U.S. Department of Energy (DOE) Bioenergy Technologies Office (BETO) 2017 Project Peer Review Production of α,ω diols from Biomass

March 9, 2017

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 (through 1/17)

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

Project Dates: 2/1/2015- 01/31/2018

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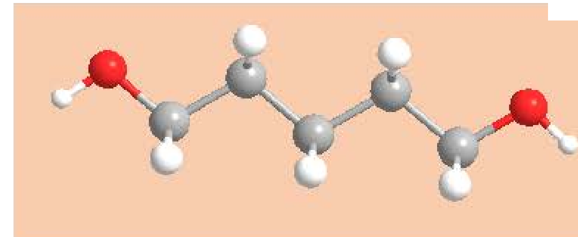
Catalytic Processes for Production of α,ω-diols from Lignocellulosic Biomass

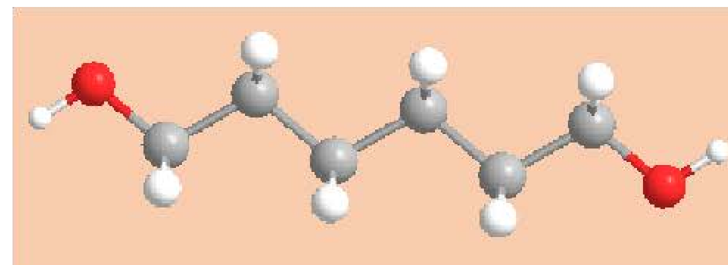
GlucanBio

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, corn stover) into 1,5 pentanediol and 1,6 hexanediol.

Argonne NATIONAL LABORATORY

Quad Chart Overview

Timeline

- Project start date: 2/1/2015
- Project end date: 1/29/2018
- Percent complete: 51%

Budget

	Total Costs FY 12 –FY 14	FY 15 Costs	FY 16 Costs	Total Planned Funding (FY 17- Project End Date)
DOE Funded	0	464,559	1,255,513	1,614,059
Project Cost Share (UW Madison)	0	107,212	256,439	342,150
Project Cost Share (Minnesota)	0	0	55,240	72,510

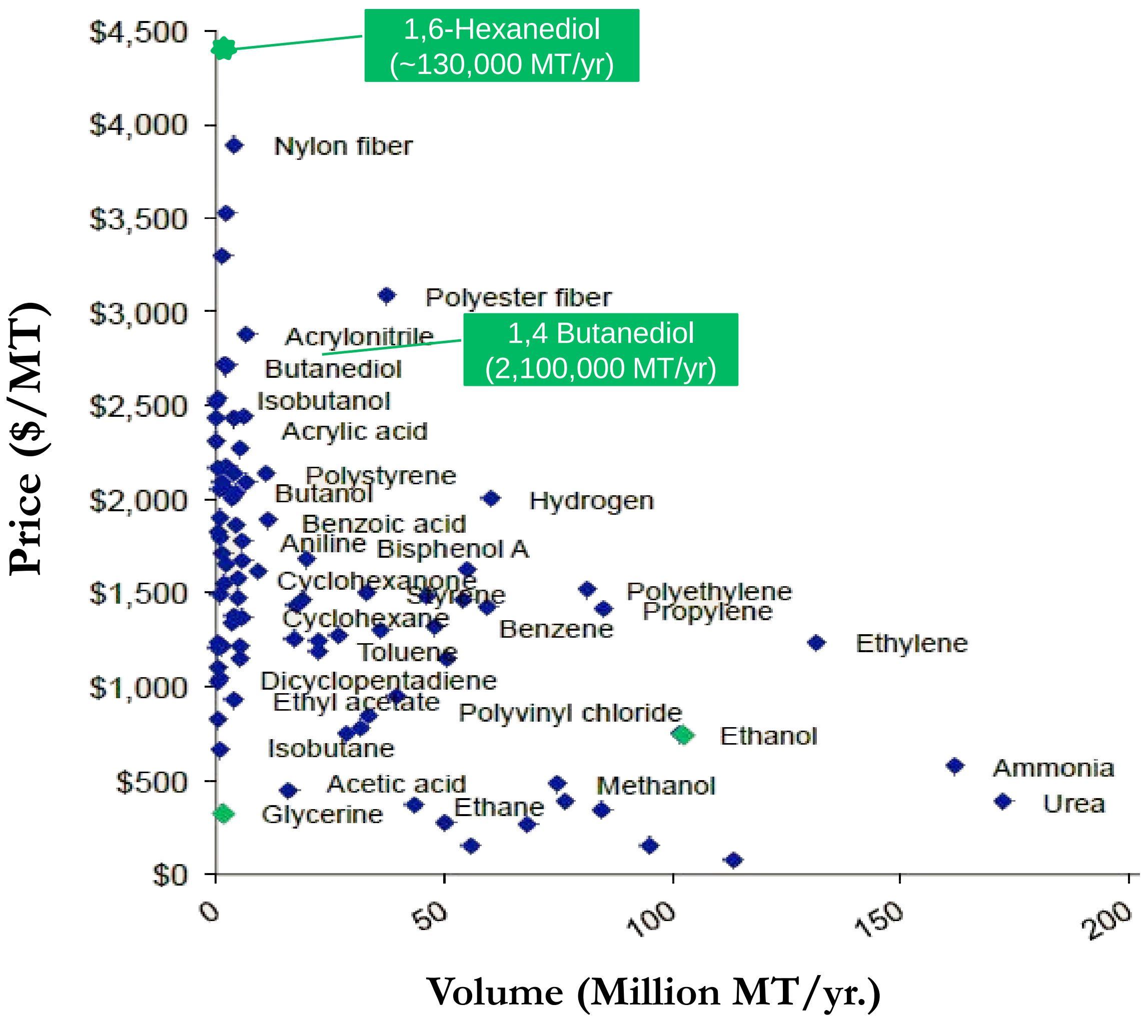
Barriers

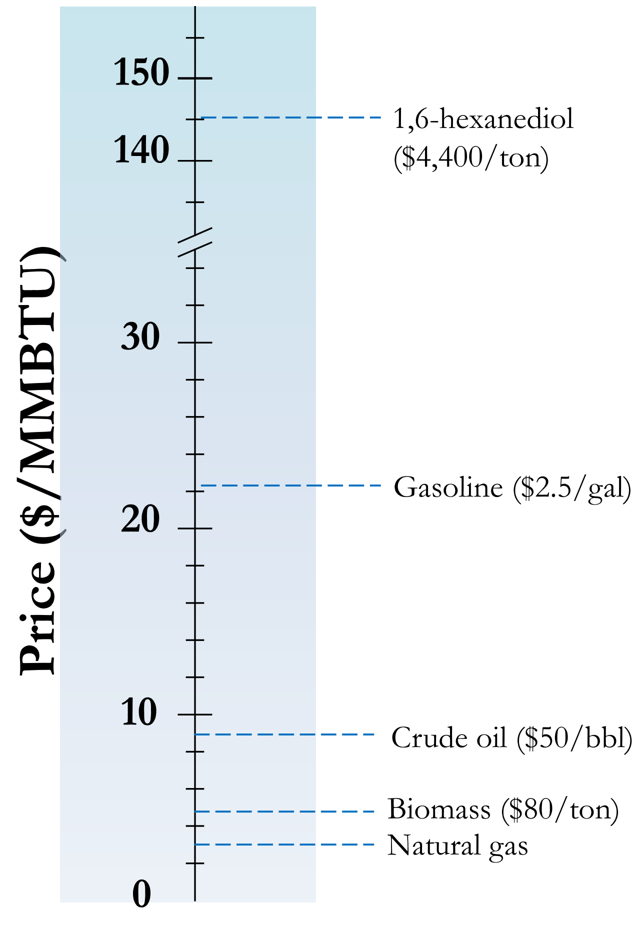
- **Ct-E.** Efficient Low-Temperature Deconstruction
- **Ct-H.** Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals
- **Ct-J.** Process Integration

Partners

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

High value infrastructure compatible oxygenated commodity chemicals from biomass



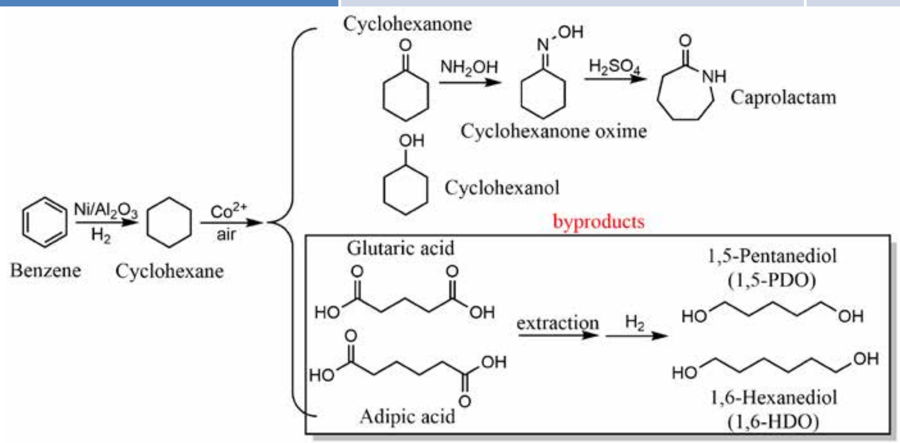


Source: ICIS, IEA

Source: Lux Research, Bio-based Materials and Chemical Intelligence Service, www.luxresearchinc.com, 2013 market prices

