GlucanBio

Argonne
NATIONAL
LABORATORY

WISCONSIN
UNIVERSITY OF WISCONSIN–MADISON

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2019 Project Peer Review
Production of α,ω diols from Biomass

March 6, 2019

Denver, CO

PI: George W Huber

Co-PIs: William Banholzer, James Dumesic, Ive Hermans, Christos Maravelias, Chris Marshall, Ilja Siepmann, Michael Tsapatsis

Post-doctoral Researchers: Jiayue He, Kefeng Huang, Bahman Elyassi

Graduate Students: Kevin J. Barnett, Zachary Brentzel, Samuel P. Burt, Robert DeJaco, Pranav U. Karanjkar, Siddarth H. Krishna, Nitish Mittal, Insoo Ro, Theodore Walker

Project Dates: 2/1/2015- 06/01/2018

Quad Chart Overview

Timeline

- Awarded as part of Biological and Chemical Upgrading for Advanced Biofuels and Products (DE-FOA-0001085)
- Start date: 2/1/2015
- Project end date: 6/1/2018
- Percent complete: 100%

Budget

	FY 12 – FY 14	FY 15	FY 16	FY 17	FY18
DOE Funded	0	354,559	1,145,513	942,883	561,176
Project Cost Share (UW Madison)	0	107,212	227,424	232,140	151,044
Project Cost Share (Minnesota)	0	0	55,240	61,031	43,917

Barriers

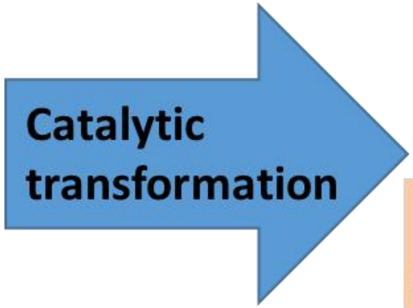
- **Qt-B Cost of Production**
- **Ct-E Improving Catalyst Lifetime**
- **Ct-F Increasing the Cost of Production**
- **Ct-J Identification and Evaluation of Potential Bioproducts**

Partners

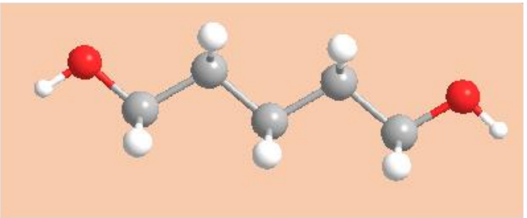
Argonne National Lab:	9%
Minnesota:	21%
GlucanBio:	4%

Catalytic Processes for Production of α,ω-diols from Lignocellulosic Biomass

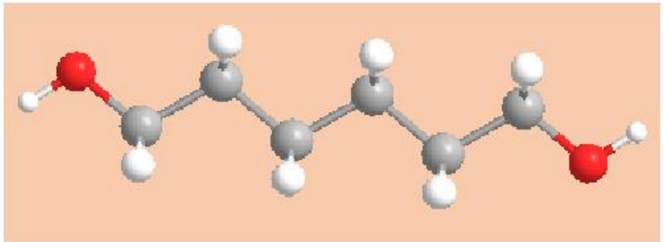
Lignocellulosic feedstock



Catalytic transformation



1,5-pentanediol



1,6-hexanediol

FOA Goals: EERE seeks diversification of the Bioenergy Technologies Office (BETO) portfolio to include a variety of chemical and biological upgrading technologies for the <u>production of a suite </u>of hydrocarbon fuels, fuel intermediates and <u>chemicals</u> (beyond ethanol) to <u>be produced in an integrated fashion from biologically or chemically derived intermediate feed streams</u>, such as but not limited to cellulosic sugars, lignocellulose derivatives, lignin, cellulosic alcohols, bio-solids and biogases.
Project Goal: Develop an economically viable approach (using inorganic catalysis) for conversion of biomass into 1,5 pentanediol (PDO) and 1,6 hexanediol (HDO) which will lower cost of cellulosic biofuels.
Project Outcome: Experimental data, process and technoeconomic model for conversion of biomass (white birch) into 1,5 pentanediol and 1,6 hexanediol.

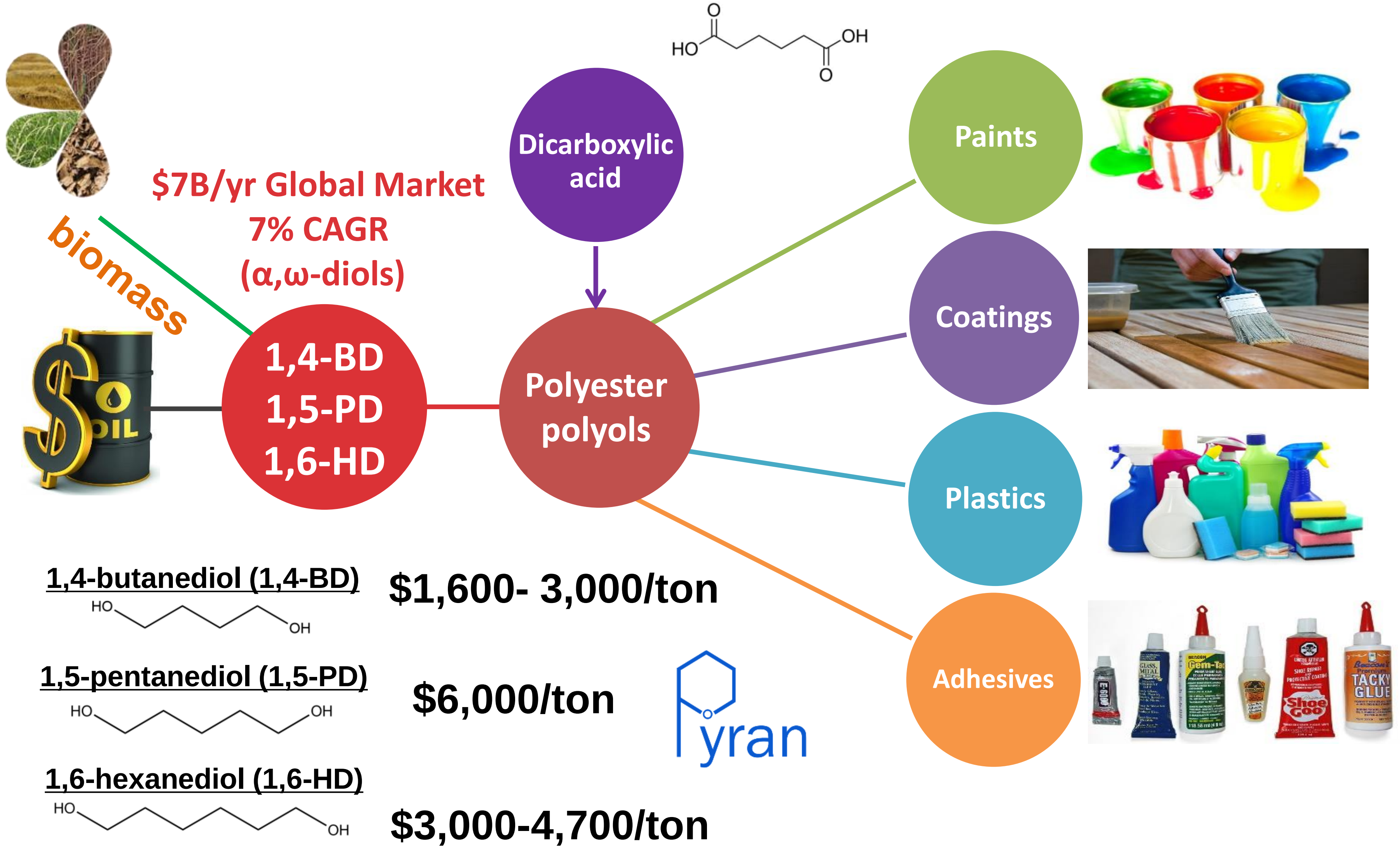
Management Approach

- UW lead and all partners report to PI
- Each institutions responsible for own tasks
- Follow workplan and make sure we can complete milestones
- Work with DOE review team to make sure workplan is consistent with goals
- UW in charge of process integration
- One senior post-doc is in charge of economic modeling which incorporates all the data
- Have regular phone calls (bimonthly to monthly) with partners
- Quarterly reports to DOE managed by senior post-doc

Key Technical Accomplishments

1. Demonstrated integrated production of 1,5-PDO and 1,6-HDO from biomass in laboratory continuous flow reactors
2. Developed techno-economic models for technologies and how they could be integrated into fuels production to reduce cost of cellulosic ethanol
3. Spun out a company to commercialize 1,5-PDO technology (Pyran)
4. Elucidated new reaction chemistry to convert biomass to α,ω-diols, identified and patented new high-value intermediates (including tetrahydrofurandimethanol and 1,2,5,6-hexanetetrol)
5. Developed new methodology to computationally predict adsorption/desorption behavior of polyols in zeolites, with correlation to experimental data
6. 17 peer-reviewed publications (3 more in preparation) and 4 patents/patent applications (2 issued patents)
7. Successfully completed all project milestones

C_4-C_6 α,ω-diols fit into $7 billion/year global market



Adipic Acid

$7B/yr Global Market
7% CAGR
(α,ω-diols)

biomass

1,4-BD
1,5-PD
1,6-HD

Dicarboxylic acid

Polyester polyols

Paints

Coatings

Plastics

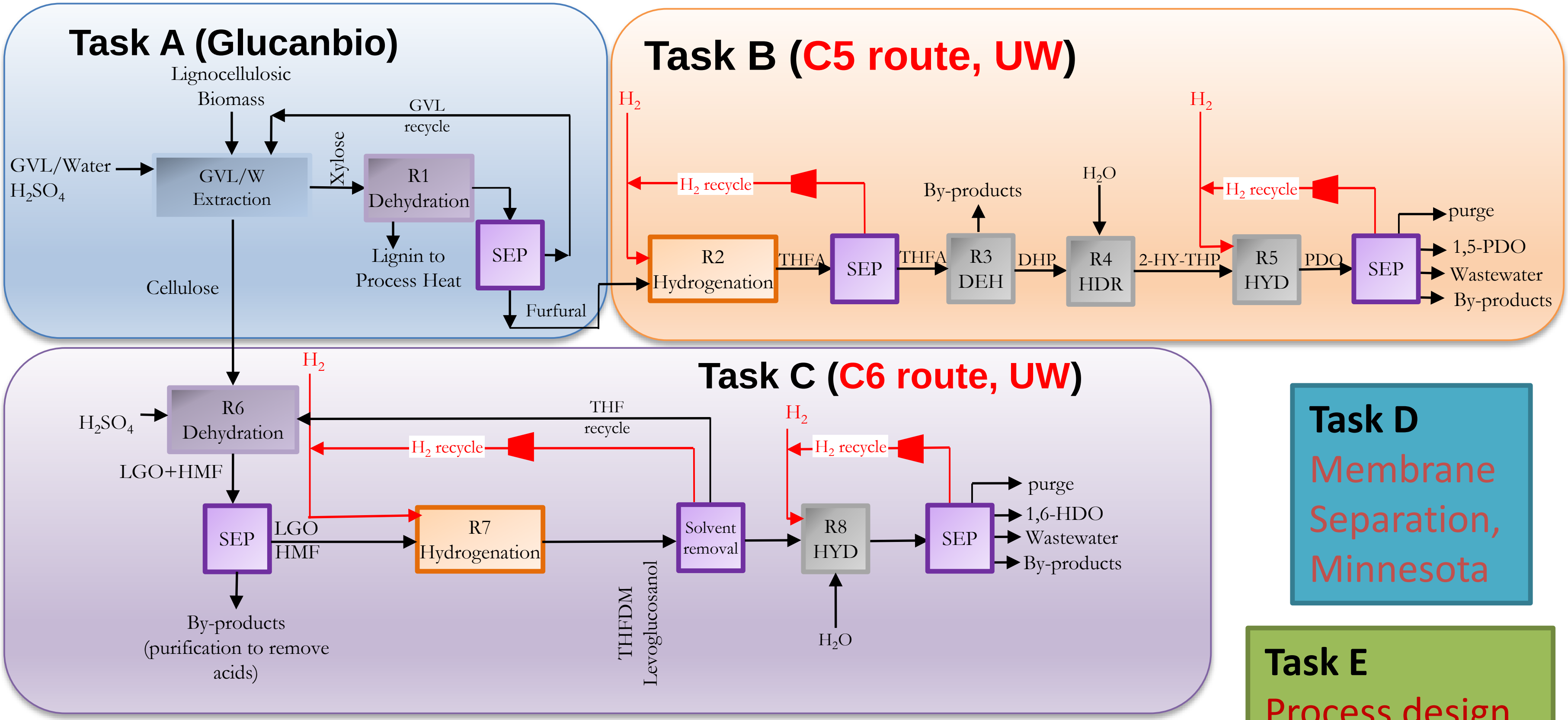
Adhesives

1,4-butanediol (1,4-BD) $1,600- 3,000/ton

1,5-pentanediol (1,5-PD) $6,000/ton

1,6-hexanediol (1,6-HD) $3,000-4,700/ton

Project involves 6 Integrated Tasks for Conversion of Lignocellulosic Biomass to PDO and HDO

