Title: Commodity Chemicals from Biomass: Combining Ring-opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural

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Chemicals from Biomass: Combining Ring-opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural

Zachary J. Brentzel, Kevin J. Barnett, Kefeng Huang, Christos T. Maravelias, James A. Dumesic*, George W. Huber*

Abstract: We have developed a process for the synthesis of 1,5-pentanediol (1,5-PD) with 84% yield from furfural, utilizing dehydration/hydration, ring-opening tautomerization, and hydrogenation reactions. Although this process has more reaction steps than the traditional direct hydrogenolysis of tetrahydrofurfuryl alcohol (THFA), techno-economic analyses demonstrate that this process is the economically preferred route for the synthesis of biorenewable 1,5-PD. 2-hydroxytetrahydropyran (2-HY-THP) is the key reaction pathway intermediate that allows for a decrease in the minimum selling price of 1,5-PD. The reactivity of 2-HY-THP is 80 times greater than that of THFA over a bimetallic hydrogenolysis catalyst. We demonstrate that this enhanced reactivity is a result of the ring-opening tautomerization to 5-hydoxyvaleraldehyde and subsequent hydrogenation to 1,5-PD.

The low cost of petroleum and large capacity of petroleum refineries, combined with challenges in implementing technologies at scale, have made it difficult to commercialize technologies to produce liquid transportation fuels from lignocellulosic biomass [1–4]. An alternative, economically viable approach, that could help transition society to a more sustainable society, is to synthesize high volume commodity chemicals from biomass [5,6]. C3-C6 α,ω-diols are a class of high value, high volume (with a α,ω-diols global production of 2.3 million tons/year) oxygenated commodity chemicals that have found a variety of applications in the production of polyurethanes, coatings, acrylates, adhesives, polyesters, and plasticizers [7-9]. α,ω-diols are expensive to produce from petroleum-derived feedstocks, because they involve a complex number of separations, selective oxidations, and reductions. 1,5-pentanediol (1,5-PD) is more challenging to produce than the other α,ω-diols, because C5 petroleum feedstocks are not available on a large scale. In contrast, C5 feedstocks, such as xylose and furfural, are produced at the industrial scale from biomass. However, current approaches for the production of 1,5-PD from furfural are expensive due to high catalyst costs and low catalytic activity [10–12]. Here we report a new approach for the production of 1,5-PD from furfural-derived tetrahydrofurfuryl alcohol (THFA) that has 2 times lower capital cost and 7 times lower operating cost (not including feedstock cost) than current approaches to make 1,5-PD from THFA. Although this process has more reaction steps than the traditional direct hydrogenolysis of tetrahydrofurfuryl alcohol (THFA), techno-economic analyses demonstrate that this process is the economically preferred route for the synthesis of biorenewable 1,5-PD. 2-hydroxytetrahydropyran (2-HY-THP) is the key reaction pathway intermediate in our approach, and we show . that the high enhanced reactivity of this intermediate is a result of the ring-opening tautomerization to 5-hydoxyvaleraldehyde and subsequent hydrogenation to 1,5-PD.

Furfural is produced on the industrial scale (300 ktons/year) by dehydration of the hemicellulose portion of biomass and has a projected annual growth rate of 11.9% [13,14]. Furfural is hydrogenated into a variety of products, including tetrahydrofurfuryl alcohol (THFA) using Cu- or Ni-based catalysts [15–17]. Research on the synthesis of 1,5-PD from THFA has focused on the direct hydrogenolysis of THFA (Fig. 1A) [10-12,18–21]. The most active and selective catalysts are comprised of Rh doped with an oxophilic promoter, such as Re or Mo. The acidity of the oxophilic promoter assists with the stabilization of the ring-opened oxocarbenium ion intermediates, producing high selectivity (97%) to 1,5-PD from THFA at 393 K [10,21]. The drawback of this direct hydrogenolysis approach is low catalytic activity and high catalyst cost.