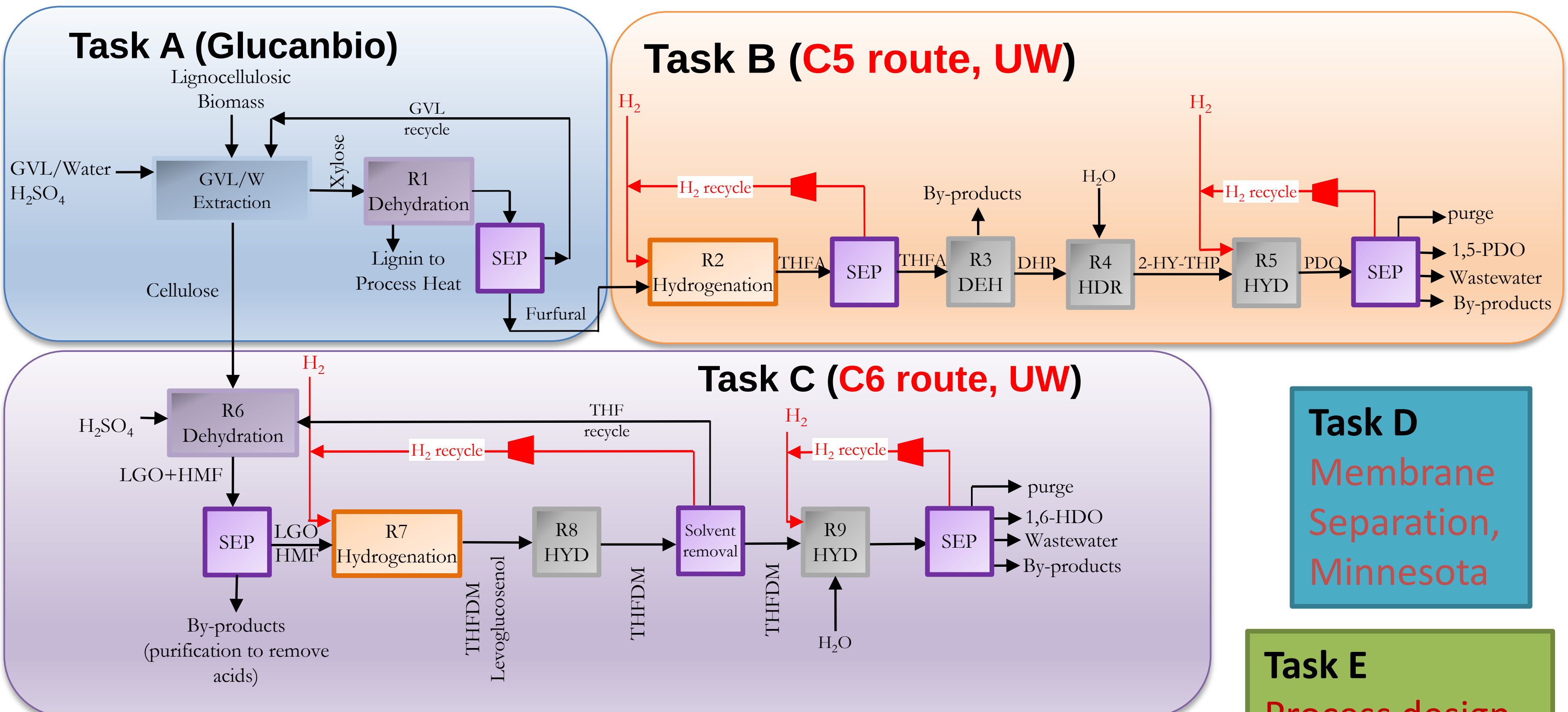
α,ω-diols have many uses in the polymer industry

Particular	1,6-Hexanediol	1,5-Pentanediol	1,4-Butanediol
Applications	▪ Polyurethanes ▪ Coatings ▪ Acrylates ▪ Adhesives ▪ Polyester Resins ▪ Plasticizers ▪ Others	▪ Polyester plastics ▪ Polyurethanes ▪ Pharmaceuticals ▪ Inks and coatings ▪ Plasticizers ▪ Solvent and industrial chemicals ▪ Others	▪ Biodegradable plastics ▪ Hot melt polyesters ▪ Coatings ▪ Polyurethanes ▪ Adhesives ▪ Pharmaceuticals ▪ Fiber particle and composite
Major players	▪ BASF ▪ Ube Industries ▪ Lanxess ▪ Perstorp AB ▪ Lishui Nanming Chemical ▪ Fushun Tianfu Chemicals	▪ BASF ▪ Ube Industries ▪ Marubeni Corporation ▪ Lishui Nanming Chemical	▪ BASF ▪ Dairen Chemicals ▪ Lyondell Chemicals ▪ Shanxi Sanwei Group ▪ ISP ▪ Invista ▪ Mitsubishi Chemicals
Current market size (2013)	$524 Million	< $10 Million	$5,550 Million



1,5-PDO and 1,6-HDO are produced from dicarboxylic acid as byproducts of caprolactam.

Approach for Conversion of Lignocellulosic Biomass to PDO and HDO



Task D
Membrane Separation, Minnesota

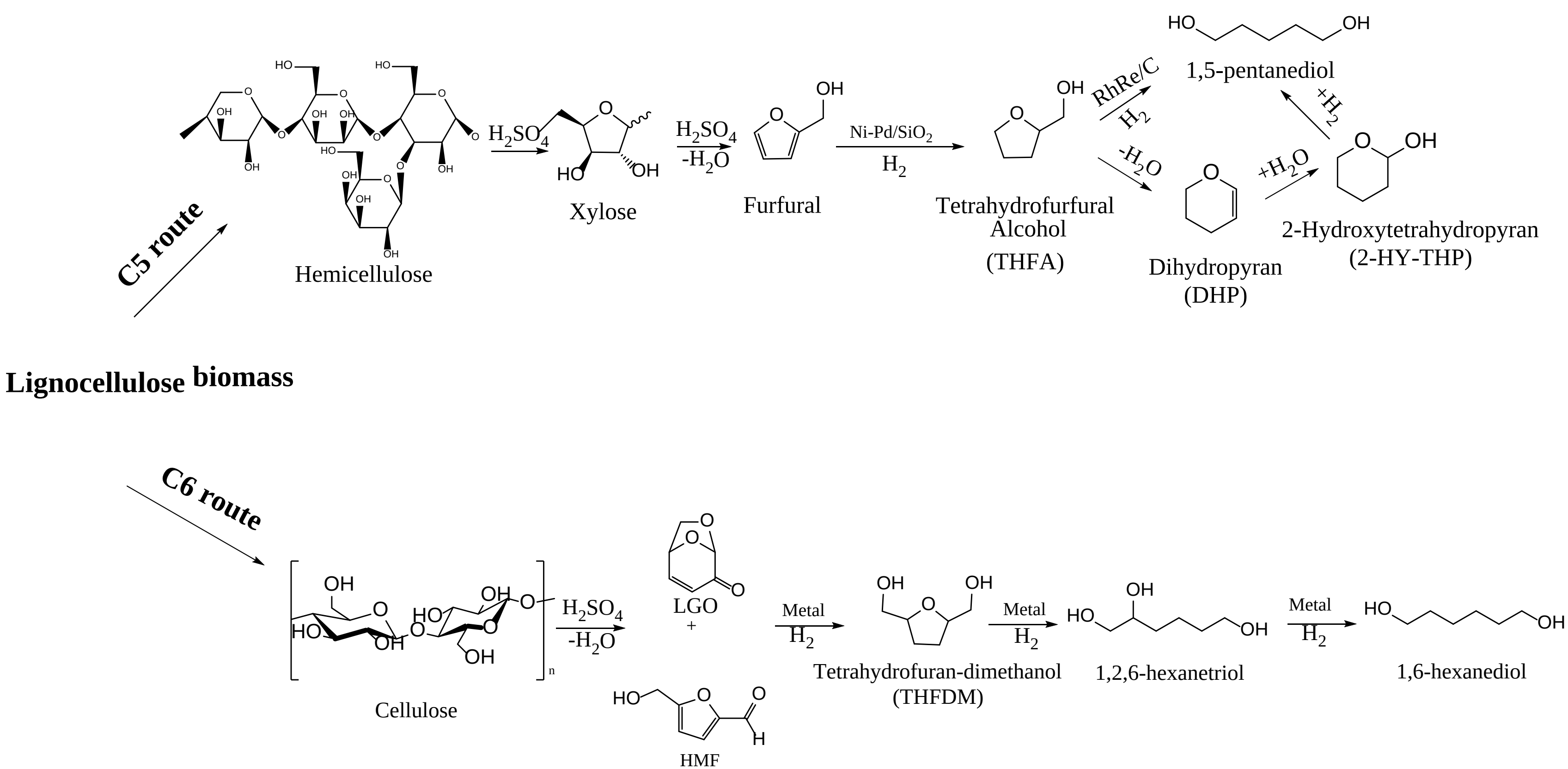
Task E
Process design and economic analysis, UW