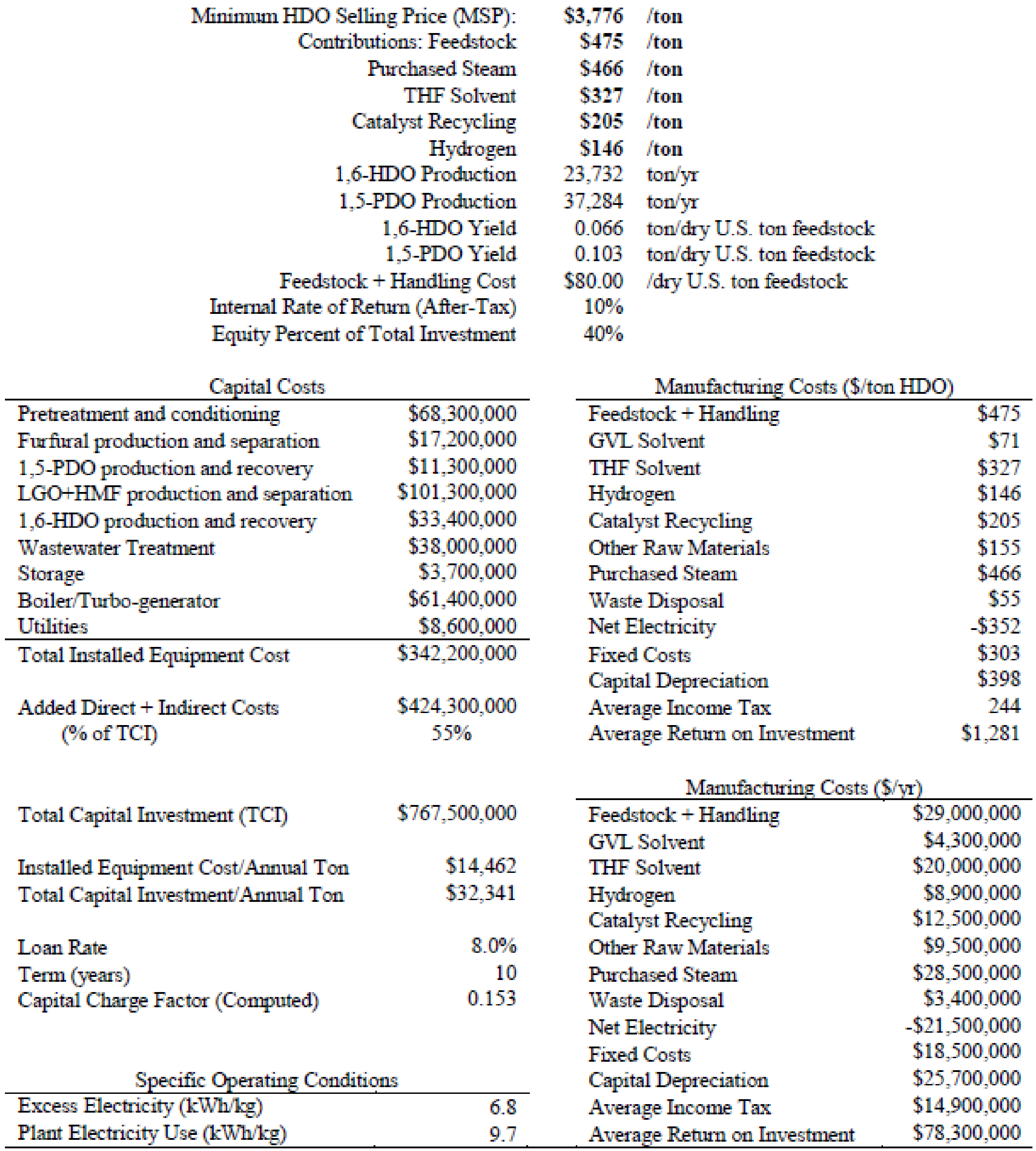


Task D
Membrane Separation, Minnesota

Task E
Process design and economic analysis, UW

Task B and C High throughput Studies at Argonne
Phase II Task F: Integration (All)

Results : Economic summary for base case process (all values in 2015$)



Minimum HDO Selling Price (MSP):	$3,776	/ton
Contributions: Feedstock	$475	/ton
Purchased Steam	$466	/ton
THF Solvent	$327	/ton
Catalyst Recycling	$205	/ton
Hydrogen	$146	/ton
1,6-HDO Production	23,732	ton/yr
1,5-PDO Production	37,284	ton/yr
1,6-HDO Yield	0.066	ton/dry U.S. ton feedstock
1,5-PDO Yield	0.103	ton/dry U.S. ton feedstock
Feedstock + Handling Cost	$80.00	/dry U.S. ton feedstock
Internal Rate of Return (After-Tax)	10%	
Equity Percent of Total Investment	40%	

Capital Costs	
Pretreatment and conditioning	$68,300,000
Furfural production and separation	$17,200,000
1,5-PDO production and recovery	$11,300,000
LGO+HMF production and separation	$101,300,000
1,6-HDO production and recovery	$33,400,000
Wastewater Treatment	$38,000,000
Storage	$3,700,000
Boiler/Turbo-generator	$61,400,000
Utilities	$8,600,000
Total Installed Equipment Cost	$342,200,000
Added Direct + Indirect Costs	$424,300,000
(% of TCI)	55%
Total Capital Investment (TCI)	$767,500,000
Installed Equipment Cost/Annual Ton	$14,462
Total Capital Investment/Annual Ton	$32,341
Loan Rate	8.0%
Term (years)	10
Capital Charge Factor (Computed)	0.153

Specific Operating Conditions	
Excess Electricity (kWh/kg)	6.8
Plant Electricity Use (kWh/kg)	9.7

Manufacturing Costs ($/ton HDO)	
Feedstock + Handling	$475
GVL Solvent	$71
THF Solvent	$327
Hydrogen	$146
Catalyst Recycling	$205
Other Raw Materials	$155
Purchased Steam	$466
Waste Disposal	$55
Net Electricity	-$352
Fixed Costs	$303
Capital Depreciation	$398
Average Income Tax	244
Average Return on Investment	$1,281

Manufacturing Costs ($/yr)	
Feedstock + Handling	$29,000,000
GVL Solvent	$4,300,000
THF Solvent	$20,000,000
Hydrogen	$8,900,000
Catalyst Recycling	$12,500,000
Other Raw Materials	$9,500,000
Purchased Steam	$28,500,000
Waste Disposal	$3,400,000
Net Electricity	-$21,500,000
Fixed Costs	$18,500,000
Capital Depreciation	$25,700,000
Average Income Tax	$14,900,000
Average Return on Investment	$78,300,000

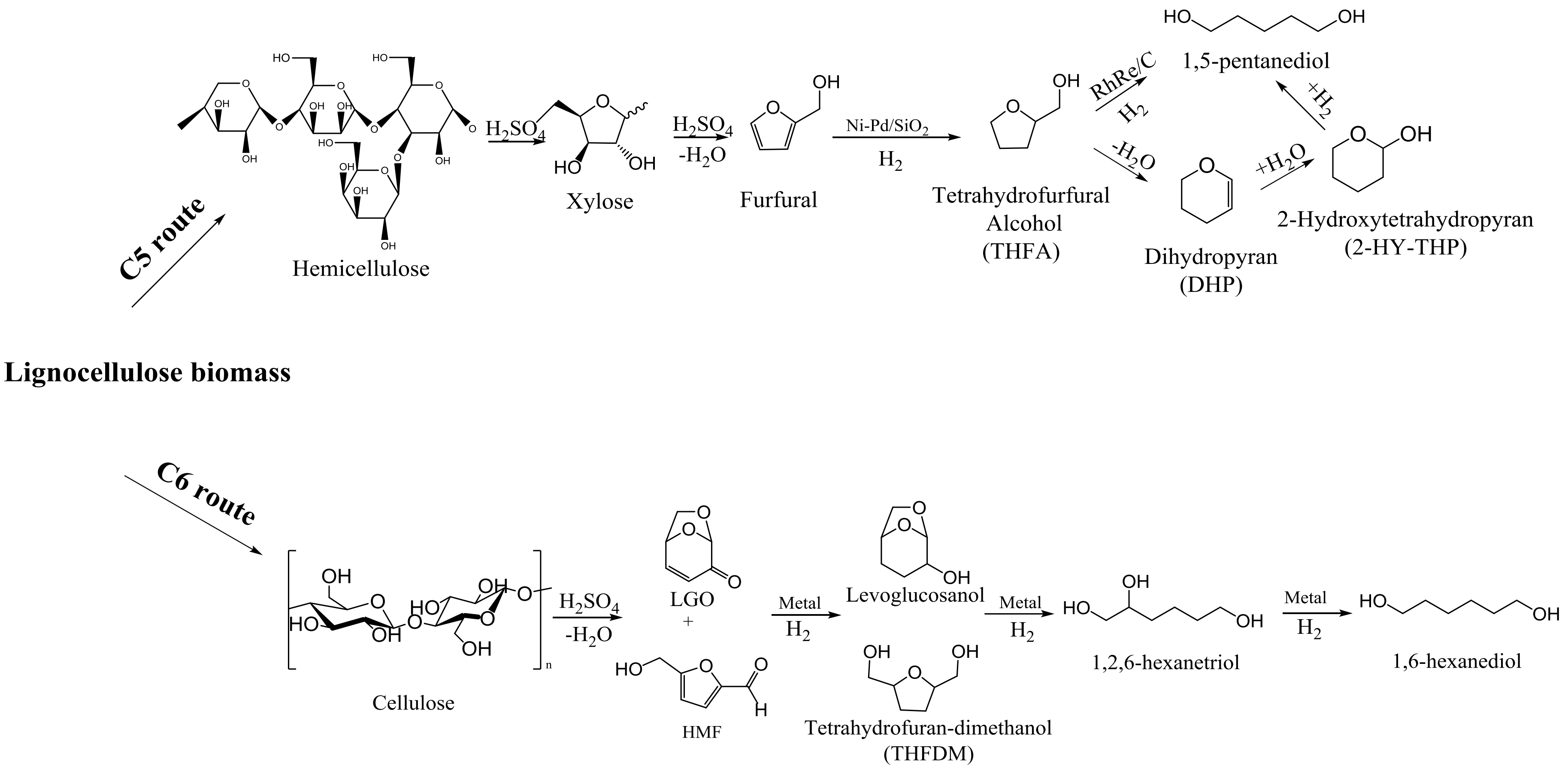
Minimum selling price is lower than current market price of 1,6 HDO and 1,5 PDO