The new pathway we report here is outlined in Figure 1B. Furfural is first hydrogenated into THFA which is then dehydrated in the gas phase (neat at 648 K, 1 atm, and a WHSV of 9 hr^{-1}) to produce dihydropyran (DHP) in 87% yield. The DHP is then hydrated to 2-hydroxytetrahydropyran (2-HY-THP) and 2-HY-THP dimers in yields up to 100% (Table S1) in the aqueous phase (20 wt% DHP in water) without a catalyst at temperatures from 343 to 403 K. 2-HY-THP is a cyclic hemiacetal that undergoes ring-opening tautomerization in the aqueous phase to form 5-hydroxyvaleraldehyde (5-HY-Val) [22,23]. The hydrogenation of 5-HY-Val in the presence of the 2-HY-THP monomers and dimers using a Ru catalyst results in 97% overall yield of 1,5-PD from DHP. This route will subsequently be referred to as the dehydration, hydration, and hydrogenation (DHH) pathway.

The results of this paper for the gas phase dehydration of THFA to DHP are consistent with the work of Geller et al. and Yamada et al. who used an activated alumina catalyst [24,25]. DHP is likely formed via acid-catalyzed dehydration of the THFA primary hydroxyl group [26], followed by simultaneous ring-opening and Wagner-Meerwein rearrangement to the 6-membered ring DHP product [27,28]. The high yields for the dehydration reaction are unique to the 5-membered ring, THFA. Studies with the 6-membered ring equivalent, 2-(hydroxymethyl)-tetrahydropyran, at the same conditions produce low yields to the 7-membered unsaturated ring, 2,3,4,5-tetrahydrooxepine (THO). The main product is cyclopentane carboxaldehyde (CPC), as predicted by the thermodynamic results for dehydration reactions of five- and six-carbon heterocyles (Table S2). Density functional theory

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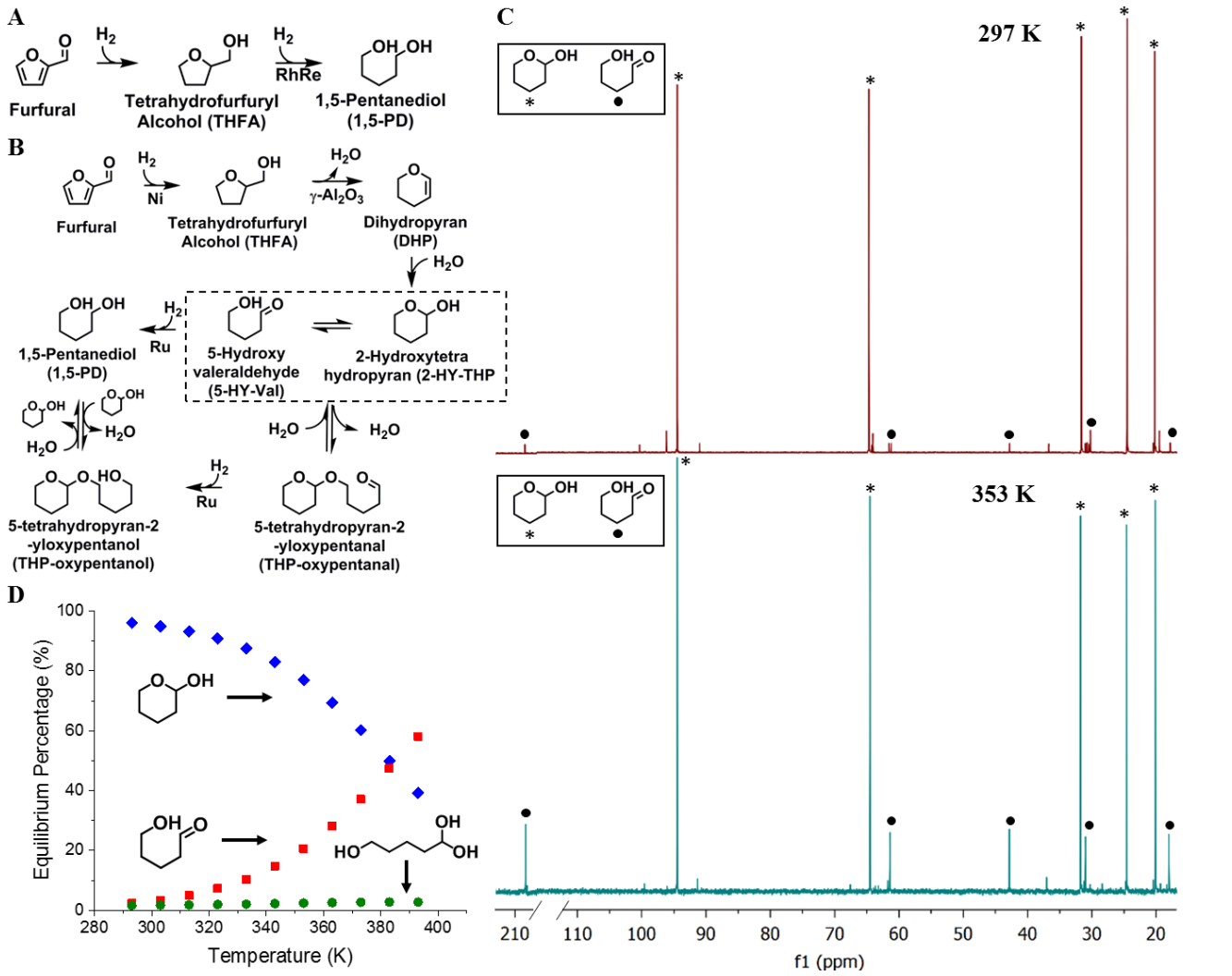