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

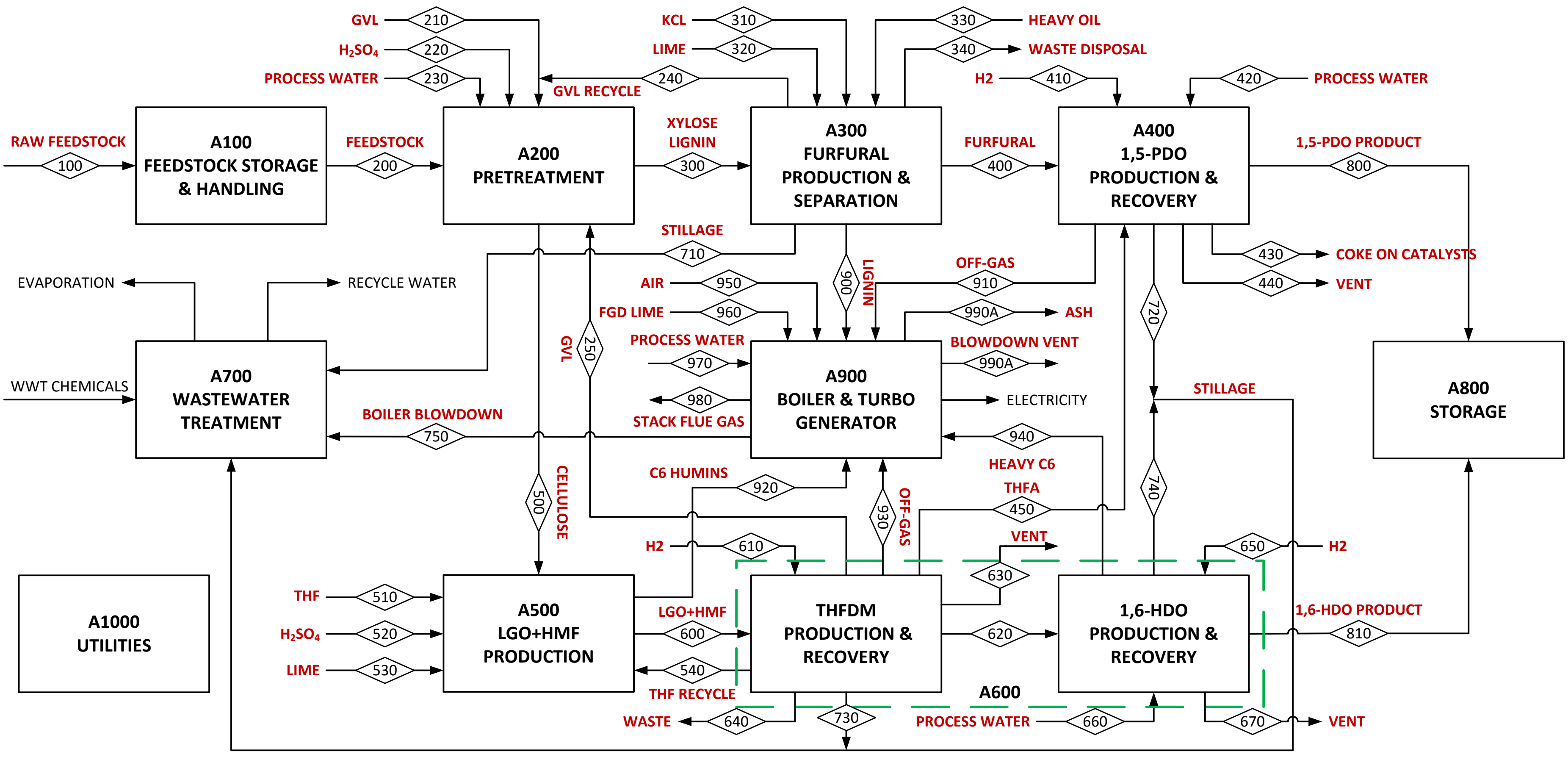
Management Approach

- 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

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



Results: Conceptual process design based on laboratory data



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

Minimum Selling Price (MSP):	**$4,089**	**/ton**
1,6-HDO Production	22,743	ton/yr
1,5-PDO Production	40,291	ton/yr
1,6-HDO Yield	0.063	ton/dry U.S. ton feedstock
1,5-PDO Yield	0.111	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%	

Installed Equipment Costs	
Pretreatment	$75,600,000
Furfural Production and Separation	$18,700,000
PDO Production and Recovery	$12,300,000
LGO+HMF Production	$106,600,000
HDO Production and Recovery	$37,600,000
Wastewater Treatment	$37,300,000
Storage	$3,600,000
Boiler and Turbo Generator	$60,300,000
Utilities	$9,400,000
Total Installed Equipment Cost	$361,400,000
Added Direct + Indirect Costs	$449,000,000
(% of TCI)	55%
Total Capital Investment (TCI)	$810,400,000
Installed Equipment Cost/Annual Ton	$15,891
Total Capital Investment/Annual Ton	$35,634
Loan Rate	8.0%
Term (years)	10
Capital Charge Factor (Computed)	0.137

Specific Operating Conditions	
Excess Electricity (kWh/kg)	2.5
Plant Electricity Use (kWh/kg)	3.5

Manufacturing Costs ($/ton HDO)	
Feedstock + Handling	$460
GVL Solvent	$59
THF Solvent	$199
Hydrogen	$153
Catalyst Recycling	$89
Other Raw Materials	172
Purchased Steam	$1,025
Waste Disposal	$18
Net Electricity	-$130
Fixed Costs	$282
Capital Depreciation	$408
Average Income Tax	$244
Average Return on Investment	$1,111

Manufacturing Costs ($/yr)	
Feedstock + Handling	$29,000,000
GVL Solvent	$3,700,000
THF Solvent	$12,500,000
Hydrogen	$9,600,000
Catalyst Recycling	$5,600,000
Other Raw Materials	$10,800,000
Purchased Steam	$64,600,000
Waste Disposal	$1,100,000
Net Electricity	-$8,200,000
Fixed Costs	$17,800,000
Capital Depreciation	$25,700,000
Average Income Tax	$15,400,000
Average Return on Investment	$74,000,000

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 PDO

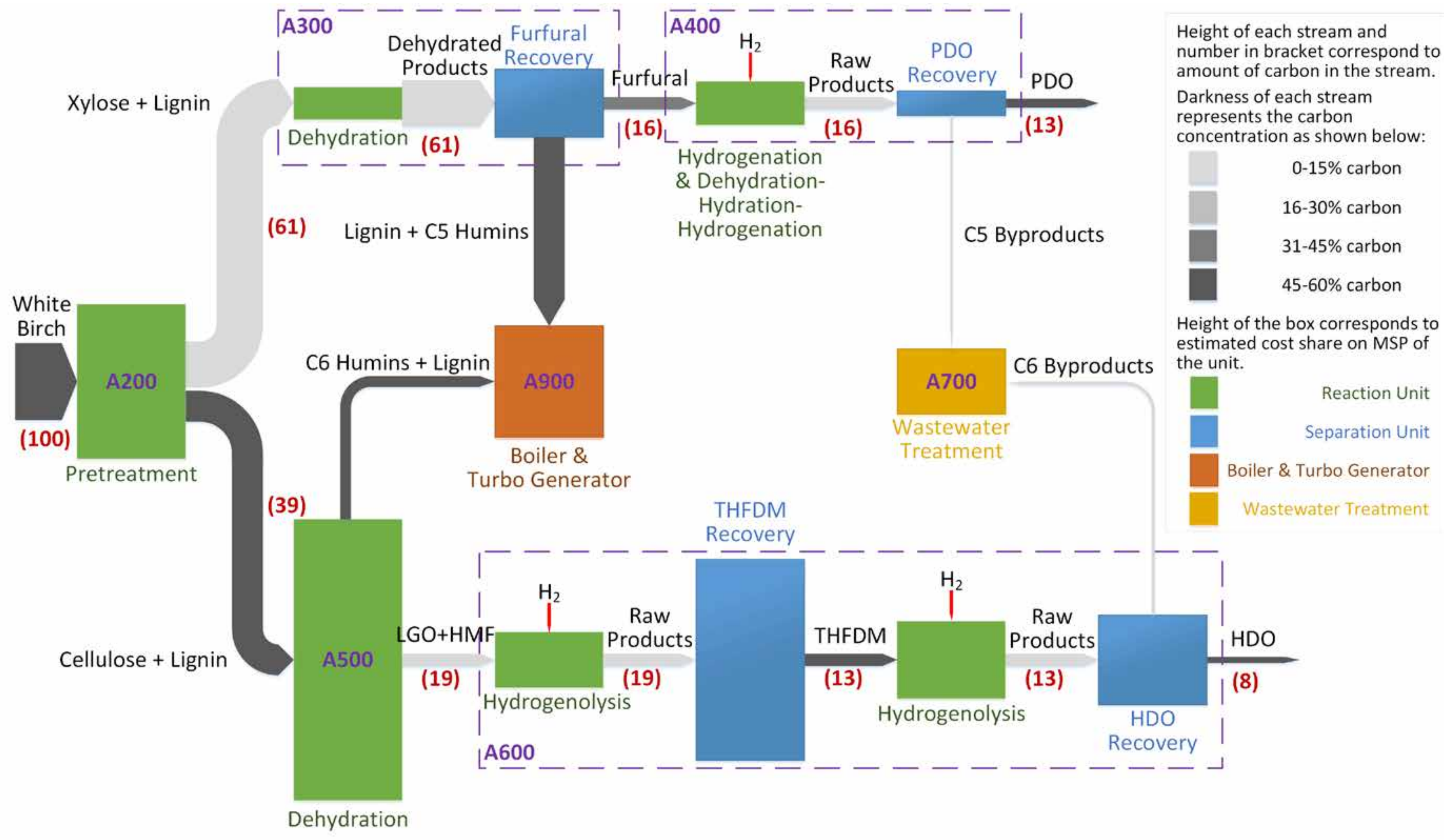
Largest operating cost is steam cost.