Produce more 1,5 PDO than 1,6 HDO

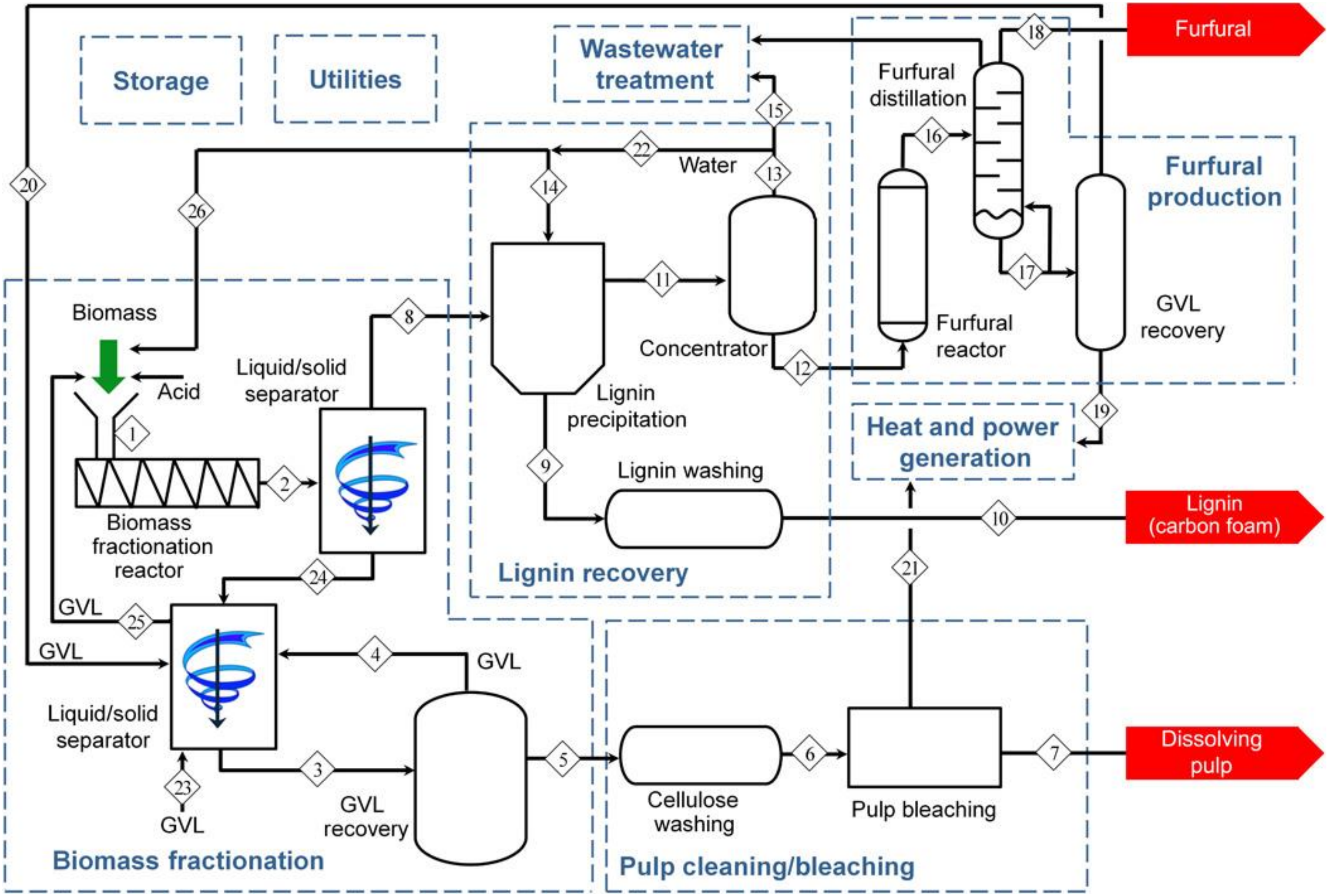
Largest operating costs are steam and feedstock

Plant size: 1000 dry metric tonne per day of **white birch** feedstock

Technical Approach: The chemistry from Lignocellulosic Biomass to PDO and HDO

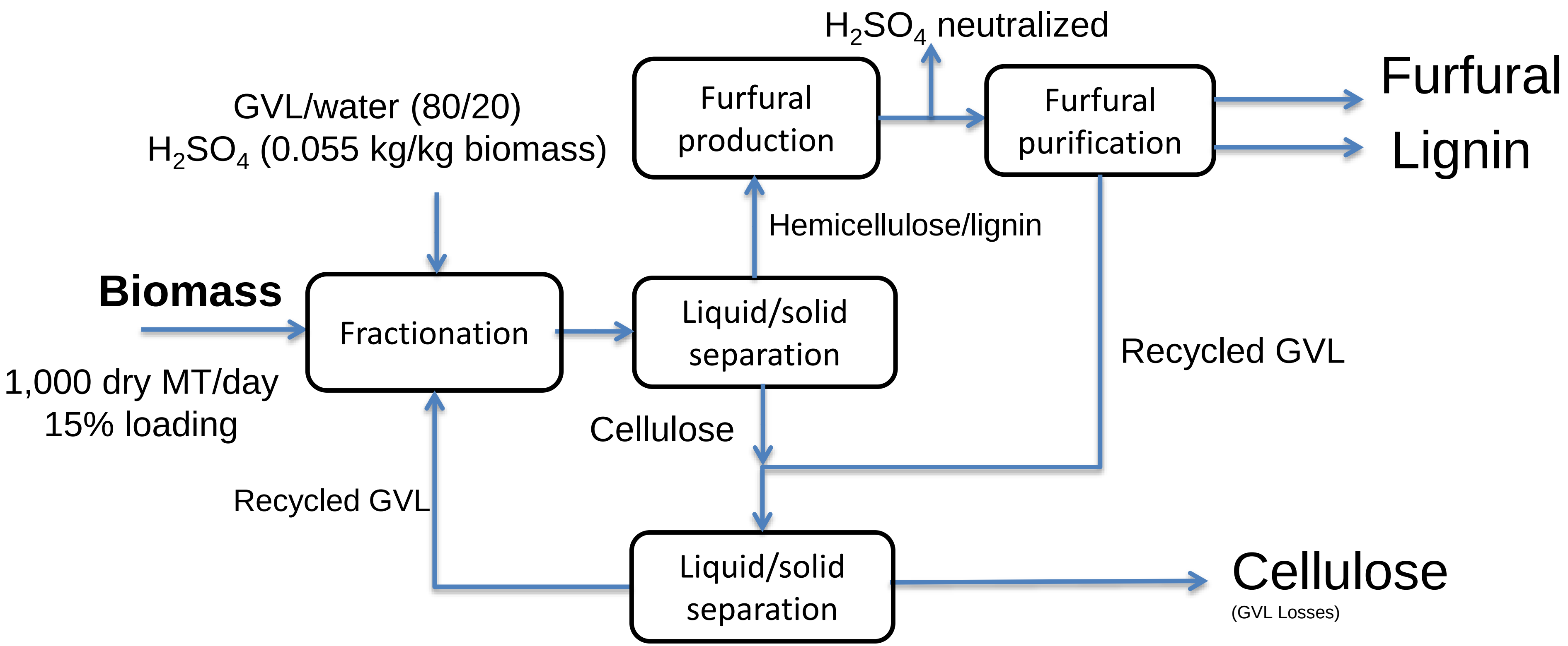


GlucanBio Triversa Process Fractionates Biomass into Furfural, Lignin and Celluose



DM Alonso et al, Increasing the revenue from Lignocellulosic Biomass: Maximizing Feedstock Utilization, Science Advances (2017) 3 e1603301

Results Task A: Cellulose, furfural, and lignin produced in labratory



H_2SO_4 neutralized

GVL/water (80/20)
H_2SO_4 (0.055 kg/kg biomass)

Furfural production

Furfural purification

Furfural

Lignin

Hemicellulose/lignin

Biomass

Fractionation

Liquid/solid separation

Recycled GVL

1,000 dry MT/day
15% loading

Cellulose

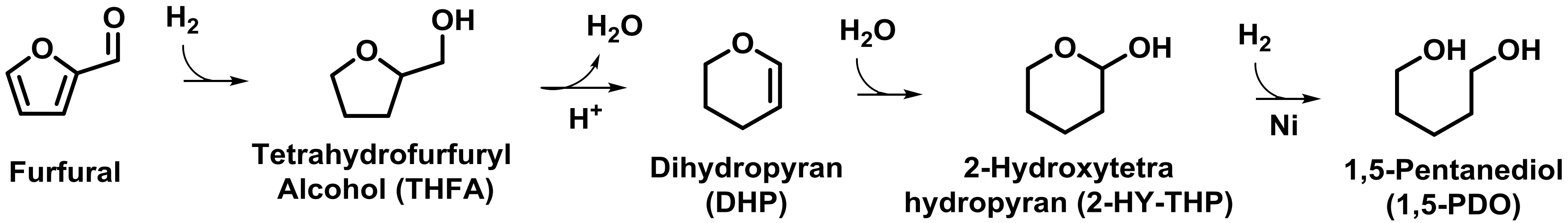
Recycled GVL

Liquid/solid separation

Cellulose
(GVL Losses)

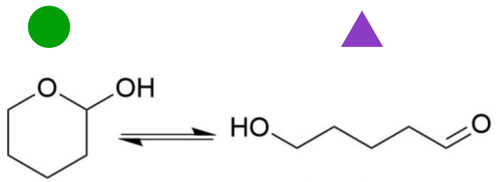
Biomass	Hemicellulose extracted (wt%)	Liquid/solid separation efficiency (%)	Furfural yield from hemicellulose (molar %)
White birch	90.8	95	86
Corn Stover	97	95	72
Switch grass	94.3	95	

Results Task B: Furfural to 1,5-Pentanediol



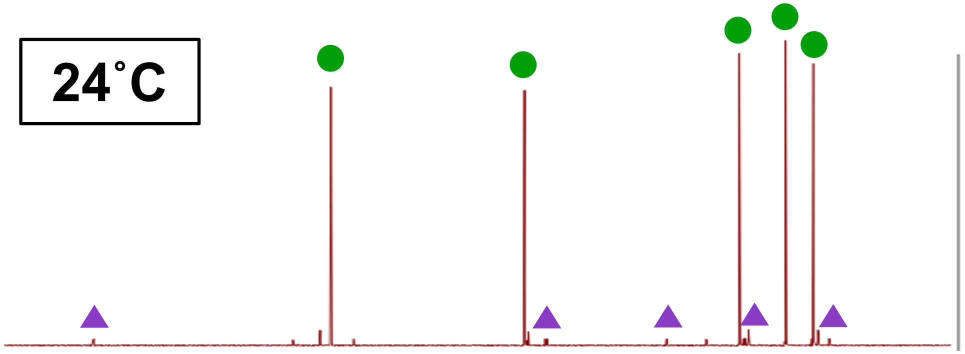
- **Step 1:** THFA Dehydration
  - γ-Al_2O_3 catalyst: 90% yield to DHP
- **Step 2:** DHP Hydration
  - No catalyst: 99% yield to 2-HY-THP + dimers
- **Step 3:** 2-HY-THP Hydrogenolysis
  - Ru/C: >96% yield to 1,5-PD
- THFA to 1,5-PDO split into 3 reactions to improve economics (“DHH Route”)
- Fully integrated process demonstrated with 85% yield

Ring-opening Tautomerization of 2-HY-THP into 5-hydroxyvaleraldehyde: NMR Studies



2-hydroxy tetrahydropyran (2-HY-THP)

5-hydroxy valeraldehyde (5HVal)

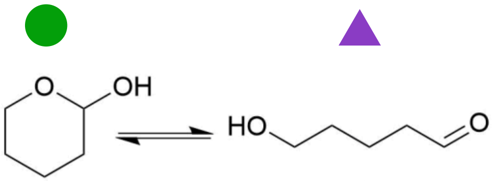


- Variable temperature quantitative ^{13}C NMR studies confirm the existence of 5-hydroxyvaleraldehyde (5HVal)

- Higher concentrations of 5HVal are observed at elevated temperatures
  - Tautomerization reaction is endothermic

ZJ Brentzel, KJ Barnett, K Huang, CT Maravelias, JA Dumesic, GW Huber, Chemicals from Biomass: Combining Ring-opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural, ChemSusChem, (2017), 10, 1351-1355.

