (HMF), which are converted with hydrogen to tetrahydrofuran-dimethanol (THFDM). HDO is then obtained from hydrogenolysis of THFDM. We will discuss the catalytic requirements of each step.

Keywords: α,ω-diols, Catalysis, Biomass.

1. Introduction (11-point boldface)

α,ω-diols, chemicals such as 1,4-butanediol (BDO) and HDO, which have a linear carbon-chain and OH groups at both terminal positions, are high value commodity chemicals with market prices of $2,000/ton and $4,400/ton, respectively [1]. α,ω-diols are monomers used predominantly for production of polyesters and polyurethanes. Both HDO and PDO synthesis routes from petroleum feedstock suffer from low conversion reactions, many reaction steps (lower yields), homogeneous chemistry involving toxic chemicals (HNO_3 or KCN), and nonrenewable, petroleum feedstocks which contribute to climate change. In this paper we demonstrate a multi-step catalytic process for production of PDO and HDO starting from white birch as shown in **Figure 1**.

2. Experimental

Experimental details can be found in reference. [2]

3. Results and discussion

First, lignocellulosic biomass is converted into cellulose, furfural and solid lignin *via the TriVersa Process™* developed by Glucan Biorenewables LLC. Furfural yields over 85% are obtained at 225°C. Furfural is converted into PDO by four catalytic steps as shown in **Figure 1** [3]: i) Furfural is hydrogenated into Tetrahydrofuran alcohol (THFA), ii) THFA is dehydrated to Dihydropyran (DHP), dehydration of neat THFA in the vapor phase gave 87% overall yield of DHP. iii) DHP is hydrated to 2-hydroxytetrahydropyran (2-HY-THP) and 2-HY-THP dimers and 4) 5-Hydroxyvaleraldehyde (5-HY-Val) is hydrogenated into PDO. This pathway will be referred to as the dehydration, hydration, and hydrogenation (DHH) route.

The catalytic conversion of cellulose into HDO includes three steps: i) hydrolysis/dehydration of cellulose into LGO and HMF in 48% yield [4], ii) hydrogenation/hydrogenolysis of LGO and HMF into THFDM [5] and iii) hydrogenolysis of THFDM into HDO (**Figure 1)**. In the second step, LGO was hydrogenated to Lgol, followed by Lgol hydrogenolysis to THFDM, tetrahydropyran-2-methanol-5-hydroxyl (THP2M5H) and 2-methyl-tetrahydrofurfurylalcohol (2MTHFA) over Pd-based catalyst.