Steam price assumes natural gas $5.6/MMBTU

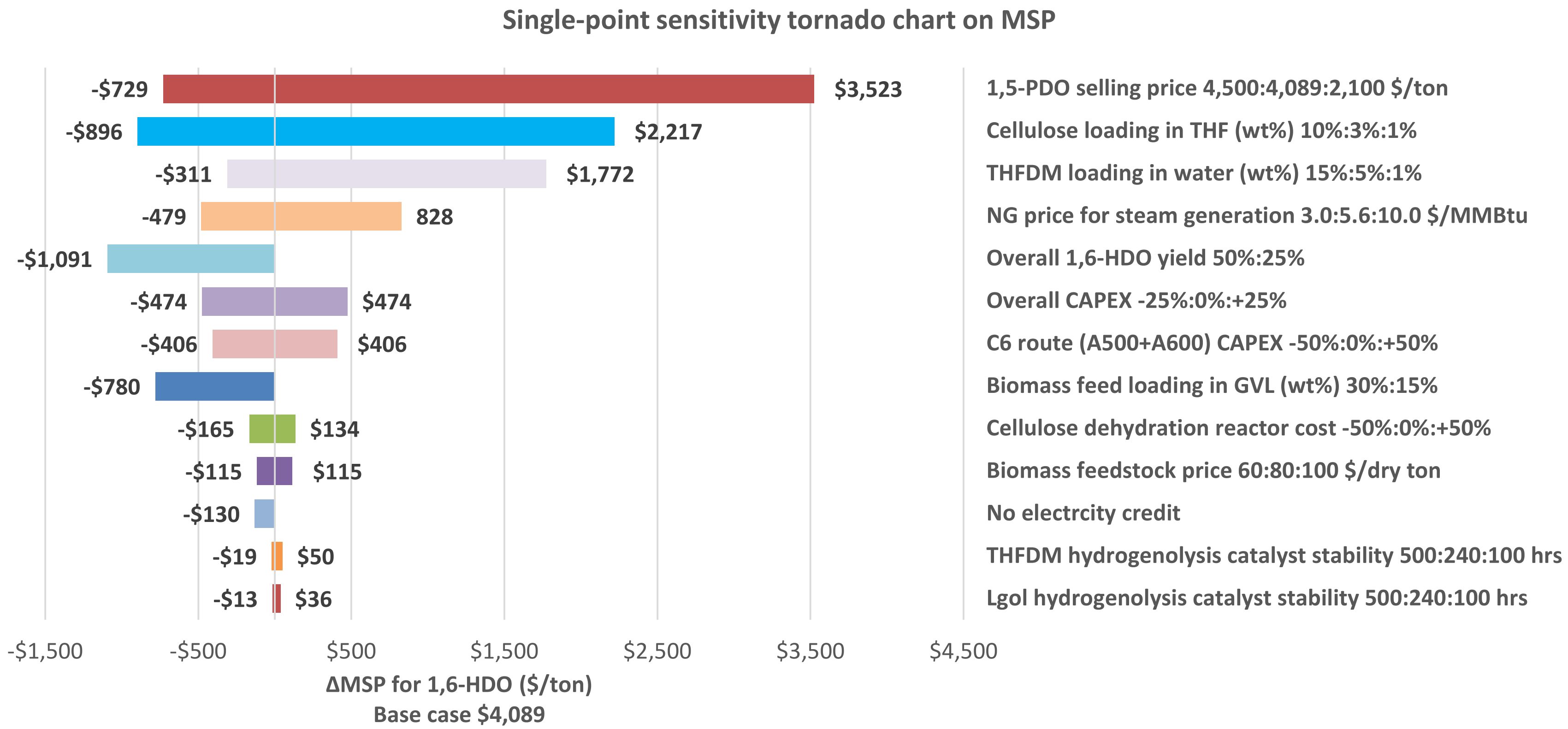
(Current US natural gas price $3.0/MMBTU)

Feedstock costs not a very large expense

Results: Sankey diagram for carbon flows and production costs

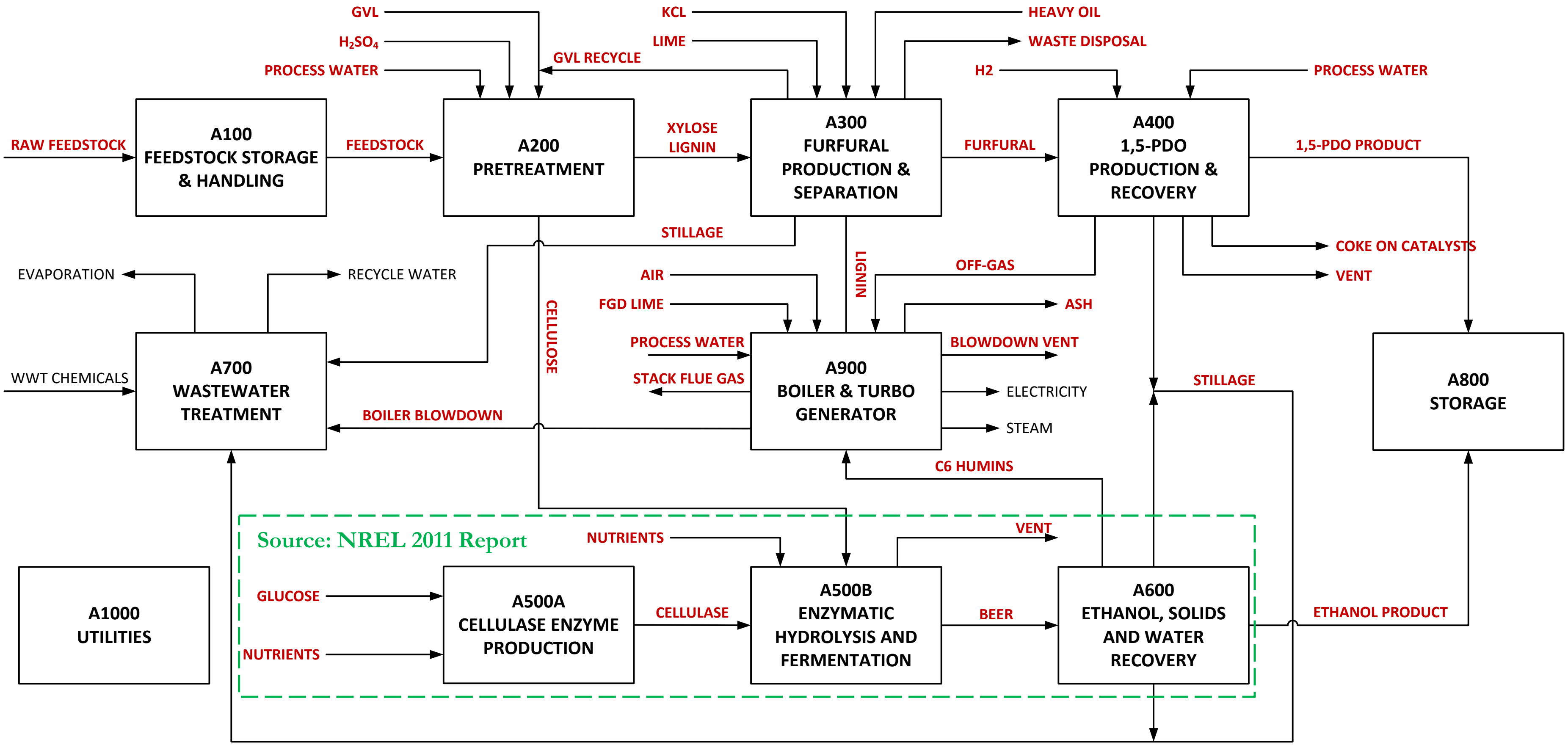


Results: There are a number of variables that can decrease the product selling price



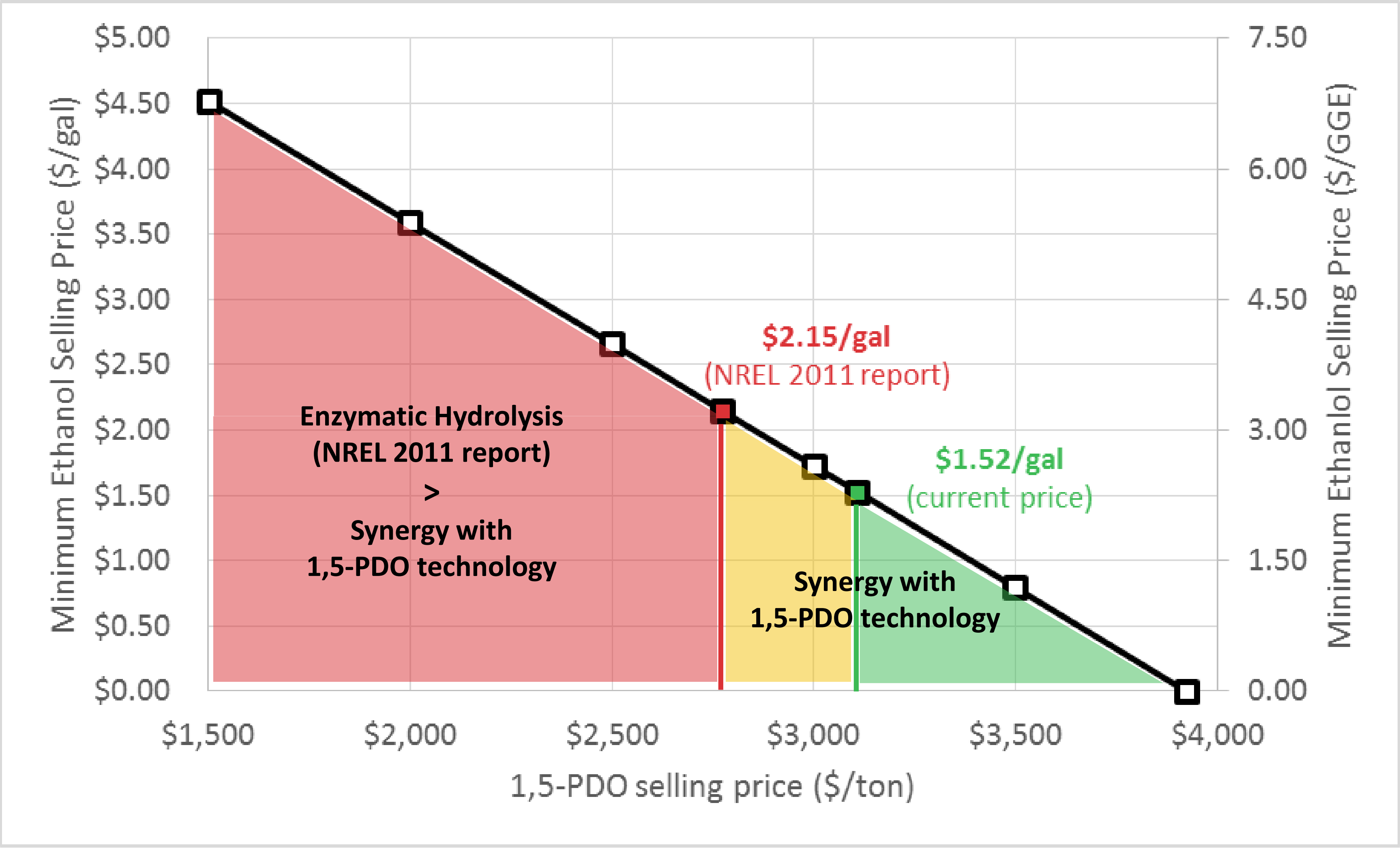
- MSP Price can decrease $1,570/ton if 1) assume current NG prices in US and 2) increase 1,6 HDO yield to 50%.
- Other opportunities for cost reduction: 1) decrease capital cost of LGO production, 2) increase biomass feed loading, 3) energy efficient separation (adsorption).