Ring-opening Tautomerization of 2-HY-THP into 5-hydroxyvaleraldehyde: NMR Studies

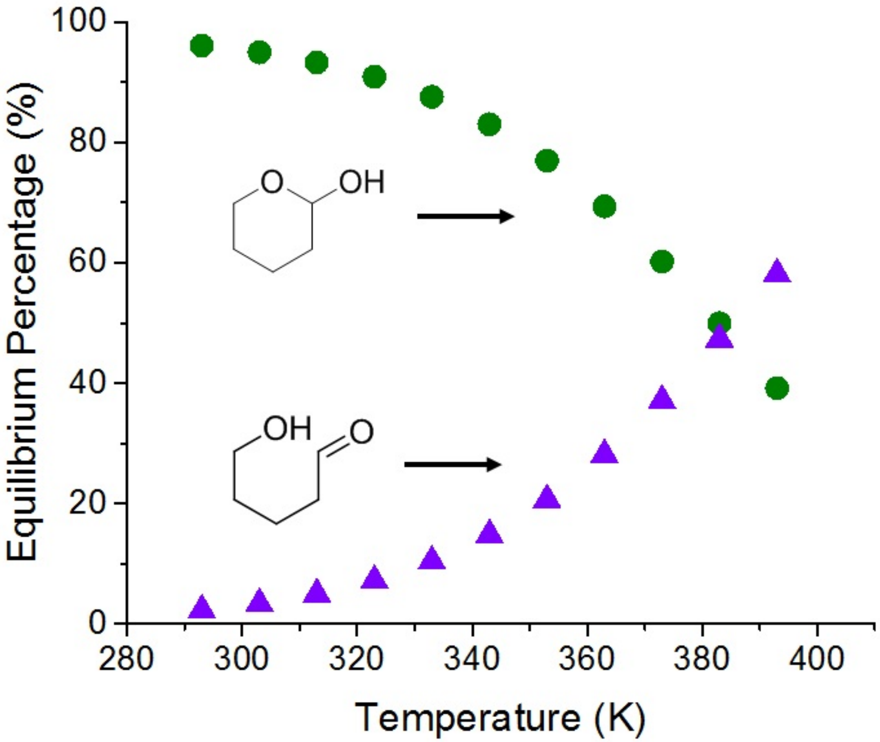


2-hydroxy tetrahydropyran (2-HY-THP)

5-hydroxy valeraldehyde (5HVal)

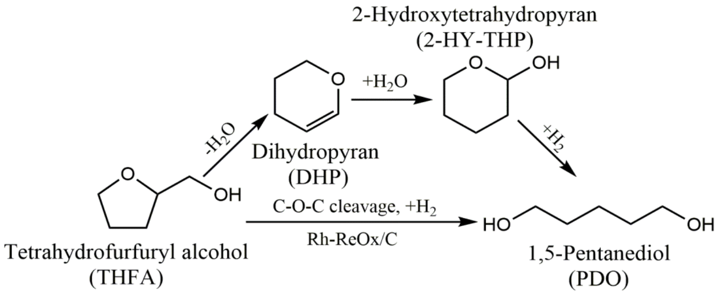
- Variable temperature quantitative ^{13}C NMR studies confirm the existence of 5-hydroxyvaleraldehyde (5HVal)

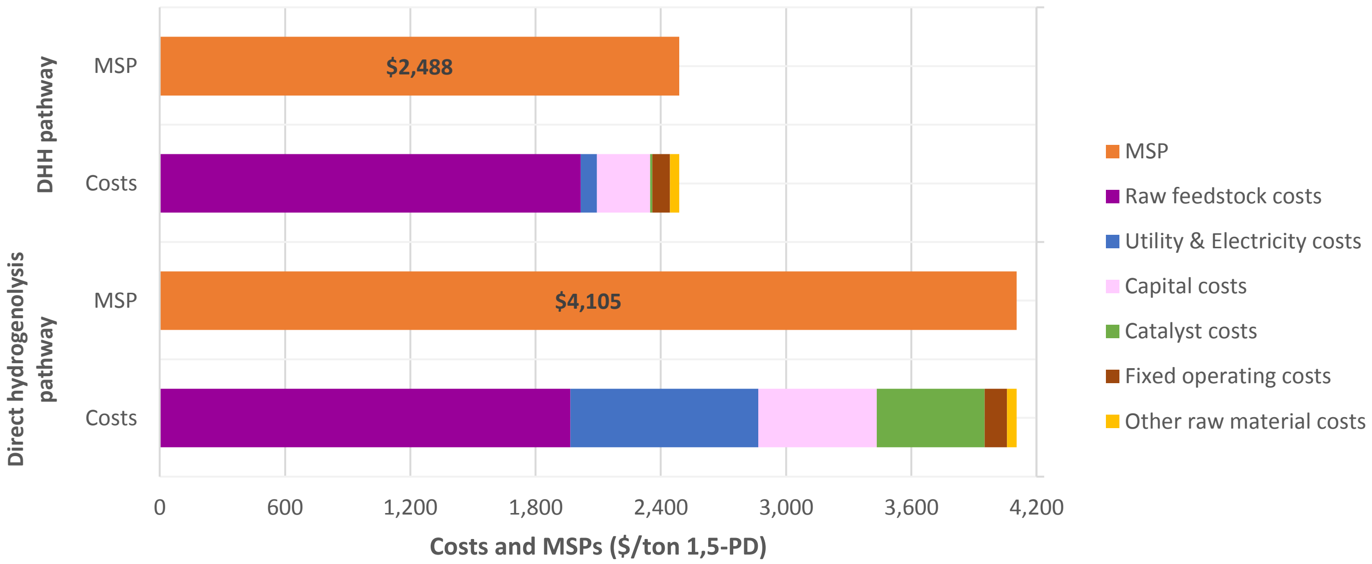
- Higher concentrations of 5HVal are observed at elevated temperatures
  - Tautomerization reaction is endothermic



ZJ Brentzel, KJ Barnett, K Huang, CT Maravelias, JA Dumesic, GW Huber, Chemicals from Biomass: Combining Ring-opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural, ChemSusChem, (2017), 10, 1351-1355.

Very promising economics for conversion of furfural into 1,5 PDO



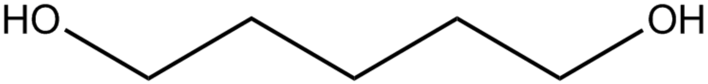


- Production cost (excluding feedstock) of DHH pathway is 4.5 times lower
- Catalyst cost of DHH pathway is 47 times lower

ZJ Brentzel, KJ Barnett, K Huang, CT Maravelias, JA Dumesic, GW Huber, Chemicals from Biomass: Combining Ring-opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural, ChemSusChem, (2017), 10, 1351-1355.

Pyran

Renewable chemicals for everyday plastics



1,5 Pentanediol (1,5 PDO)

Kevin Barnett (PhD student)

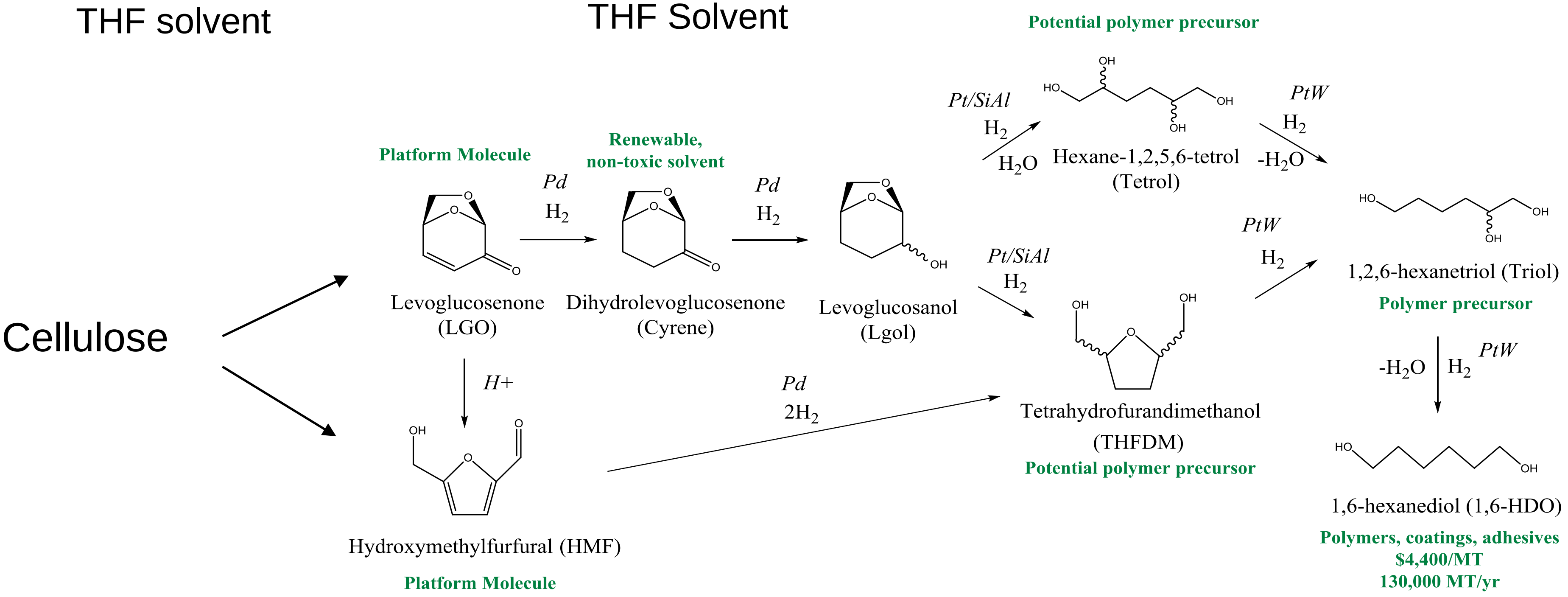
Dr Kefeng Huang (post-doc)

Task C: Cellulose to 1,6 HDO

Step 1: LGO and HMF production in THF solvent

Step 2: Hydrogenation in THF Solvent

Step 3: Hydrogenolysis in H2O



Cellulose

Platform Molecule

Levoglucosenone (LGO)

Pd H_2

Renewable, non-toxic solvent

Dihydrolevoglucosenone (Cyrene)

Pd H_2

Levoglucosanol (Lgol)

H+

Hydroxymethylfurfural (HMF)

Platform Molecule

Pd $2H_2$

Pt/SiAl H_2 H_2O

Potential polymer precursor

Hexane-1,2,5,6-tetrol (Tetrol)

PtW H_2 $-H_2O$

Pt/SiAl H_2

Tetrahydrofurandimethanol (THFDM)

Potential polymer precursor

PtW H_2

1,2,6-hexanetriol (Triol)

Polymer precursor

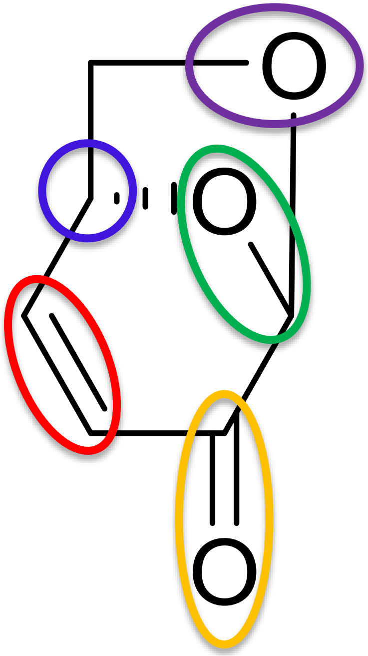
$-H_2O$ H_2 *PtW*

1,6-hexanediol (1,6-HDO)

Polymers, coatings, adhesives
$4,400/MT
130,000 MT/yr

- LGO is a platform molecule for the production of renewable chemicals from biomass
- LGO upgrading involves metal catalysts (hydrogenation), acid catalysts (C-O cleavage), and bifunctional catalysts (hydrogenolysis)
- Selective production of target molecules requires careful control of catalyst metal-acid properties

Levoglucosenone (LGO)



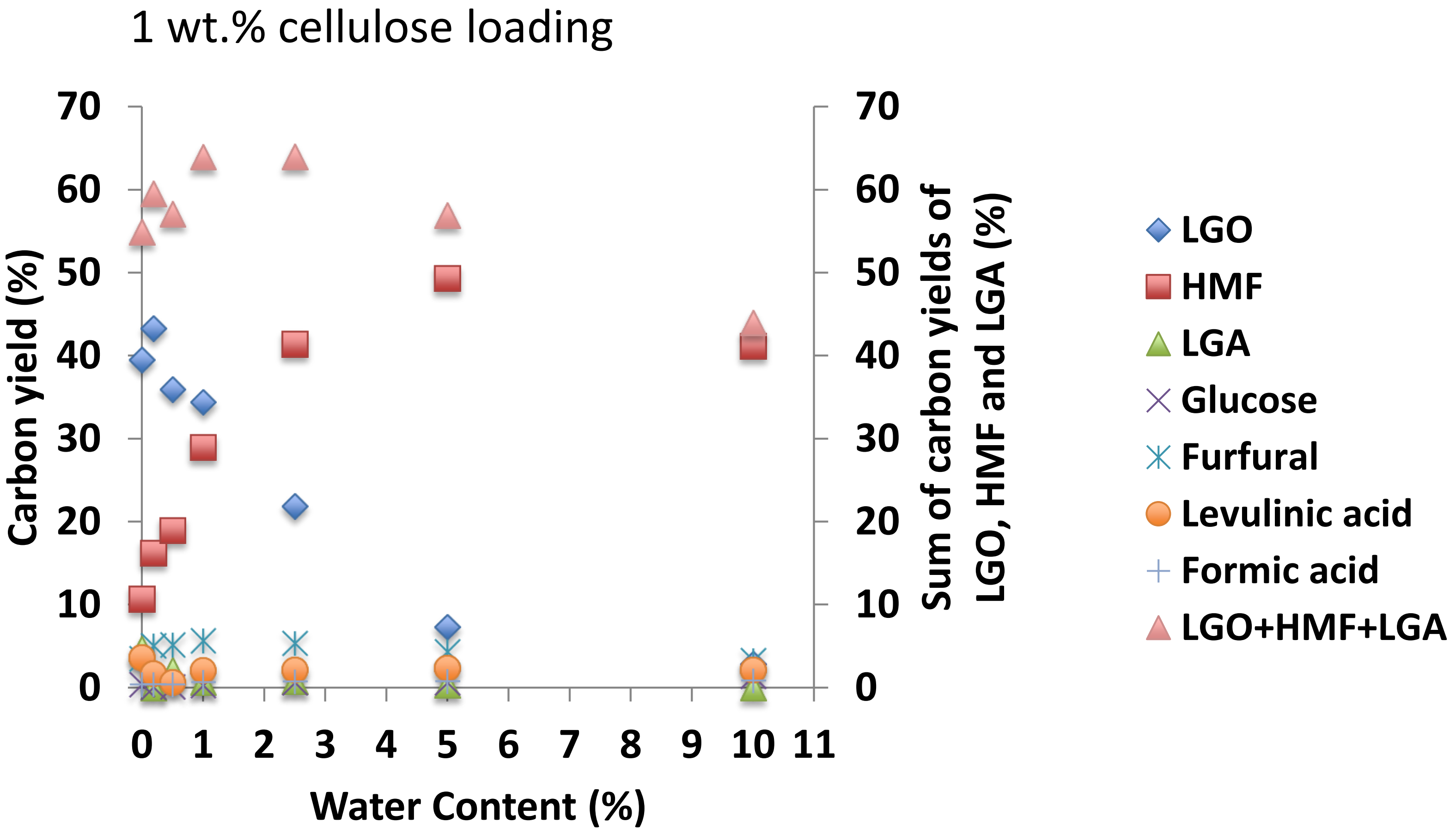
- **Chiral carbon**
- **Double bond** conjugated with a **ketone**
- Protected **aldehyde**
- Two protected **hydroxyl groups**