Figure 1 Route to produce 1,5-pentanediol from furfural. **(A)** Reaction pathway for the direct hydrogenolysis of tetrahydrofurfuryl alcohol (THFA). (**B**) Reaction pathway for the dehydration, hydration, and hydrogenation (DHH) of tetrahydrofurfuryl alcohol (THFA). (**C**) Quantitative ^{13}C NMR spectra of 10 wt% 2-hydroxytetrahydropyran (2-HY-THP) in D_2O at 297 and 353 K. (**D**) Equilibrium percentage of 2-HY-THP, 5-hydroxyvaleraldehyde (5-HY-Val), and 1,1,5-pentanetriol from 297 to 393 K based on quantitative ^{13}C variable temperature NMR results.

calculations show that the isomerization of THO to CPC at 648 K has a Gibbs free energy change of -72.2 kJ mol^{-1}, whereas the isomerization of DHP to cyclobutane carboxaldehyde is an endergonic reaction, with a Gibbs free energy change of 15.8 kJ mol^{-1}.

Vapor phase continuous flow studies were conducted to determine the stability of the γ-Al_2O_3 catalyst versus time on stream (Fig. S1) for the dehydration of THFA to DHP. The fresh γ-Al_2O_3 catalyst had a first order deactivation rate constant of 0.026 hr^{-1}. Coking was the primary mode of deactivation, and the catalyst was thus regenerated by a calcination treatment at 673 K for 3 hours in air. After calcination, the catalyst regained its initial activity but deactivated more rapidly, with a first order deactivation rate constant of 0.039 hr^{-1}. The low cost of alumina allows for replacement of the catalyst every 24 hours without the need for regeneration, as we have demonstrated in more detail in our techno-economic analyses.

DHP can be hydrated in water at temperatures from 343 to 433 K. Yields of 2-HY-THP ranged from 90-92% at temperatures of 373 and 403 K in one hour of reaction time (Table S1). Two dimer products were also detected, 2-tetrahydropyranyl ether (2,2'-HY-THP) and 5-tetrahydropyran-2-yloxypentanal (THP-oxypentanal) (Fig. 1B). These dimers are also precursors to 1,5-PD since they can undergo reversible hydrolysis back to monomers at the reaction conditions [29]. Thus, the yield of 1,5-PD precursors (2-HY-THP and etherified dimers) is approximately 100%. Similar yields can be obtained at 343 K with longer residence times (e.g., 12 h). At elevated temperature, 433 K, conversion of dihydropyran resulted in the formation of solid polymers in the reactor and lower yields to 2-HY-THP and upgradable dimers (~71%).