Results: 1,5-PDO process can improve economics of cellulosic ethanol



- 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)

Results: 1,5 Pentanediol technology could lower the price of cellulosic ethanol



Results: Most Project Milestones for Phase 1 are Complete

Task A: Production of furfural from lignocellulosic biomass

- 86% yield of furfural production from hemicellulose with hemicellulose extraction from White birch.
- **Completed all milestones**

Task B: Conversion of furfural into 1,5-PDO

- Overall yield of 85% 1,5-PDO from THFA was obtained with "DHH" process.
- Economic analysis indicates 1,5 PDO can be produced (*from furfural-derived THFA*) at costs comparable to 1,4 butanediol in a large scale biorefinery
- **Completed all milestones**

Task C: Conversion of cellulose into 1,6-HDO

- Overall yield of 35% of 1,6 HDO from cellulose with current work focused on improving this
- **All milestones complete except slurry reactor for cellulose dehydration**

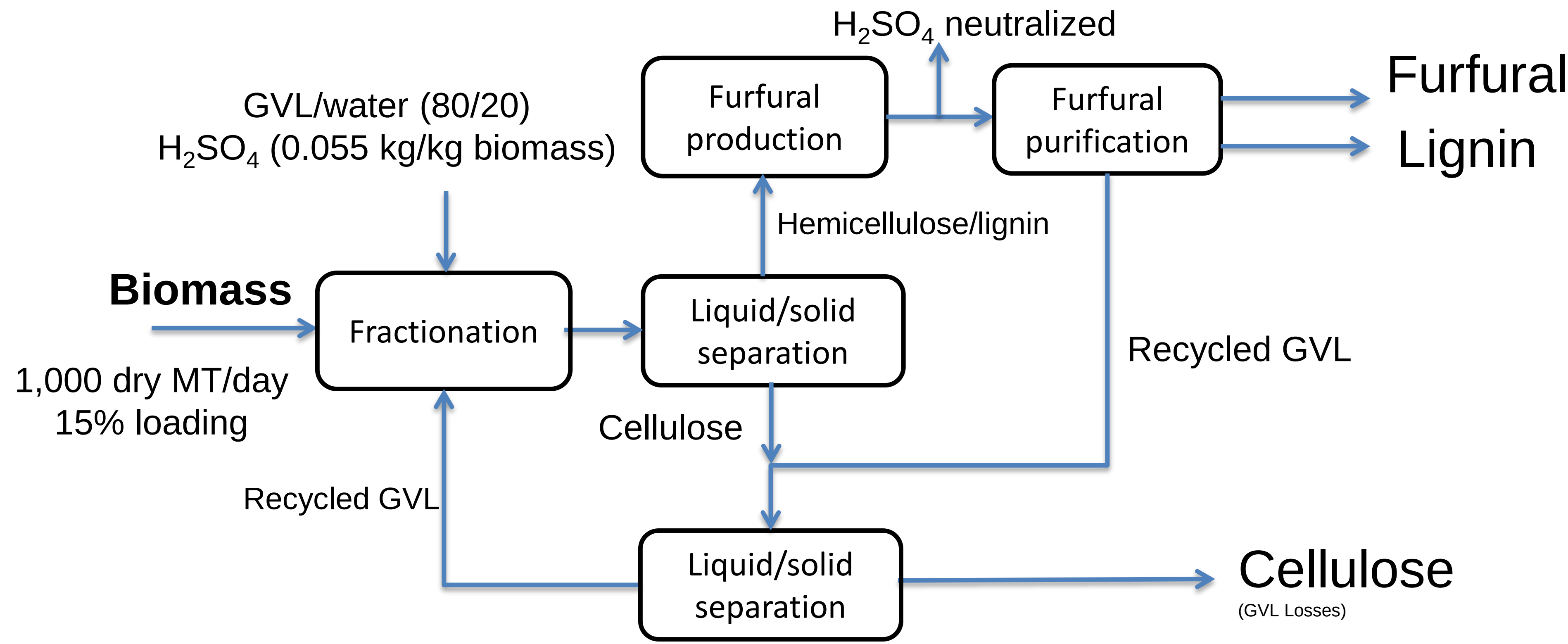
Task D: Separation of polyols with an optimized combination of zeolite membranes, adsorbents and liquid/liquid extraction

- Subtask D.1:-D.2 Screening of zeolites for 1,5-PDO separation from reaction intermediates and cyclic byproducts **(Complete)**
- Subtask D.3-D5: Investigate liquid—liquid extraction for 1,5-PDO separation **(Still in progress)**

Task E: Conceptual process design and technoeconomic modeling

- **Completed all milestones**

Results Task A: Cellulose, furfural, and lignin production

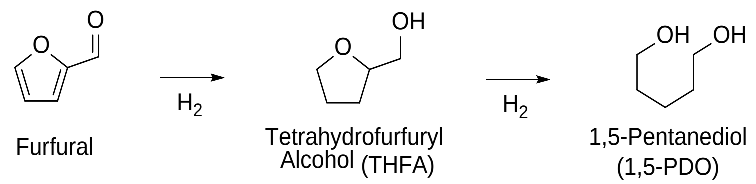


Biomass	Hemicellulose extracted (wt%)	Liquid/solid separation efficiency (%)	Furfural yield from hemicellulose (molar %)
White birch	90.8	95	86
Corn Stover	97	95	72
Switch grass	94.3	95	

GlucanBio

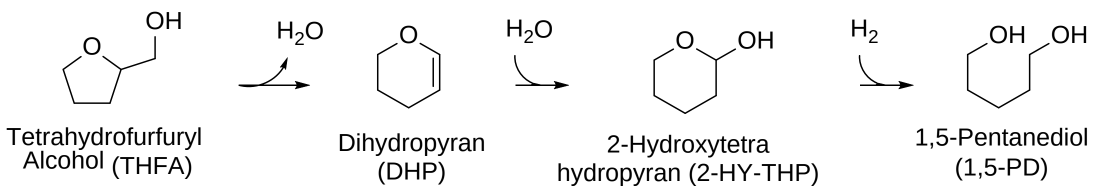
Results Task B: Furfural to 1,5-Pentanediol

Initial validation: RhRe Hydrogenolysis Route



	1,5-PDO yield from THFA (%)
RhRe Route	46
DHH Route	**87**

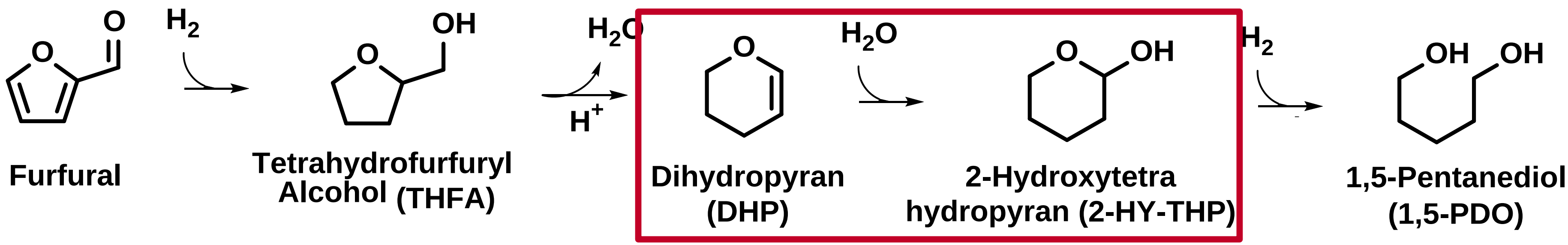
Intermediate validation : THFA Dehydration at UW



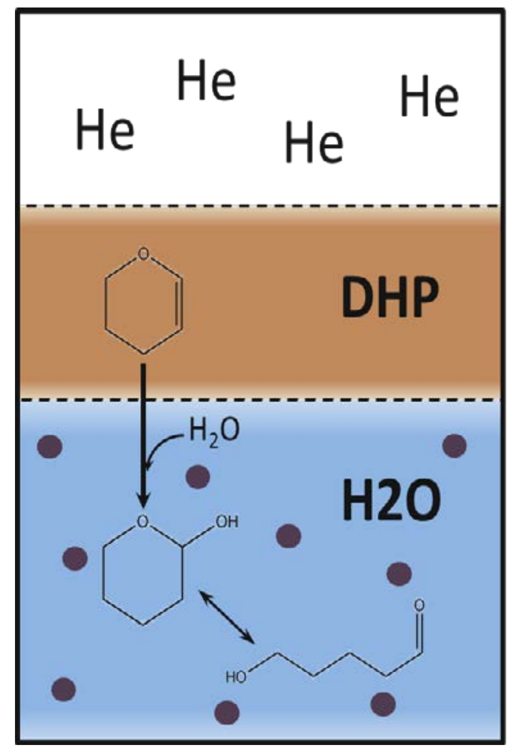
- **Step 1:** THFA Dehydration
  - γ-Al_2O_3 catalyst: 90% yield to DHP
- **Step 2:** DHP Hydration
  - No catalyst: 99% yield to 2-HY-THP + dimers
- **Step 3:** 2-HY-THP Hydrogenolysis
  - Ru/C: >96% yield to 1,5-PD