Sometimes referred to as “the next HMF”

Circa (http://www.circagroup.com.au/levoglucosenone/) producing 50 tons/year
Technoeconomic analysis suggest at larger scale LGO can be produced ~$4/kg

F Cao, TJ Schwartz, D McClelland, S Krishna, JA Dumesic, GW Huber, Dehydration of Cellulose to Levoglucosenone using Polar Aprotic Solvents, EES, (2015) 4 1808-1885.

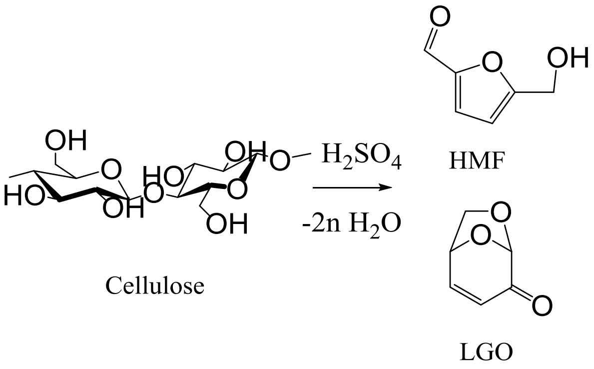
LGO and HMF can be selectively produced from Cellulose depending on water content



Reaction conditions: Cellulose (1 wt%, 0.53 g), THF (60 mL), H_2SO_4 (64 µL Conc., 20 mM)

J. He *et al* "Production of levoglucosenone and 5-hydroxymethylfurfural from cellulose in polar aprotic solvent–water mixtures" *Green Chemistry*, 19 (2017) 3642 – 3653

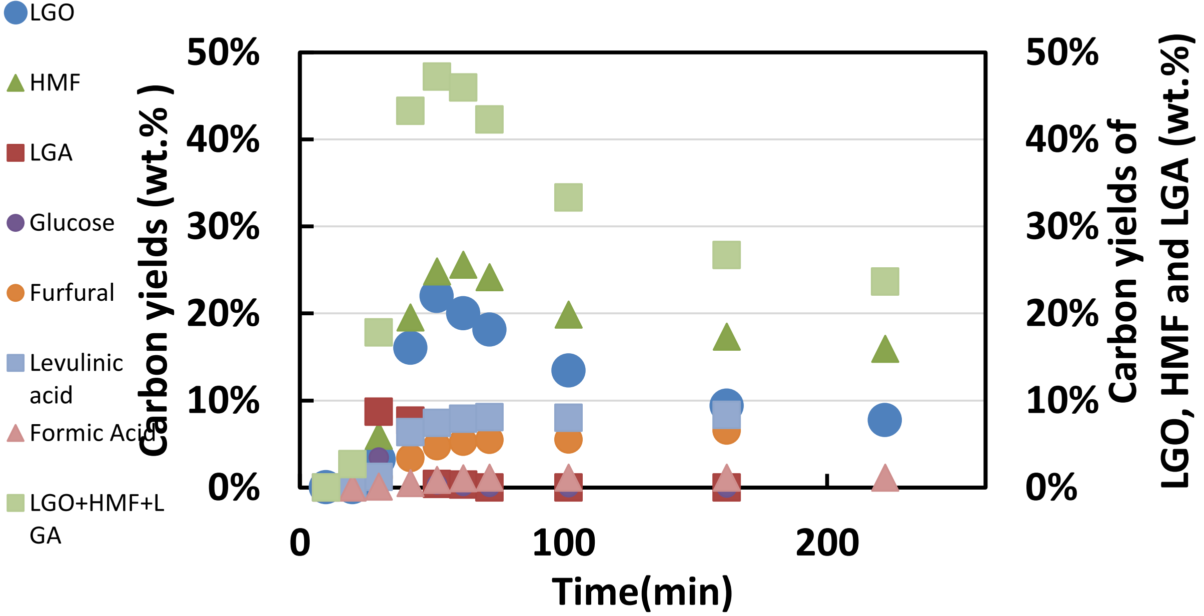
Similar LGO-HMF yields from pure cellulose and white birch-derived cellulose



Sigma Cellulose

GlucanBio Cellulose

3 wt.% cellulose loading, 1 wt.% water



Reaction conditions: Cellulose (1.65 g, 3 wt.%), THF (60 mL), H_2SO_4 (64 uL), 210 C, 500 psi He, 700 rpm.

Feedstock	Carbon yield (%)	
	LGO	HMF
Sigma Cellulose	22	24.8
GlucanBio Cellulose*	17	25.5

*Normalized to hexosan

- Cellulose loading optimized for lowest product selling price, not highest yield

1,6-HDO Yields Maintained in Integrated Process

Dehydration

Step 1 (THF Solvent)

Yield: 43%

Hydrogenation

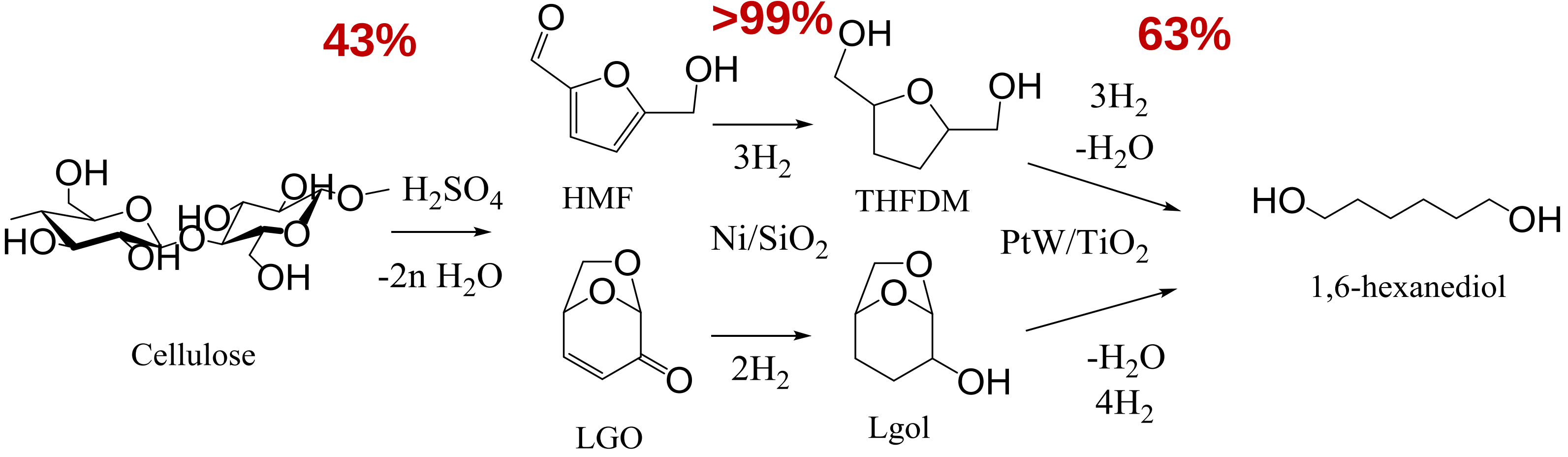
Step 2 (THF Solvent)

Yield: >99%

Hydrodeoxygenation

Step 3 (water solvent)

Yield: 63%



- **Overall 1,6-HDO yields**:

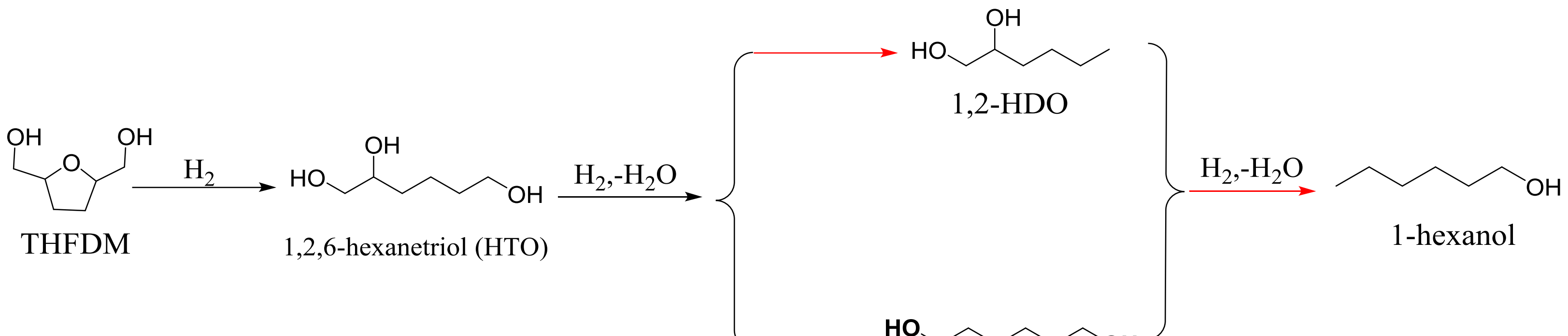
~60% from LGO + HMF monomers

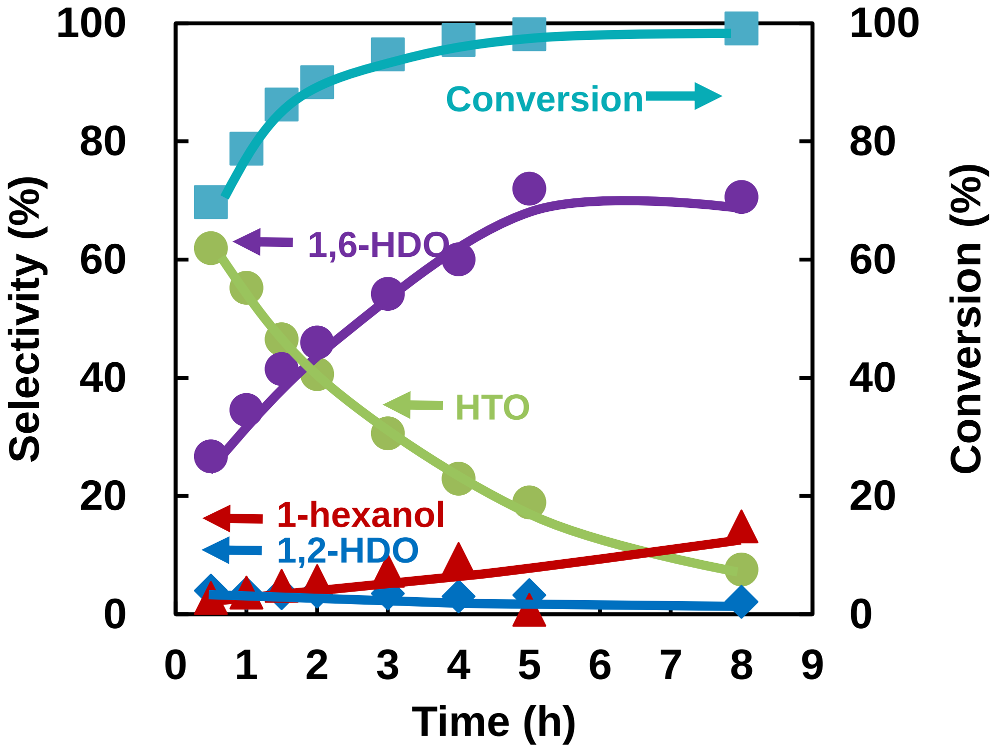
~ 27% from biomass-derived cellulose

- Similar yields as with pure components

Color of Reaction Products at Different Stages

Conversion of THFDM to 1,6-HDO with Pt-WO_x/TiO_2





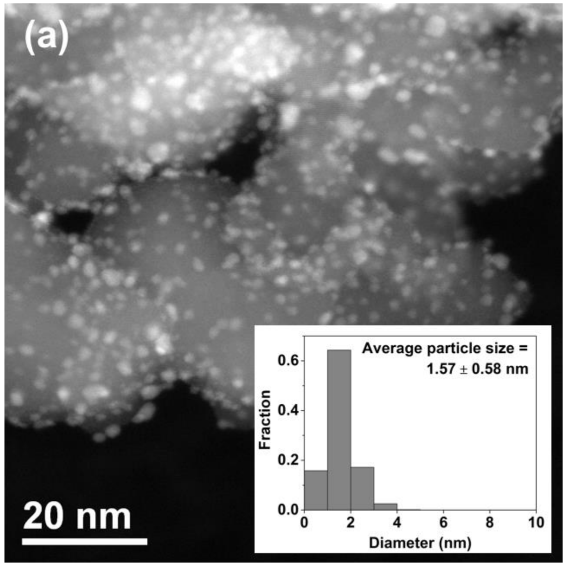
- 1,6-hexanediol yield is 70%.
- HTO is the primary product from THFDM.
- 1,2-HDO and 1-hexanol are the major side products.