The rate of 1,5-PD production from 2-HY-THP with a Rh-Re/Carbon catalyst is 80 times faster than the rate from THFA over the same catalyst. This high reactivity of 2-HY-THP is related to

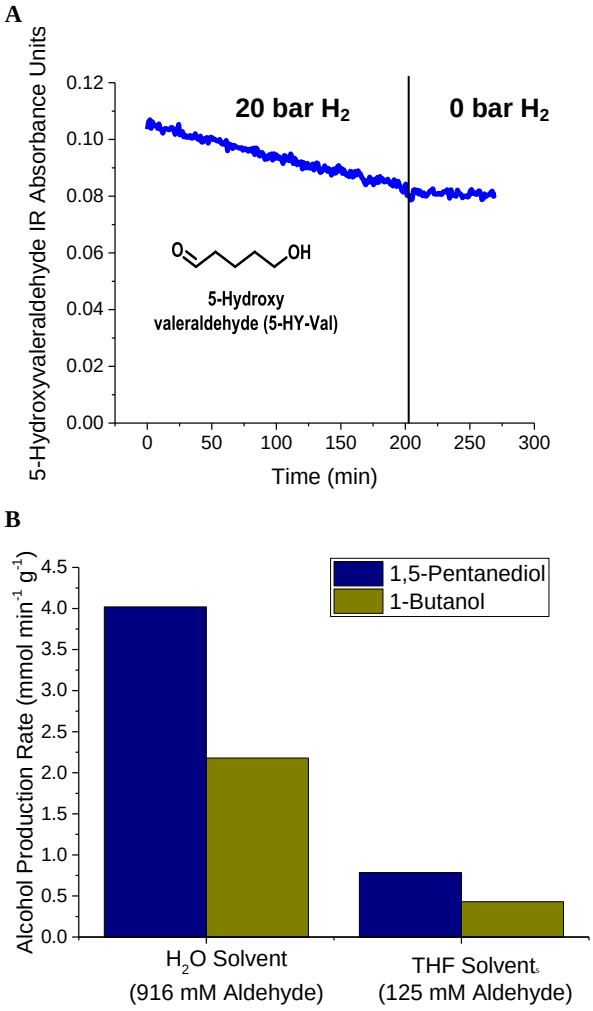

Figure 2 Results from *in situ* infrared spectroscopy and reactivity experiments. (A) 5-Hydroxyvaleraldehyde (5-HY-Val) carbonyl absorbance from *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy of the ring-opening tautomerization and hydrogenation of 20 wt% 2-hydroxytetratropyran (2-HY-THP) in water using 1 wt % Ru/TiO_2 at 383 K and 20 bar H_2. (**B**) Comparison of the alcohol production rates over 1 wt % Ru/TiO_2 at 383 K and 20 bar H_2. The production rate of 1,5-pentanediol (1,5-PD) from 2-HY-THP was compared against the production rate of 1-butanol from butanal in H_2O and tetrahydrofuran (THF) solvents. The concentration of butanal used was calculated based on the concentration of ring-opened 5-HY-Val determined by NMR.

its ring-opening tautomerization to 5-HY-Val, as shown by ^{13}C variable temperature NMR experiments (Fig. 1C), because the rate of hydrogenation of an aldehyde group is typically higher than the rate of hydrogenolysis of a cyclic ether linkage [12,30]. The ring-opening tautomerization is an endothermic reaction. Therefore, the equilibrium composition of 5-HY-Val increases with temperature (from 2.4% at 297 K to 19.2 % at 353 K), as shown in Figure 1D. Aldehydes exist in equilibrium with their hydrated forms, geminal diols. We used butanal as a probe aldehyde to study the equilibrium between an aldehyde and its geminal diol with ^{13}C variable temperature NMR experiments in D_2O, since 1,1,5-pentanetriol was below the detection limits. The calculated equilibrium concentration of geminal diol, 1,1,5-pentanetriol, is estimated to be less than 3% at all temperatures. At the hydrogenation temperatures of 383 and 393 K used in this study, the equilibrium concentrations of 5-HY-Val are 47 and 58%, respectively.