- THFA to 1,5-PDO split into 3 reactions to improve economics (“DHH Route”)

Task B Experimental Results



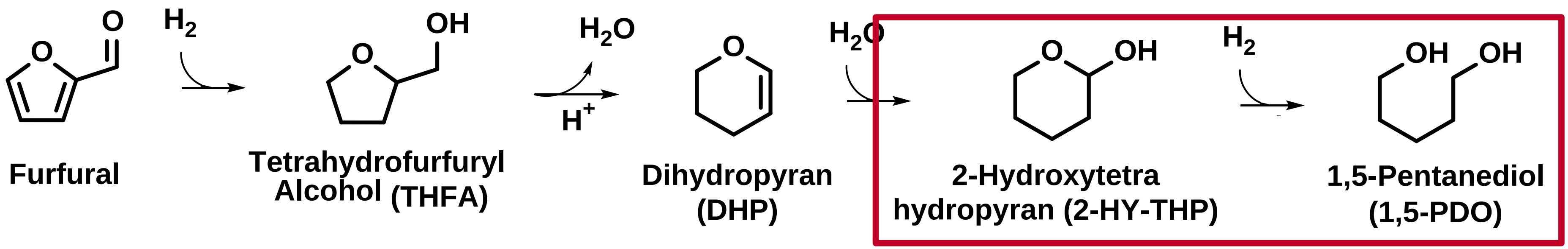
- **Phase 1:**
  - Hydration proceeded non-catalytically in water
- **Phase 2:**
  - Solid acids increase hydration rate
  - Hydration successfully scaled to continuous flow reactor

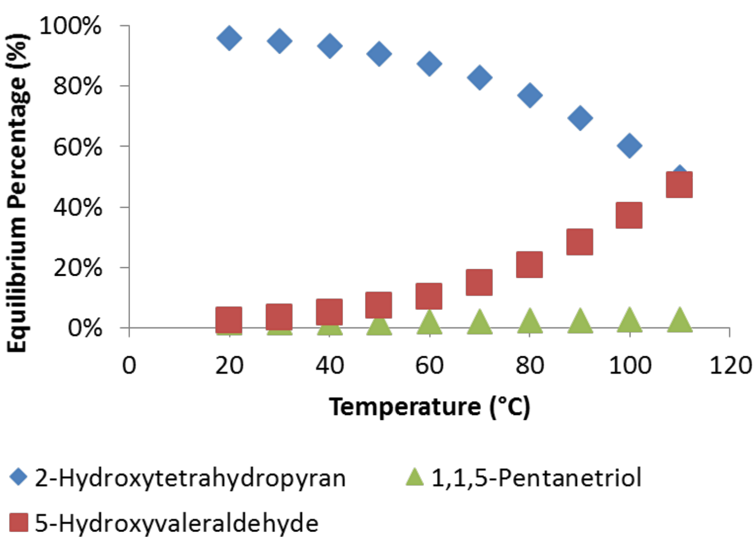


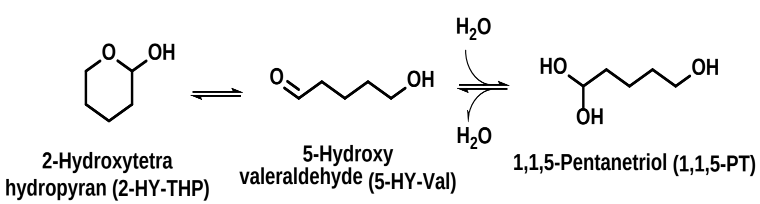
Catalyst	Catalyst mass (mg)	2-HY-THP Yield	Reaction Rate (μmol/gcat-min)	Total Acid Sites (mmol/g)	Bronsted Acid Sites (mmol/g)	Bronsted site TOF (s^{-1})
No Catalyst	-	0	0	-	-	-
γ-Al2O3	500	0	0	0.43[a]	0.17[a]	0.000
SiO2-Al2O3	300	7.8%	13	0.43[a]	0.34[a]	0.0006
CsPTA	20	28.0%	722	-	-	
Nafion SAC-13	20	45.8%	1180	0.14[a]	0.14[a]	*0.140*
ZrP	20	48.8%	1258	1.41[a]	1.36[a]	0.015
				0.84[b]	0.81[b]	0.026
HZSM5	4	21.9%	2822	0.80[c]	0.41[c]	*0.115*
H-Beta	2	20.1%	5178	-	-	-
Amberlyst-15	0.5	22.0%	*22662*	2.86[a*]	2.86[a*]	*0.132*
Amberlyst-70	**0.5**	**25.3%**	***26017***	**2.86[a]**	**2.86[a]**	***0.152***

(a) Weingarten et. al (2011) (b) Ning Li et. al (2011) (c) Yu-Ting et. al. (2012) *Amberlyst-70 acid site density

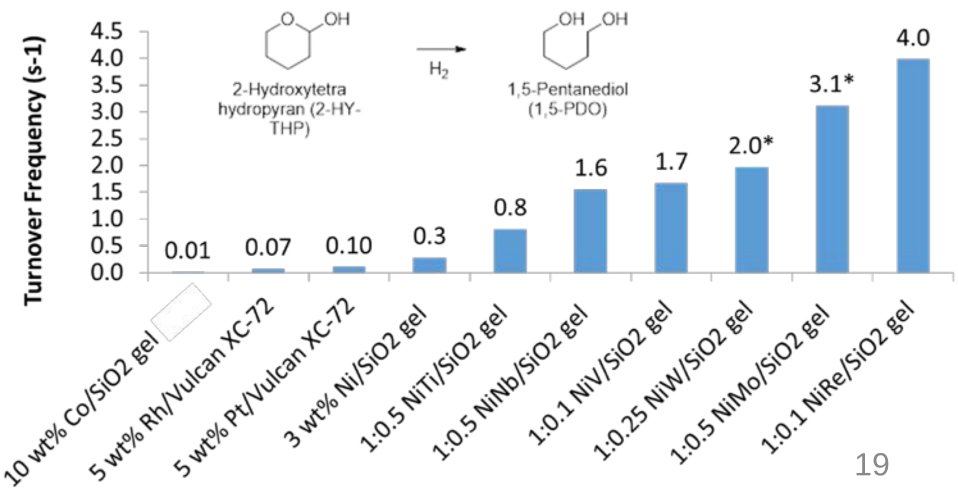
Task B Experimental Results



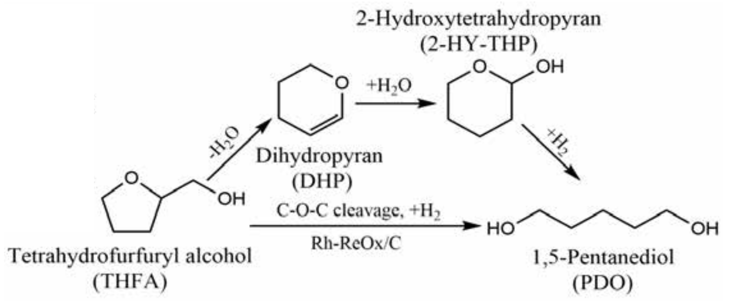


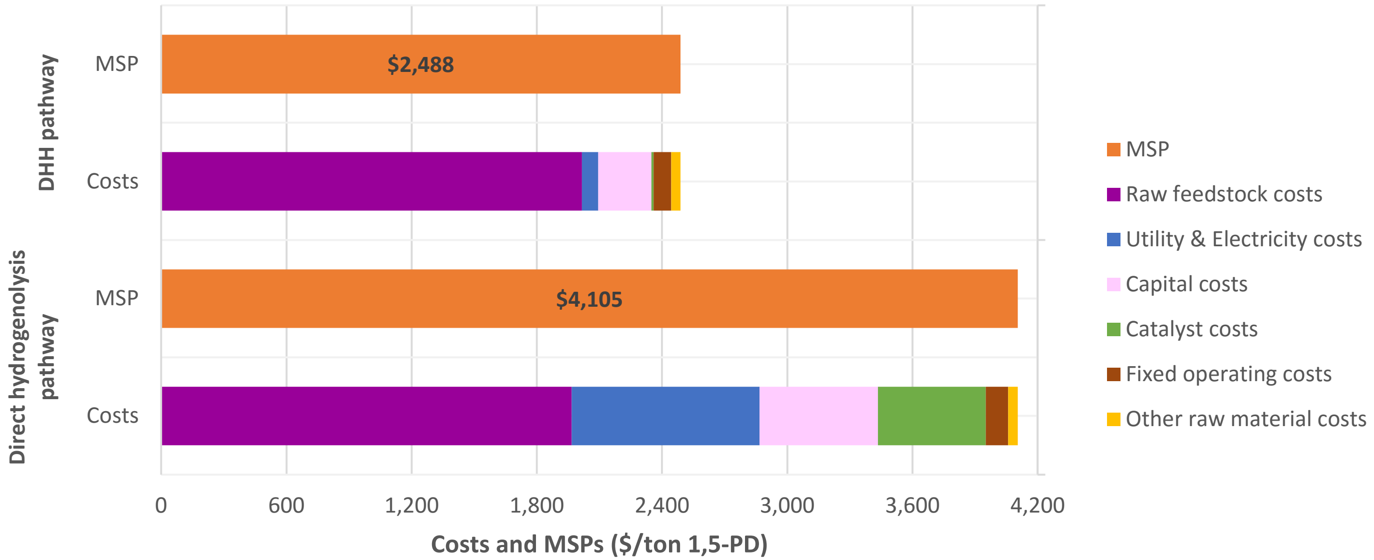


- 2-HY-THP in equilibrium with ring-opened tautomer, 5-HY-Val (left)
- >99% 1,5-PDO yields over monometallic catalysts
- Currently studying base metal stability and effect of promoter on rates (below)