Reaction conditions: Reactant (5 wt.% in H_2O, 20 mL), Pt-WO_x/TiO2 (10 wt.% Pt, 10 wt% W 0.50 g), 160 ˚C , 800 psi H_2, 700 rpm.

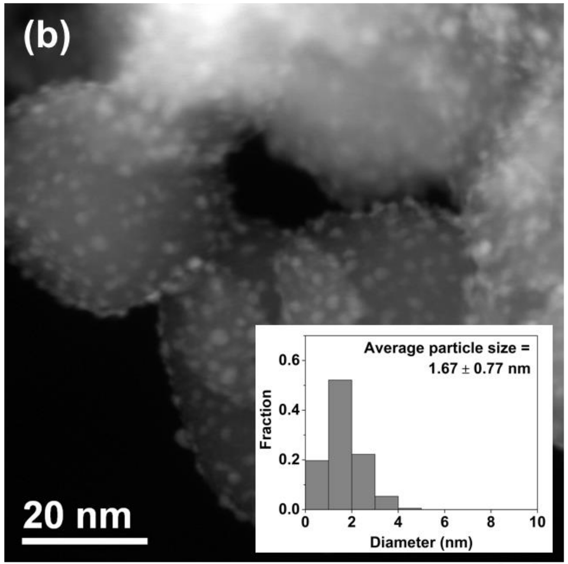
J. He, SP Burt, M Ball, D Zhao, I Hermans, JA Dumesic and GW Huber "Synthesis of 1,6-Hexanediol from cellulose derived tetrahydrofuran dimethanol (THFDM) with Pt-WO_x/TiO_2 catalysts". ACS Catalysis (2018), 8, 1427-1439

Pt particle size is not affected by tungsten loading

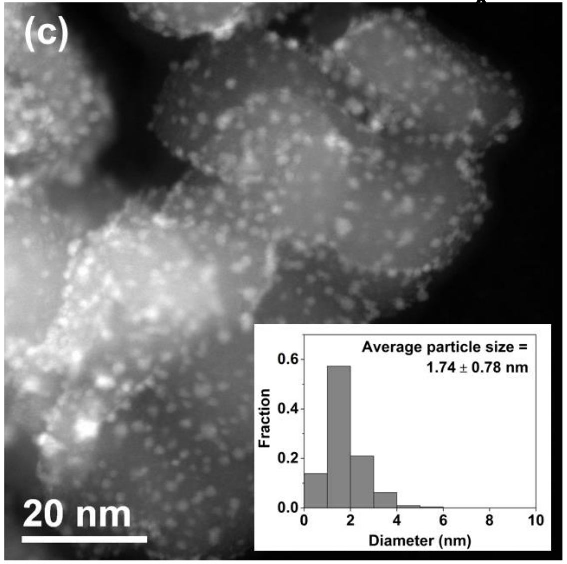
10 wt.% Pt-4 wt.% WO_x/TiO_2



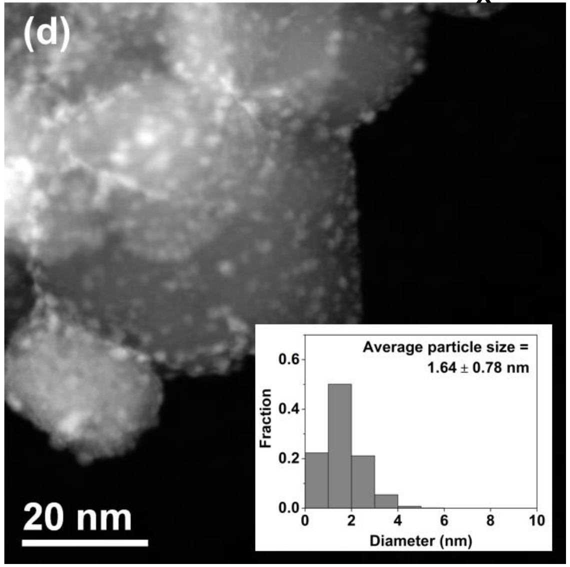
10 wt.% Pt-7 wt.% WO_x/TiO_2



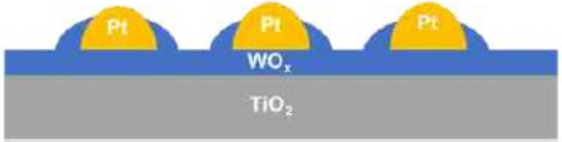
10 wt.% Pt-10 wt.% WO_x/TiO_2



10 wt.% Pt-20 wt.% WO_x/TiO_2



- Pt particle size is between 1.57-1.74 nm.
- Pt particle size is very similar regardless of tungsten loadings.



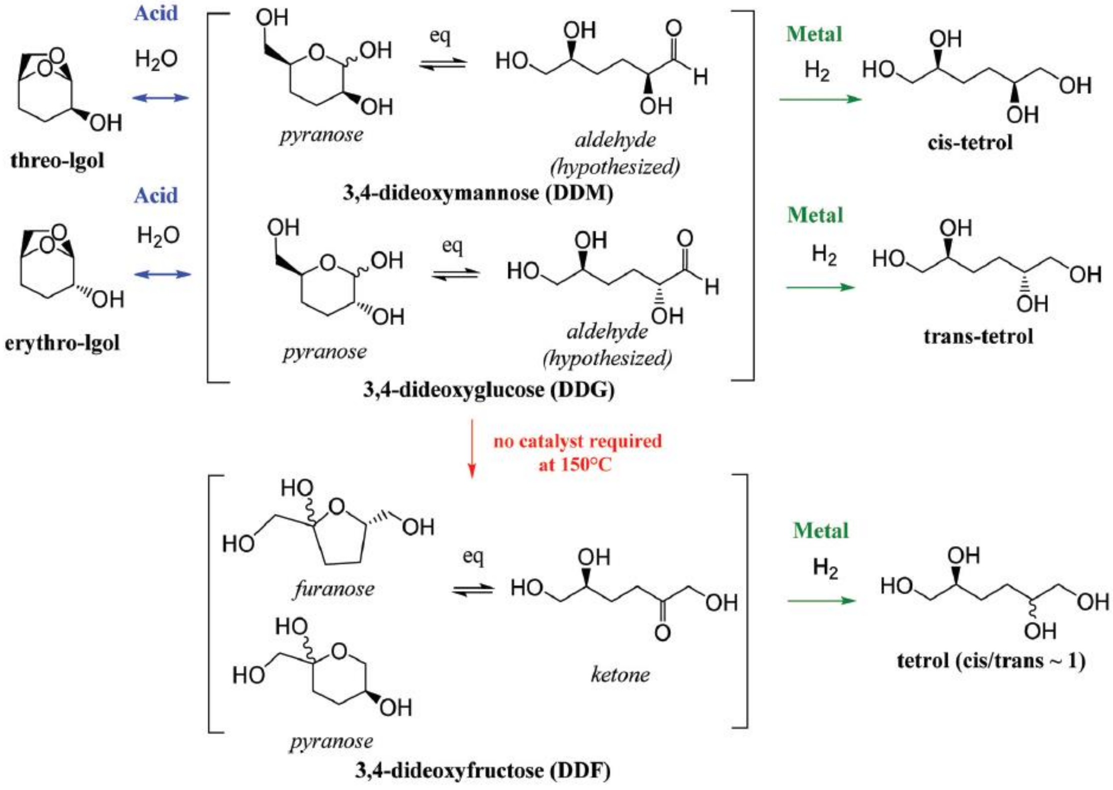
Pt (golden), WO_x (blue), TiO_2 (grey).

Production of Tetrol (new polyol) from LGO derived chemical

- New pathway to produce hexane-1,2,5,6-tetrol (potential polymer precursor) from levoglucosanol in up to 90% yield with bifunctional Pt/SiAl catalyst

<u>Reaction Network:</u>

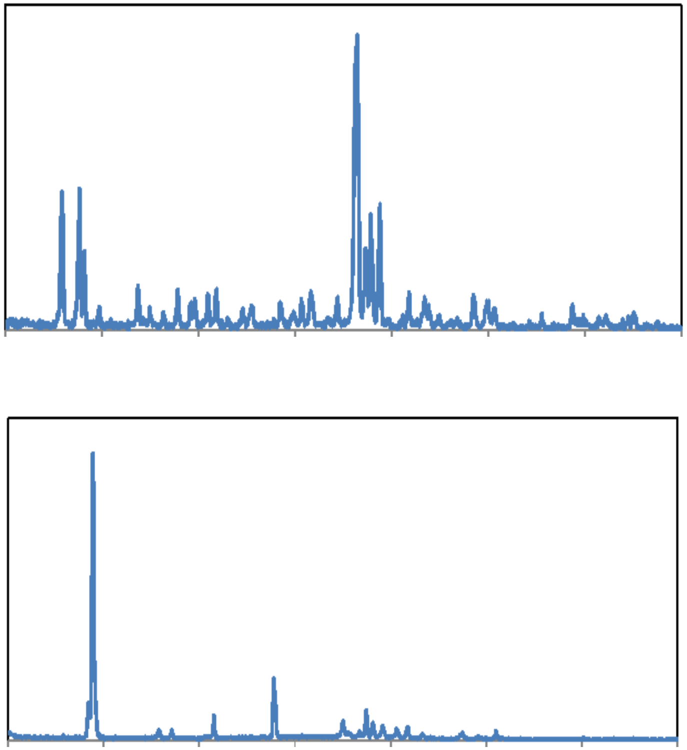
- Lgol undergoes acid-catalyzed hydrolysis to DDM and DDG
  - C_2 stereochemistry preserved
- At higher temperatures (150C), DDM/DDG undergo aldose-ketose isomerization to DDF without added catalyst
  - C_2 stereochemistry erased
- DDM, DDG, and DDF can then be hydrogenated to tetrol over metal sites



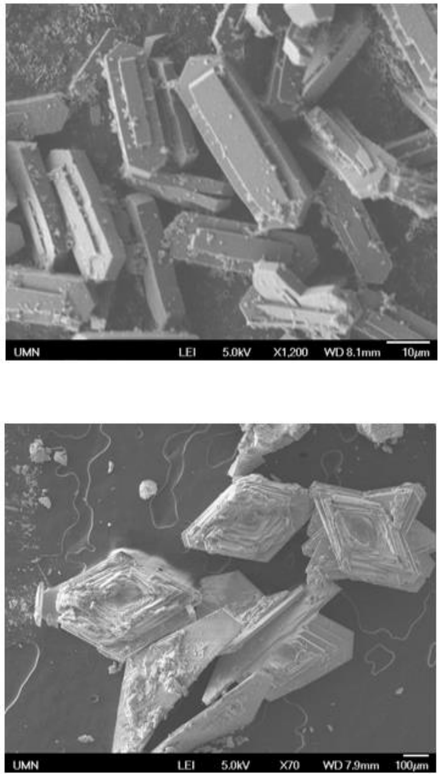
S. H. Krishna, M. De bruyn, Z. R. Schmidt, B. M. Weckhuysen, J. A. Dumesic and G. W. Huber, "Catalytic production of hexane-1,2,5,6-tetrol from bio-renewable levoglucosanol in water: effect of metal and acid sites on (stereo)-selectivity," *Green Chemistry*, 2018, **20**, 4557-4565.