The relative rates of ring-opening tautomerization of 2-HY-THP and hydrogenation of 5-HY-Val over a Ru/TiO_2 catalyst were studied in a batch reactor equipped with *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy to monitor the carbonyl stretch of 5-HY-Val at reaction conditions. A step change in the hydrogen pressure was employed to determine the relative rate of ring-opening compared to hydrogenation (Fig. 2A). In both water and tetrahydrofuran (THF) solvents, the 5-HY-Val concentration remained constant when stepping the hydrogen pressure from 20 to 0 bar, indicating that the rate of ring-opening is quasi-equilibrated relative to the hydrogenation. Therefore, the rate determining step in the conversion of 2-HY-THP to 1,5-PD is hydrogenation of the aldehyde.

Further experiments were performed to confirm that the reaction mechanism is a ring-opening and subsequent hydrogenation rather than direct hydrogenolysis of 2-HY-THP. Butanal hydrogenation was used as a probe reaction to compare with respect to the rate of ring-opening and hydrogenation of 2-HY-THP. Butanal concentrations were chosen based on the calculated 5-HY-Val concentrations determined from ^{13}C variable temperature NMR of 2-HY-THP in H_2O and THF solvents. In each solvent system, the rate of butanol production was proportional to the rate of 1,5-PD production (Fig. 2B), indicating that the rate of production of 1,5-PD is proportional to the concentration of aldehyde present in solution. Under the same reaction conditions, Ru/TiO_2 was not active for the hydrogenolysis of a probe acetal molecule, 2-methoxytetrahydropyran, in a THF solvent. In water, however, the acetal was hydrolyzed to 2-HY-THP and methanol, leading to high activity for production of 1,5-PD. Accordingly, results from variable temperature NMR, ATR-FTIR, and reaction kinetics measurements in different solvents demonstrate that the high reactivity of 2-HY-THP compared to THFA is caused by ring-opening tautomerization of 2-HY-THP followed by hydrogenation of the aldehyde intermediate, which is faster than hydrogenolysis of the α-alcohol ether linkage in THFA.

The conversion of 2-HY-THP over the Ru/TiO_2 catalyst was studied at various weight hourly space velocities (WHSV) in a continuous flow reactor to determine product selectivities as a function of conversion. The selectivity for production of 1,5-PD from 2-HY-THP is 100% at full conversion (96.5% from 1,5-PD precursors) and decreases as the conversion decreases (Fig. S2). These results are consistent with 2-HY-THP synthesized from commercial DHP and DHP from THFA dehydration. The lower 1,5-PD selectivity at high WHSVs is offset by an increase in the extent of dimer formation, most notably THP-oxypentanal and 5-

tetrahydropyran-2-yloxy pentanol (THP-oxypentanol). THP-oxypentanal is formed from the etherification of 5-HY-Val and 2-HY-THP. THP-oxypentanol is the hydrogenation product of THP-oxypentanal. These data suggest that the feed monomers undergo parallel reactions: i) hydrogenation to 1,5-PD and ii) etherification to THP-oxypentanal and 2,2'-HY-THP. The cleavage of these dimers results in 1,5-PD formation and is responsible for the high 1,5-PD yields at low space velocities.

The stabilities with respect to time on stream of Ru/TiO_2 and Ru/C catalysts were studied for the conversion of 2-HY-THP in continuous flow reactors (Fig. S3). These reaction kinetics studies were performed using 2-HY-THP feeds formed from DHP hydration at high feed concentrations (> 20 wt%). At both 343 and 393 K, the Ru/TiO_2 catalyst displayed more than 50% loss of activity in less than 24 hours. At 343 K, after an initial 35 hour period of rapid deactivation, the catalyst displayed more gradual deactivation with a first order deactivation constant of 0.0086 hr^{-1}. The Ru/TiO_2 catalyst was not fully regenerable by either re-reduction at 573 K for 2 hours or calcination at 603 K for 30 minutes and reduction at 573 K for 2 hours. The Ru/C catalyst was more stable than the Ru/TiO_2 catalyst, with a deactivation rate constant of 0.0020 hr^{-1} for 500 hours of time on stream. Re-reduction of the Ru/C catalyst at 573 K for 2 hours regenerated the activity from 38% back to 65% of the initial activity. The deactivation rate constant for the regenerated catalyst was 0.0037 hr^{-1}. Prior studies with glucose hydrogenation over Ru catalysts demonstrated similar findings, i.e., the oxide-supported catalyst, Ru/Al_2O_3, displayed deactivation as a result of support restructuring under hydrothermal conditions [31], while the carbon-supported catalyst did not deactivate since there were no morphological changes to the support [32].