Results: DHH Route has Economic Improvement over Hydrogenolysis Route





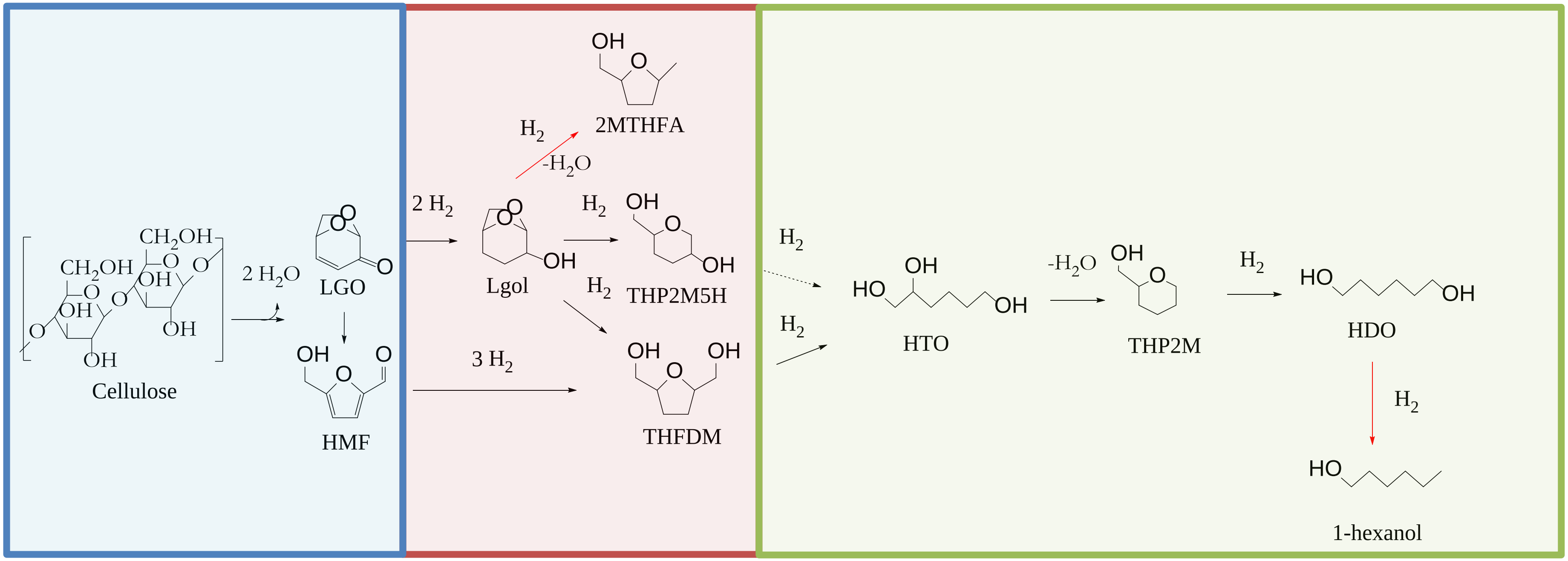
- Production cost (excluding feedstock) of DHH pathway is 4.5 times lower
- Catalyst cost of DHH pathway is 47 times lower

Results Task C: Proposed reaction pathway for 1,6-HDO production from cellulose

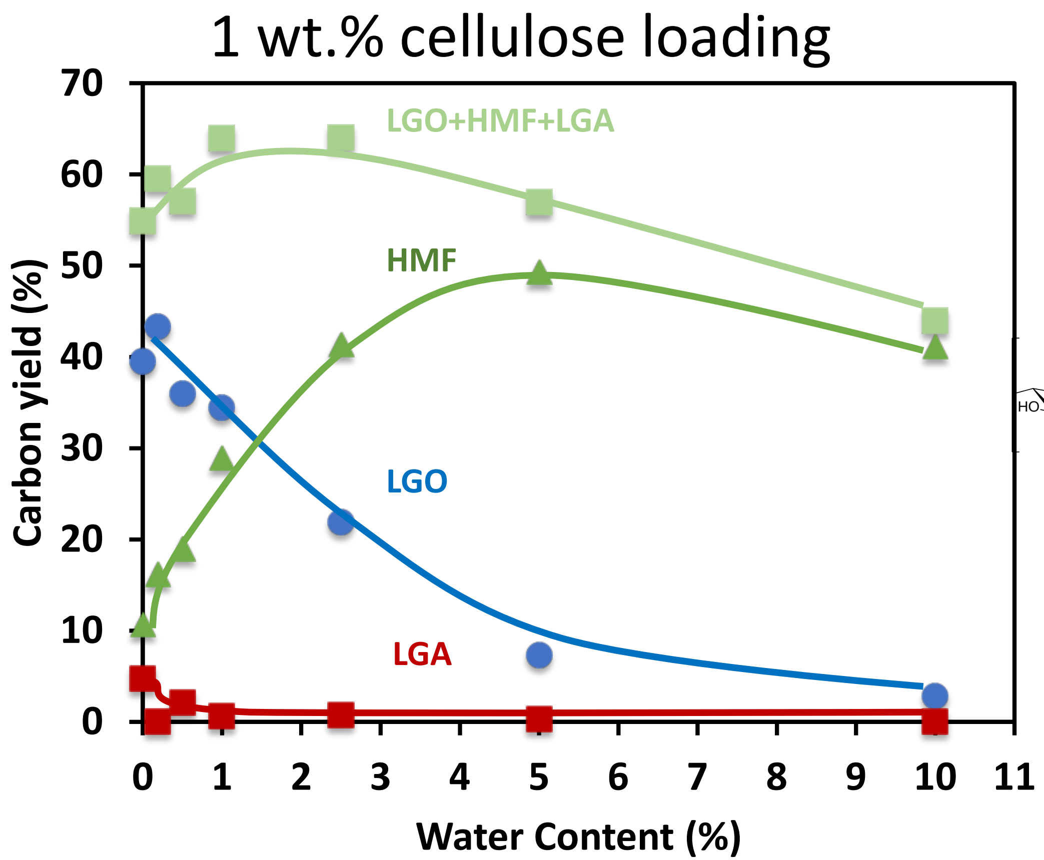
Step 1 (R1)
Dehydration in THF

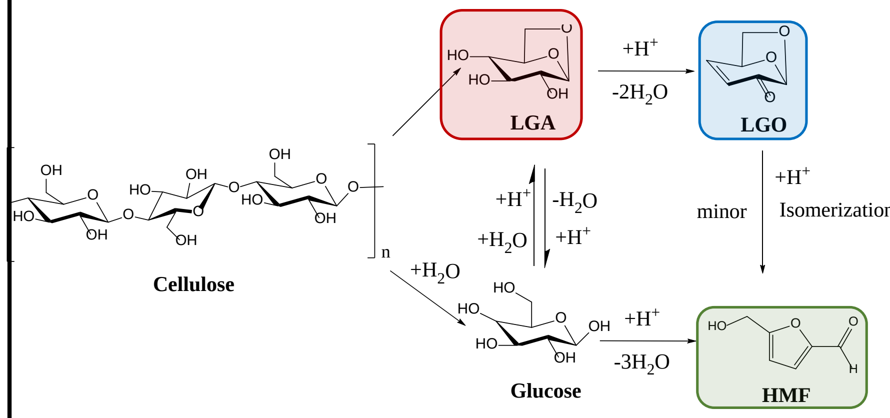
Step 2 (R2)
Hydrogenation in THF

Step 3 (R3)
Hydrodeoxygenation in H2O



LGO and HMF can be selectively produced depending on water content

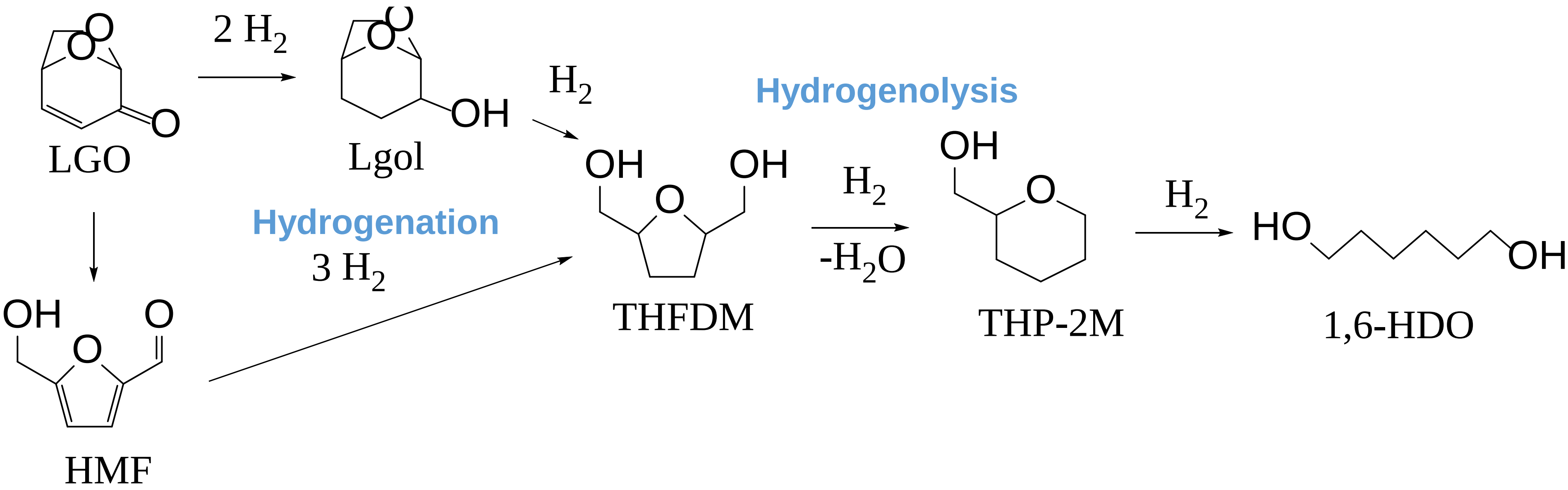




Reaction conditions: Cellulose (1 wt%, 0.53 g), THF (60 mL), H_2SO_4 (64 µL Conc., 20 mM), 1000 psi He, 483 K, 700 rpm.