Screening Zeolitic Adsorbents for 1,5-PDO Separation

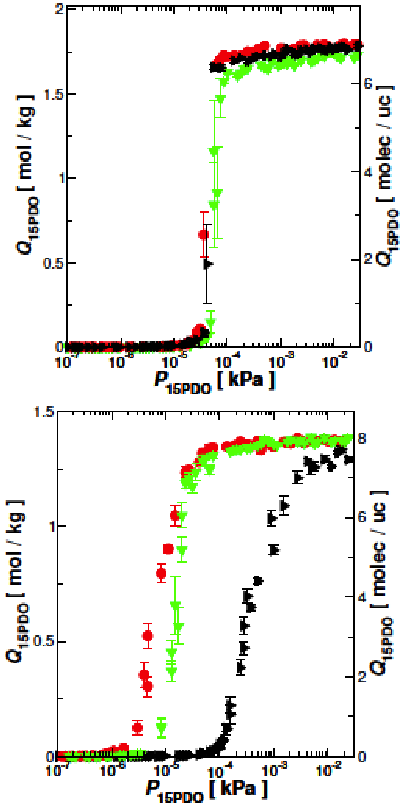
- 256 structures from IZA-SC (International Zeolite Association - The Structure Commission) database screened and found 11 frameworks that exhibit favorable adsorption of 1,5-PDO
- Computation of binary 1,5-PDO /H_2O adsorption isotherms yields two framework types with high capacity and high selectivity



X-ray Powder Diffraction Patterns



Scanning Electron Microscopy Images

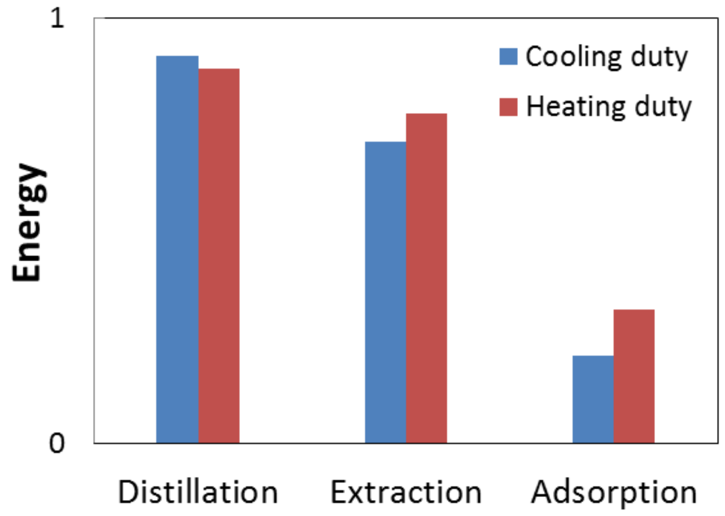


Mixture Isotherms

Techno-economic Analysis of Alternative Separation Processes for 1,5-PDO Recovery

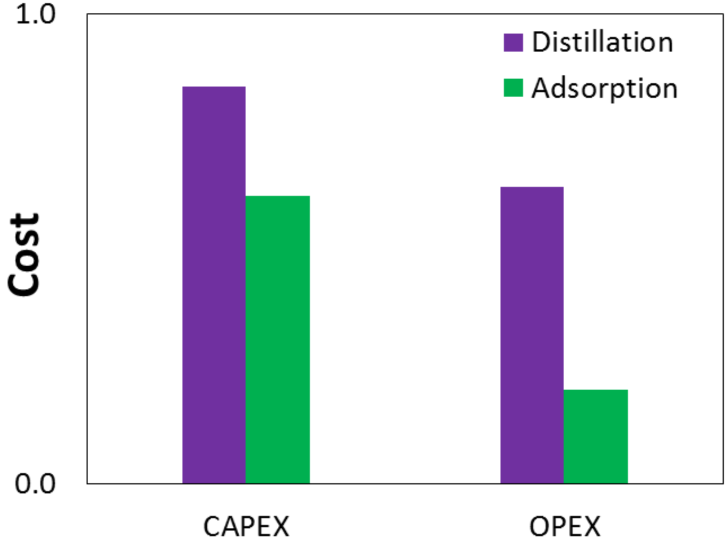
Energy Savings:

- Liquid–liquid extraction using low-boiling *n*-octane and adsorptive separation using promising zeolite were investigated as potential alternative to distillation
- Extraction shows only marginal improvement over direct 1,5-PDO/H_2O distillation while adsorption yields energy savings larger than a factor of 2

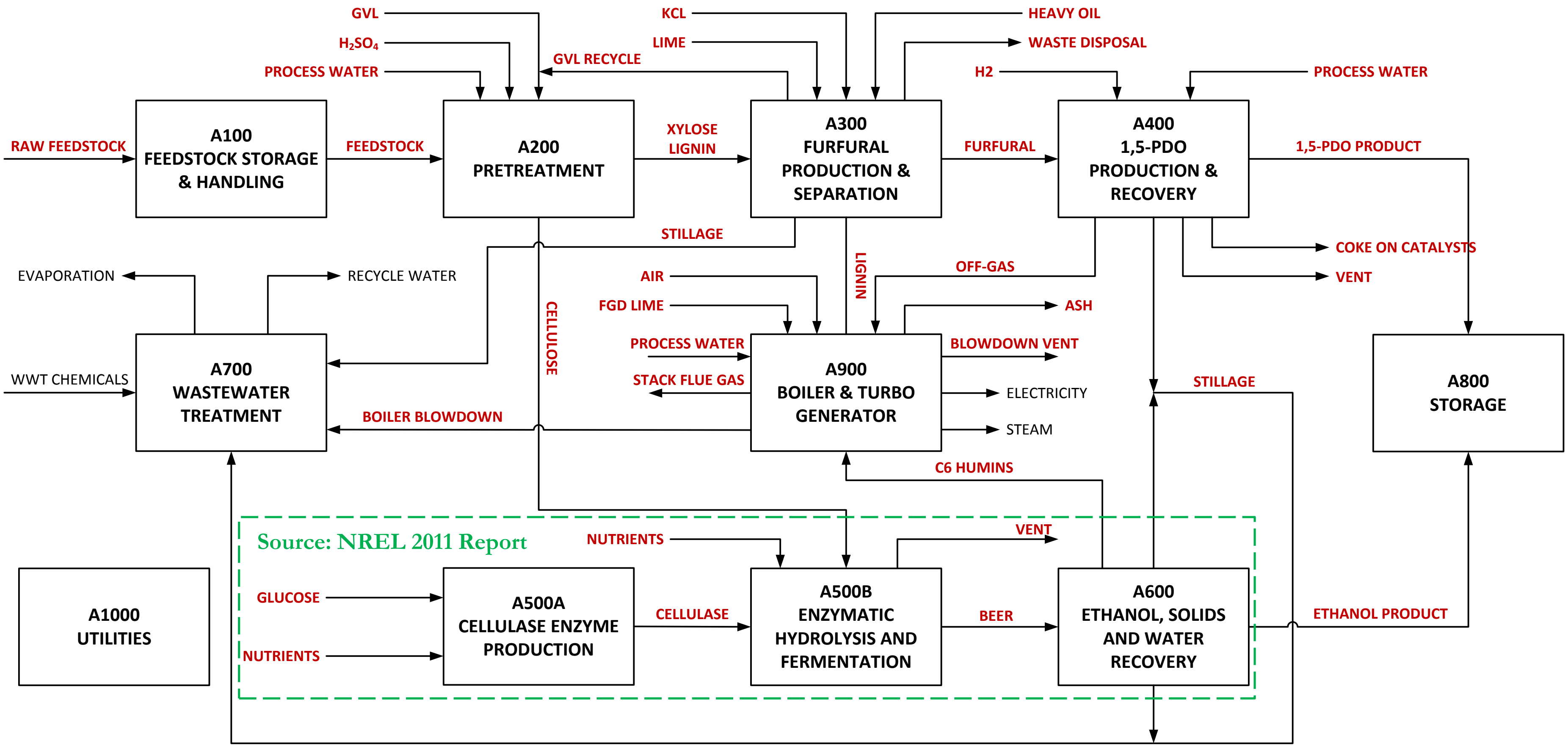


Economic Analysis:

- Economic analysis was carried out for only adsorption process due to its significant benefits over distillation
- Adsorption process results in similar capital cost, but operating cost is only about 1/3rd compared to distillation process



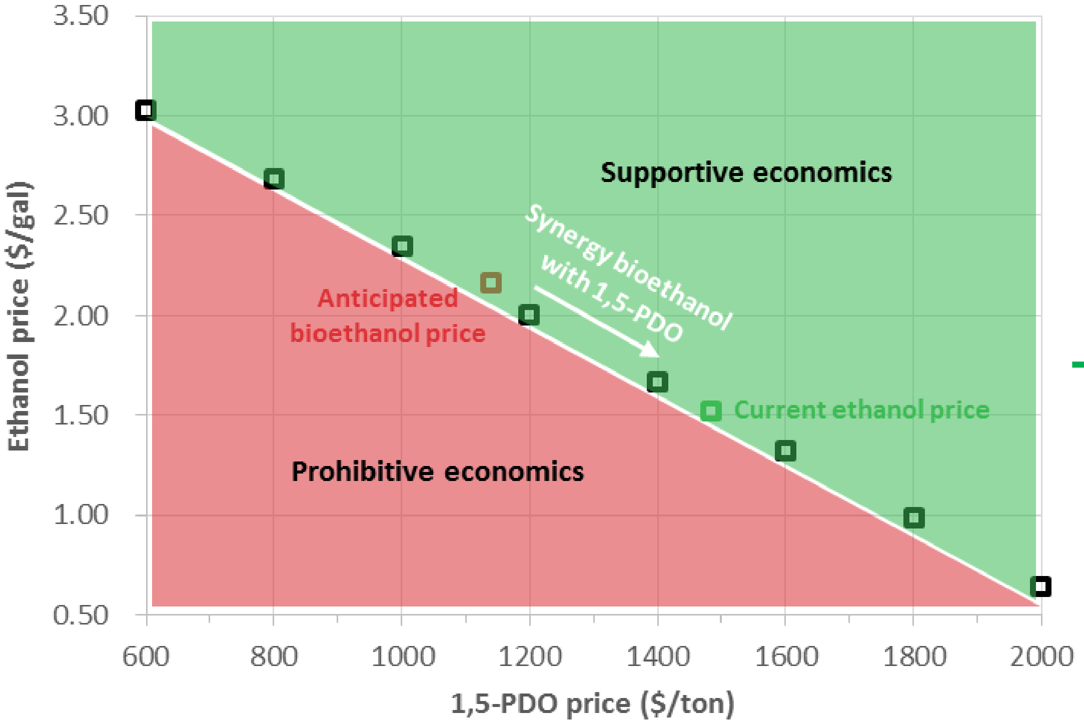
1,5-PDO integration with cellulosic ethanol



GVL
H_2SO_4
PROCESS WATER
GVL RECYCLE
KCL
LIME
HEAVY OIL
WASTE DISPOSAL
H2
PROCESS WATER
RAW FEEDSTOCK
A100
FEEDSTOCK STORAGE & HANDLING
FEEDSTOCK
A200
PRETREATMENT
XYLOSE
LIGNIN
A300
FURFURAL PRODUCTION & SEPARATION
FURFURAL
A400
1,5-PDO PRODUCTION & RECOVERY
1,5-PDO PRODUCTION
STILLAGE
LIGNIN
OFF-GAS
COKE ON CATALYSTS
VENT
EVAPORATION
RECYCLE WATER
AIR
FGD LIME
ASH
CELLULOSE
PROCESS WATER
BLOWDOWN VENT
WWT CHEMICALS
A700
WASTEWATER TREATMENT
STACK FLUE GAS
A900
BOILER & TURBO GENERATOR
ELECTRICITY
STEAM
STILLAGE
A800
STORAGE
BOILER BLOWDOWN
C6 HUMINS
Source: NREL 2011 Report
NUTRIENTS
VENT
GLUCOSE
NUTRIENTS
A1000
UTILITIES
A500A
CELLULASE ENZYME PRODUCTION
CELLULASE
A500B
ENZYMATIC HYDROLYSIS AND FERMENTATION
BEER
A600
ETHANOL, SOLIDS AND WATER RECOVERY
ETHANOL PRODUCT

K Huang, W Won, KJ Barnett, ZJ Brentzel, DM Alonso, GW Huber, JA Dumesic, CT Maravelias, Improving economics of lignocellulosic biofuels: An integrated strategy for coproducing 1,5-pentanediol and ethanol, Applied Energy (2018) 23, 585-594.