Rigorous techno-economic analyses were carried out using the current product yields and neat THFA as a feedstock. This techno-economic model suggests that a pioneer plant applying the DHH pathway could produce 1,5-PD at a minimum selling price (MSP) of \$2,488/ton, versus \$4,105/ton for the direct hydrogenolysis pathway (Fig. 3A). A description of the model and further explanation are available in the supplemental materials. The most substantial savings come from the reduced catalyst cost and lower utility costs (Fig. 3A). Specifically, with the increase in hydrogenation activity of Ru/C compared to Rh-Re/C and the decrease in metal material costs (\$31,000/kg and \$1,500/kg for Rh and Ru [33], respectively) there is a 47 times decrease in catalyst cost (Table S3). The Rh cost accounts for greater than 90% of the total Rh-Re/C catalyst cost. Furthermore, transitioning from a 5 to 20 wt% feed from the direct hydrogenolysis pathway to the DHH pathway decreases the utility costs for the separation and recovery of 1,5-PD product by a factor of 12 (Table S4). Correspondingly, the total 1,5-PD production costs (excluding the cost of the THFA feedstock) decrease from \$2,137/ton for the hydrogenolysis route to \$473/ton for the DHH route. In addition, the DHH pathway leads to a high overall 1,5-PD yield without requiring large recycle stream used in the hydrogenolysis pathway (Fig. 3B), which could save over 6 times the installed capital costs on the separation and recovery systems. Using the nth plant cost analysis, the MSP of 1,5-PD for the DHH pathway and the direct hydrogenolysis pathway decreases to \$2,292/ton and \$3,467/ton, respectively. Furfural prices have fluctuated between \$500-\$2,000/ton over the past 15 years [34]. An analysis on the sensitivity of the 1,5-PD MSP to the furfural and THFA feedstock costs demonstrates that the MSP of 1,5-PD can range from \$1,500-\$3,000 (Fig. S4). This price is lower than the price of 1,6-hexanediol and within the same price range of 1,4-butanediol, the two largest α,ω-diols (with the exception of ethylene glycol) that are used commercially today. The techno-economic analyses suggest that our approach can produce infrastructure compatible renewable high volume oxygenated commodity chemicals that in an economically viable way. We envision an approach where an analogous chemistry could be used to make 1,6-hexanediol and 1,4-butanediol from biomass-derived feedstocks.

In summary, we have demonstrated an economically feasible alternative pathway to synthesize 1,5-PD from lignocellulosic biomass. Prior approaches have focused on the direct hydrogenolysis of THFA.