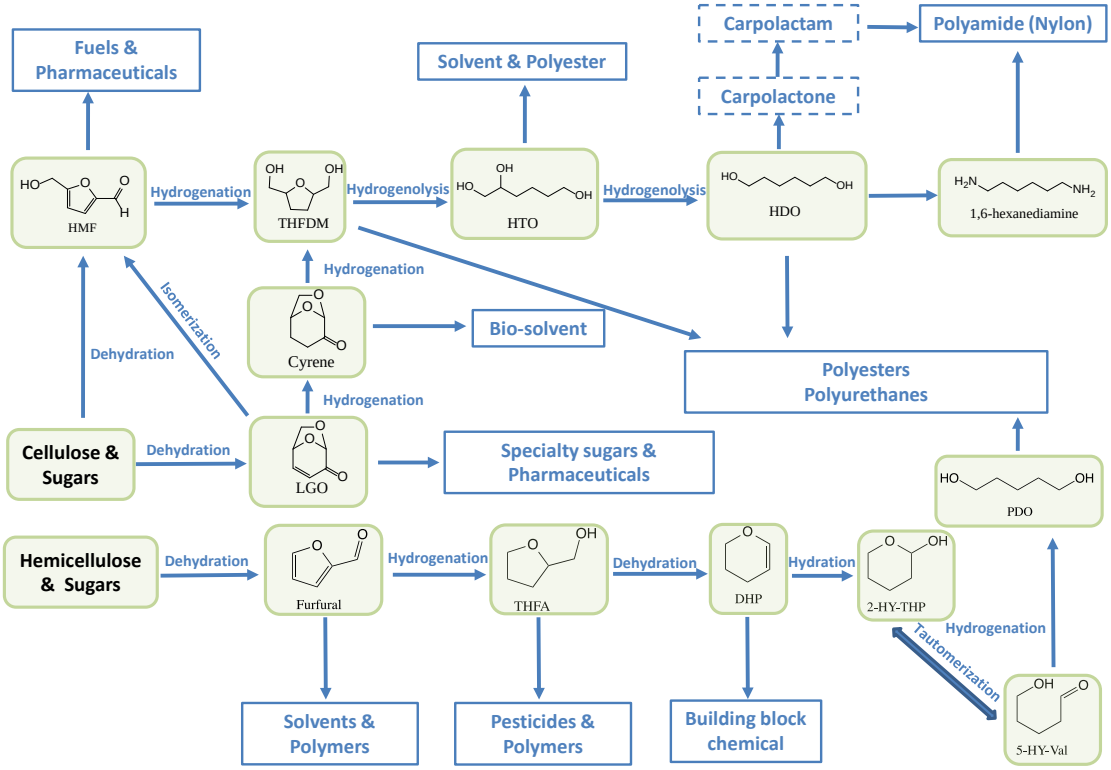

Figure 1. Potential products produced from cellulose and hemicellulose

4. Conclusions

We have demonstrated a pathway to synthesize PDO and HDO from lignocellulosic biomass. In the *TriVersa Process*^{TM} (Glucan Biorenewables LLC), a white birch biomass feedstock was solubilized by dilute sulfuric acid to produce a high purity solid cellulose (90-94.5% purity and 35-42% yield), a soluble hemicellulose (>90% of hemicellulose in biomass feedstock), and a lignin stream in GVL/H_2O (80/20) solvent. The soluble hemicellulose was converted into furfural at 85% yield in less than 30 seconds. Furfural has been shown to form THFA in 96% yields by vapor phase hydrogenation [6]. THFA was converted into PDO in 84% overall yield via the three-step DHH process. THFA was converted into DHP in 87% yield by vapor phase dehydration with γ-Al_2O_3. Uncatalyzed DHP hydration in water produced 2-HY-THP and 2-HY-THP dimers in 99% yield. Ru catalysts hydrogenated 2-HY-THP to PDO in 97% yield. This conversion represents an 80% yield of PDO from furfural. HDO was produced from the cellulose by first dehydrating cellulose into LGO and HMF (48% yield) in a THF/H_2O mixture with acid catalysts. This mixture was then hydrogenated using Ni/SiO_2 followed by hydrogenolysis over Pd/SiO_2-Al_2O_3 to 85% overall selectivity to THFDM. A 90% selectivity to HDO from THFDM was obtained with Pt-based catalysts. A process model was developed to estimate the economics of this process for a 1,000 ton biomass per day plant. The minimum selling price for production of HDO and PDO is $4,090/ton, which is similar to the market price of HDO derived from petroleum.

References

(1) MarketsandMarkets. *1,6-Hexanediol Market by Application (Polyurethanes, Coatings, Acrylates, Adhesives, Unsaturated Polyester Resins, Plasticizers, and Others) - Trends and Forecasts to 2019*; 2014.

(2) He, J.; Huang, K.; Barnett, K. J.; Krishna, S.; Alonso, D. M.; Brentzel, Z. J.; Burt, S. P.; Walker, T.; Banholzer, W. F.; Maravelias, C. T.; Hermans, I.; Dumesic, J. A.; Huber, G. W. *Faraday Discuss.* **2017**.

(3) Brentzel, Z. J.; Barnett, K. J.; Huang, K.; Maravelias, C. T.; Dumesic, J. A.; Huber, G. W. *ChemSusChem* **2017**.

(4) He, J.; Liu, M.; Huang, K.; Walker, T. W.; Maravelias, C. T.; Dumesic, J. A.; Huber, G. W. *Green Chem.* **2017**, *19*, 3642–3653.

(5) Krishna, S. H.; McClelland, D. J.; Rashke, Q. A.; Dumesic, J. A.; Huber, G. W. *Green Chem.* **2017**, *19*, 1278–1285.

(6) Nakagawa, Y.; Nakazawa, H.; Watanabe, H.; Tomishige, K. *ChemCatChem* **2012**, *4* (11), 1791–1797.