1,5 PDO process can lower the cost of cellulosic ethanol process



1,5-PDO market price: $6000/ton

- Biomass feed (white birch: 1,000 dtpd)
- Hemicellulose to 1,5-PDO, cellulose to ethanol
- 1,5-PDO: 36,000 ton/yr; ethanol: 19.3 MMgal/yr
- NREL 2011 report for biomass to ethanol: $2.15/gal (2,000 dtpd feed rate)

K Huang, W Won, KJ Barnett, ZJ Brentzel, DM Alonso, GW Huber, JA Dumesic, CT Maravelias, Improving economics of lignocellulosic biofuels: An integrated strategy for coproducing 1,5-pentanediol and ethanol, Applied Energy (2018) 23, 585-594.

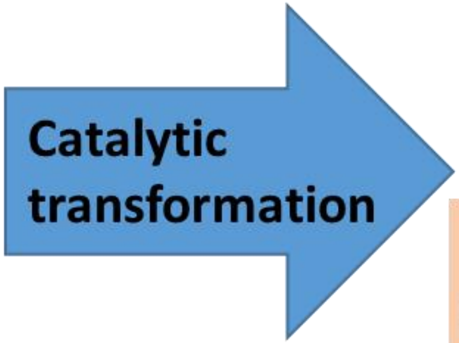
Relevance to FOA and Program Objectives

- Producing high value oxygenated commodity chemicals that can be integrated with fuels (cellulosic ethanol) from renewable resource, which helps addressing the environmental challenges from petroleum derived plastics.
- New technology/approach: No current routes exist to make these chemicals from biomass or non-oil source.
- Technology could lower the price of cellulosic ethanol, which could promote prosperity of renewable energy.
- Demonstrating each step in the pathway for the efficient low-temperature deconstruction (Barrier Ct-E) and the efficient catalytic upgrading of sugars/sromatics, gaseous and bio-Oil Intermediates to fuels and chemicals (Barrier Ct-H).
- Integrating all steps in a process (barrier Ct-J).
- Providing realistic data with process economic analysis
- Technoeconomic analysis driving the research

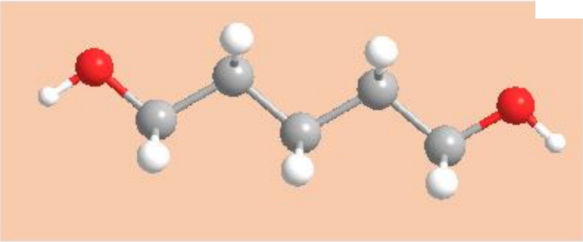
Catalytic Processes for Production of α,ω-diols from Lignocellulosic Biomass

GlucanBio

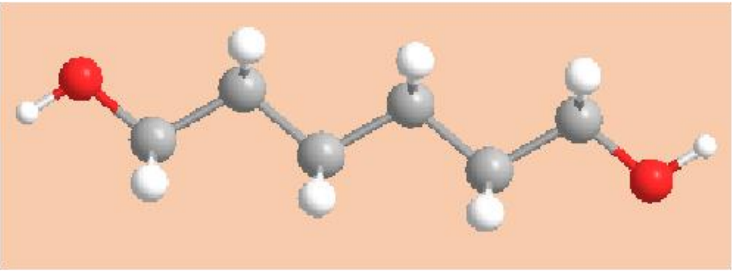
Lignocellulosic feedstock



Catalytic transformation



1,5-pentanediol



1,6-hexanediol

Project Goal: Develop an economically viable approach (using inorganic catalysis) for conversion of biomass into 1,5 pentanediol (PDO) and 1,6 hexanediol (HDO) which will lower cost of cellulosic biofuels.

Project Outcome: Experimental data, process and technoeconomic model for conversion of biomass (white birch) into 1,5 pentanediol and 1,6 hexanediol.

Argonne NATIONAL LABORATORY

Appendix: Addressing Comments from 2017 Review

Comment #1: Proposed technology is too complex with too many processing steps; it would be better to focus on diol production from intermediates (e.g. furfural)

Response : We were required by BETO to start from lignocellulosic biomass for this project. We agree that starting from intermediates (e.g. furfural, cellulose) would be simpler and take less time/resources to develop. Pyran is focusing on the concept here as outlined by this reviewer.

Comment #2: The project should also study i) proving out polymer synthesis from diols and comparing to commercial diols, and ii) production of high-value cellulose-derived intermediates such as 1,2,6-hexanetriol and 1,2,5,6-hexanetetrol

Response : We fully agree this is one of the most promising outcomes from this project. While these two topics were outside the scope of the FOA for this project, we are actively seeking funding to pursue these two areas of research.

Comment #3: The diol market is too small; only 2-3 plants would fill market demand, so the fuel co-production strategy may not have a significant impact.

Response: The current production of 1,4-butanediol and 1,6-hexanediol is 2,500 and 138 ktons/year respectively. These markets are growing at over 5% year. Therefore, the annual growth of the diols market volume is about 130 ktons. Thus if our technology was to become the low cost producer of α,ω-diols and capture the growth of this market then 2-3 plants would have to be built *each year*.

Appendix: Publications

1. S. H. Krishna, D. J. McClelland, Q. A. Rashke, J. A. Dumesic and G. W. Huber, "Hydrogenation of levoglucosenone to renewable chemicals," *Green Chemistry*, 2017, **19**, 1278-1285.

2. S. H. Krishna, T. W. Walker, J. A. Dumesic and G. W. Huber, "Kinetics of Levoglucosenone Isomerization," *ChemSusChem*, 2017, **10**, 129-138.

3. S. H. Krishna, R. S. Assary, Q. A. Rashke, Z. R. Schmidt, L. A. Curtiss, J. A. Dumesic and G. W. Huber, "Mechanistic Insights into the Hydrogenolysis of Levoglucosanol over Bifunctional Platinum Silica–Alumina Catalysts," *ACS Catalysis*, 2018, 3743-3753.

4. J. He, M. Liu, K. Huang, T. Walker , C. T. Maravelias, J. A. Dumesic, George W. Huber "Production of LGO and HMF from cellulose in water-polar aprotic solvents," Green Chemistry 19 (15), 3642-3653

5. J. He, S. P. Burt, M. Ball, D. Zhao, I. Hermans, J. A. Dumesic, and G. W. Huber, "Synthesis of 1,6-Hexanediol from cellulose derived molecules with Pt-WOx/TiO2 catalysts", ACS Catalysis 8 (2), 1427-1439

6. F. Cao, T. J. Schwartz, D. J. McClelland, S. H. Krishna, J. A. Dumesic, and G. W. Huber, "Dehydration of cellulose to levoglucosenone using polar aprotic solvents", Energy Environ. Sci., 2015, 8, 1808—1815.

7. S. H. Krishna, M. De bruyn, Z. R. Schmidt, B. M. Weckhuysen, J. A. Dumesic and G. W. Huber, "Catalytic production of hexane-1,2,5,6-tetrol from bio-renewable levoglucosanol in water: effect of metal and acid sites on (stereo)-selectivity," *Green Chemistry*, 2018, **20**, 4557-4565.

8. J. He, K. Huang, K. J. Barnett, S. H. Krishna, D. M. Alonso, Z. J. Brentzel, S. P. Burt, T. Walker, W. F. Banholzer, C. T. Maravelias, I. Hermans, J. A. Dumesic and G. W. Huber, "New catalytic strategies for alpha,omega-diols production from lignocellulosic biomass," *Faraday Discussions*, 2017, 202, 247-267.

9. S. H. Krishna, K. Huang, K. J. Barnett, M.D. bruyn, J. He, B. M. Weckhuysen, C. T. Maravelias, J. A. Dumesic, G. W. Huber, " Oxygenated commodity chemicals from chemo-catalytic conversion of biomass derived heterocycles", *AICHE Journal*, 2018

10. T. W. Walker, A. K. Chew, H. Li, B. Demir, Z. C. Zhang, G. W. Huber, R. C. Van Lehn and J. A. Dumesic, "Universal kinetic solvent effects in acid-catalyzed reactions of biomass-derived oxygenates," Energy & Environmental Science, 2018.

Appendix: Publications Continued

11. Z.J. Brentzel, K.J. Barnett, K. Huang, C.T. Maravelias, J.A. Dumesic, G.W. Huber. Chemicals from Biomass: Combining Ring-Opening Tautomerization and Hydrogenation Reactions to Produce 1,5-Pentanediol from Furfural. *ChemSusChem* **2017**.*10,* 1351-1355.
12. K. Huang, Z.J. Brentzel, K.J. Barnett, J.A. Dumesic, G.W. Huber, C.T. Maravelias. Conversion of Furfural to 1,5-Pentanediol: Process Synthesis and Analysis. *ACS Sustainable Chemistry and Engineering.* **2017**. *5* (6), 4699-4706.
13. K.J. Barnett, D.J. McClelland, G.W. Huber. Autocatalytic Hydration of Dihydropyran to 1,5-Pentanediol Precursors via in situ Formation of Liquid- and Solid-phase Acids. *ACS Sustainable Chemistry and Engineering.* **2017**. *5* (11), 10223-10230.
14. K.Huang, W.Won, K.J. Barnett, Z.J. Brentzel, D.M. Alonso, G.W. Huber, J.A. Dumesic, C.T. Maravelias. Improving Economics of Lignocellulosic Biofuels: An Integrated Strategy for Coproducing 1,5-Pentanediol and Ethanol. *Applied Energy.* **2018**. *213, 585-594.*
15. S. P. Burt, K. J. Barnett, D. J. McClelland, P. Wolf, J. A. Dumesic, G. W. Huber and I. Hermans, Production of 1,6-hexanediol from tetrahydropyran-2-methanol by dehydration-hydration and hydrogenation, *Green Chemistry,* ***2017****, 19, 1390-1398.*
16. L Li, KJ Barnett, DJ McClelland, D Zhao, G Liu, GW Huber, Gas-phase dehydration of tetrahydrofurfuryl alcohol to dihydropyran over γ-Al2O3, *Applied Catalysis B: Environmental* **(2019)** 245, 62-70.
17. R. F. DeJaco, B. Elyassi, M. D. d. Mello, N. Mittal, M. Tsapatsis and J. I. Siepmann, Understanding the unique sorption of alkane-α, ω-diols in silicalite-1, *The Journal of Chemical Physics*, **2018**, 149, 072331.

Submitted/In preparation:

18. J. He, S.P. Burt, M. B. Ball, I. Hermans, J A. Dumesic, G.W. Huber, Catalytic C-O bond hydrogenolysis of tetrahydrofuran-dimethanol over Metal supported WOx/TiO2 catalysts (submitted).
19. DeJaco, R.F.; Elyassi, B.; De Mello, M.D.; Tsapatsis, M.; Siepmann, J.I. Assessment of Options for Determining the Total Adsorption Uptake from Liquid Solution: Alkane-α,ω-Diols/(Water or Ethanol) onto Silicalite-1.(In preparation.)
20. J. He, S.H. Krishna, K. Huang, D.M. Alonso, C.T. Maravelias, J.A. Dumesic, G.W. Huber, Integrated Catalytic Production of 1,6-Hexanediol from Biomass-Derived Cellulose (in preparation).
21. J. He,# M. De bruyn,# T. Ran, J.A. Dumesic, B.M. Weckhuysen, and G.W. Huber Flow stable PtW/TiO2 catalyst for the hydrolysis and hydrodeoxygenation of levoglucosanol to hexane-1,2,5,6-tetrol and 1,2,6-hexantriol", (in preparation).
22. J. He,# L. Zhang,# J.M. Venegas, I. Hermans, J. A Dumesic, G.W Huber, Accelerated C-O cleavage of THFDM with stable Atomic layer deposition prepared Pt-WOx/TiO2 in aqueous phase, (in preparation).

Appendix: Patents/Patent Applications

1. **U.S. Patent 9376451B1**. Method for selectively preparing levoglucosenone (LGO) and other anhydrosugars from biomass in polar aprotic solvents. (issued 6/30/16)

2**. U.S. Patent 10,077,224 B1**. Production of 1,5-pentanediol via Upgrading of Tetrahydrofurfuryl Alcohol: Solid-acid Catalyzed Hydration of Dihydropyran (issued 9/18/18)

3**. U.S. Patent Application 2017/0210688 A1**. Production of 1,5-pentanediol via Upgrading of Tetrahydrofurfuryl Alcohol.

4. “Catalytic Production of 1,2,5,6-hexanetetrol from Levoglucosenone”, (submitted). Application number: 62/660517, 4/20/18