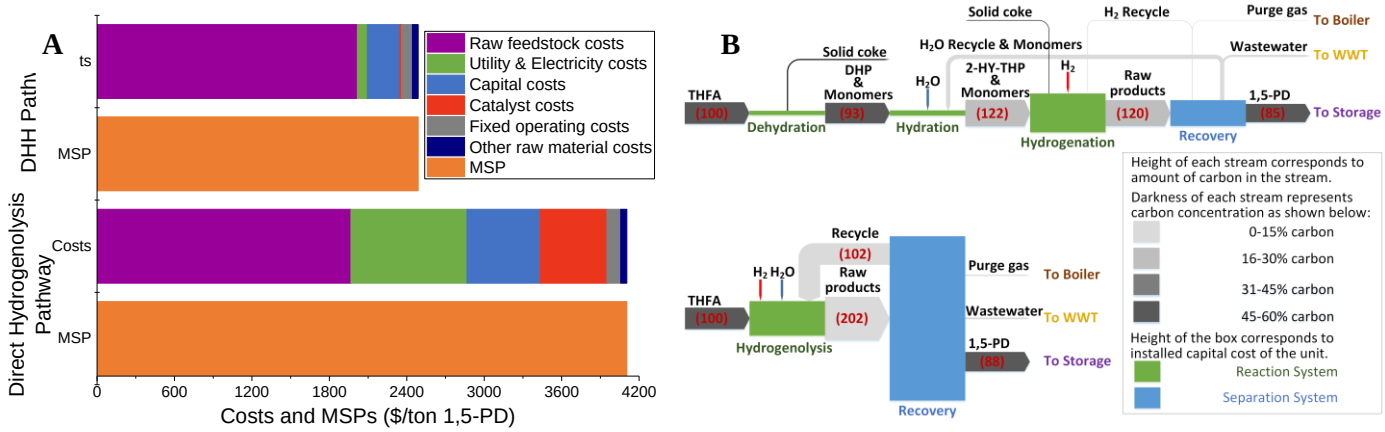

Figure 3 Process techno-economics for the synthesis of 1,5-pentanediol from furfural. (A) Comparison of costs and minimum selling prices (MSPs) for the dehydration, hydration, and hydrogenation (DHH) pathway with the direct hydrogenolysis pathway. (B) Sankey diagram for the i) DHH pathway and ii) direct hydrogenolysis pathway.

Technoeconomic analyses suggest that the 1,5-PD minimum selling prices for our route and the direct hydrogenolysis approach are $2,488/ton and $4,105/ton, respectively. Our pathway is also applicable to both C4 and C6 biomass-derived chemicals and allows for the ability to synthesize C4-C6 biorenewable α,ω-diols. The tautomerization-hydrogenation chemistry shown for C5 molecules in this work has been applied to C6 chemistry to produce 1,6-hexanediol from tetrahydropyran-2-methanol [35,36]. NMR results confirmed the analogous ring-opening tautomerization chemistry, and the C6 process achieved 1,6-hexanediol yields of 34% from tetrahydropyran-2-methanol [35].

Our approach utilizes two more reactions but no additional separation units. The vapor phase dehydration of THFA is performed with γ-Al2O3 and gives 87% yield to DHP. Uncatalyzed DHP hydration in water can produce up to 99% yield to 2-HY-THP and its dimers. Ru catalysts are 99% selective for the hydrogenation of 2-HY-THP to 1,5-PD.

The key intermediate in this alternative pathway is the cyclic hemiacetal, 2-HY-THP. The cyclic hemiacetal is equilibrated with its ring-opened tautomer, 5-HY-Val. Results from ^{13}C NMR spectroscopy measurements, ATR-FTIR spectroscopy measurements, and probe aldehyde hydrogenation reactions have demonstrated that the increased reactivity of 2-HY-THP compared to THFA is a result of quasi equilibrated ring-opening and subsequent hydrogenation.

Acknowledgments

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Keywords: α,ω-diols • biomass • catalysis • hydrogenation • sustainable chemistry

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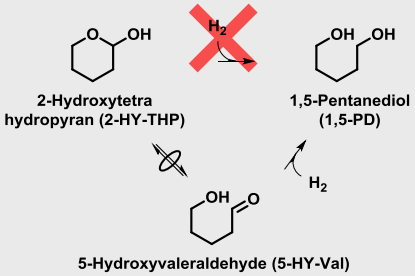
COMMUNICATION

α,ω-diols are promising targets for the upgrading of lignocellulosic biomass. An alternative to prior direct hydrogenolysis approaches has been developed. This new pathway utilizes a highly active intermediate, 2-hydroxytetrahydropyran. The reaction proceeds via ring-opening tautomerization of the hemiacetal and subsequent hydrogenation. Technoeconomic analyses demonstrate that the new pathway is economically preferred over the direct hydrogenolysis approaches.



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