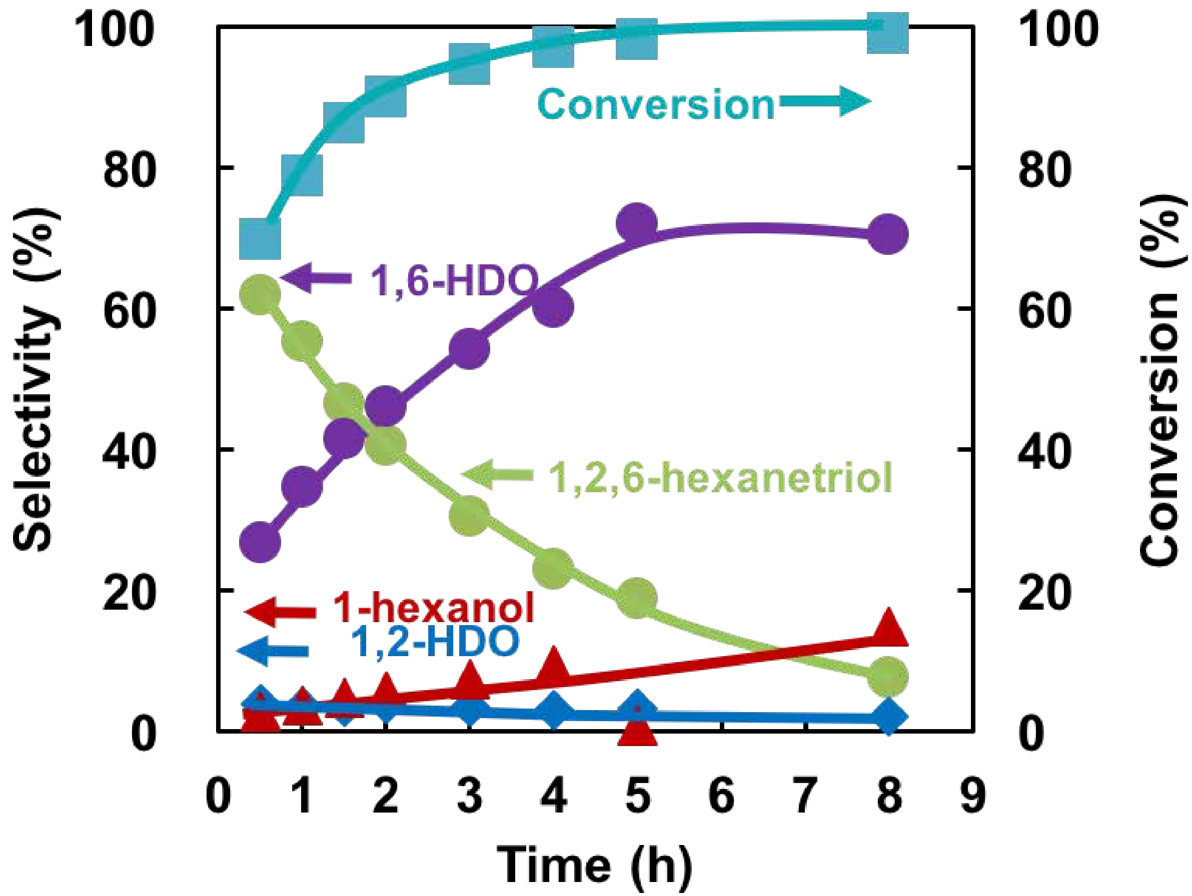
J. He, M.Liu, T. Walker, S.H. Krishna, K. Huang, C.T. Maravelias, J. A. Dumesic G. W. Huber Effect of water and solvents on the production of LGO and HMF from Cellulose", in preparation

Results: LGO/HMF undergo multi-step hydrogenation process to produce 1,6-hexanediol



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.
2. S. H. Krishna, T. W. Walker, J. A. Dumesic and G. W. Huber, "Kinetics of Levoglucosenone Isomerization," *ChemSusChem*, 2017, **10**, 129-138.
3. A.M. Allgeier, e. Korovessi, C.A. Menning, J.C Ritter, S.K. Sengupta, C.S Stauffer, " Process for preparing 1,6-hexanediol (US 8865,940 B2)," *USA Pat.,* 2014.
4. T. Buntara, S. Noel, P. H. Phua, I. Melián-Cabrera, J. G. de Vries and H. J. Heeres, "Caprolactam from Renewable Resources: Catalytic Conversion of 5-Hydroxymethylfurfural into Caprolactone," *Angewandte Chemie International Edition*, 2011, **50**, 7083-7087.

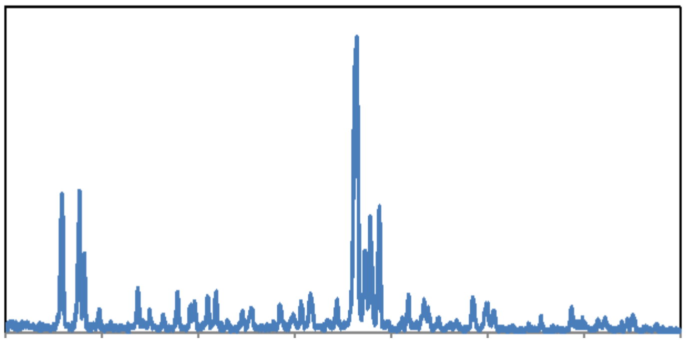
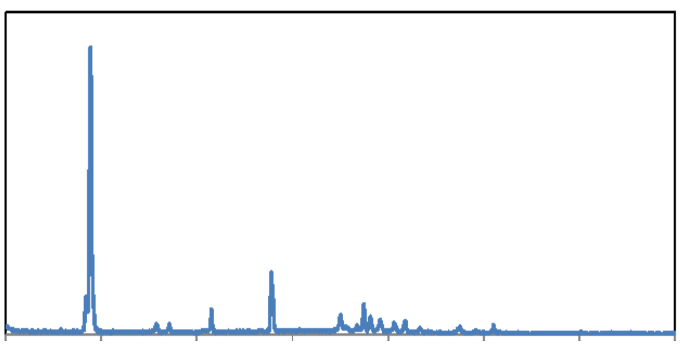
Results: THFDM can be converted into 1,6-HDO



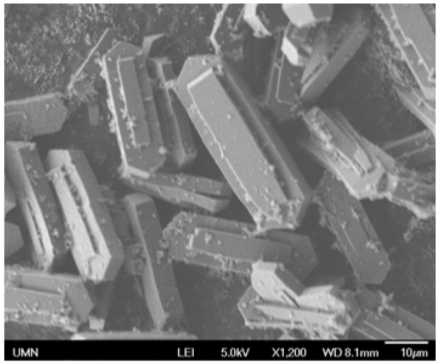
Hydrogenolysis of THFDM conversion in Batch reactor. Reaction conditions: THFDM (5 wt.% in H_2O, 20 mL), 1.0 gm of metal catalyst A, 160 C, 800 psi H_2, 700 rpm.

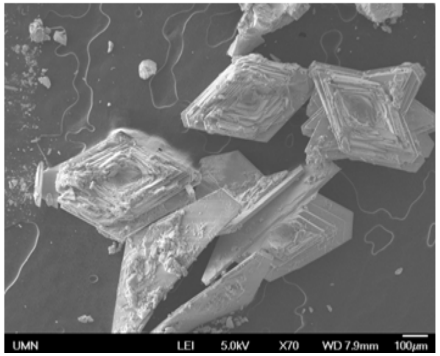
Screening Zeolitic Adsorbents for 1,5-PDO Separation

- 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

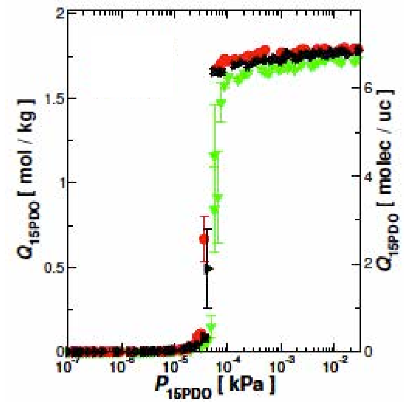



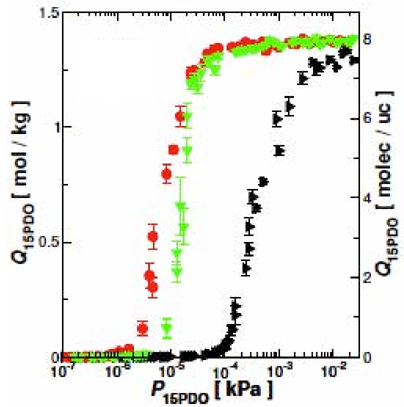
X-ray Powder Diffraction Patterns





Scanning Electron Microscopy Images



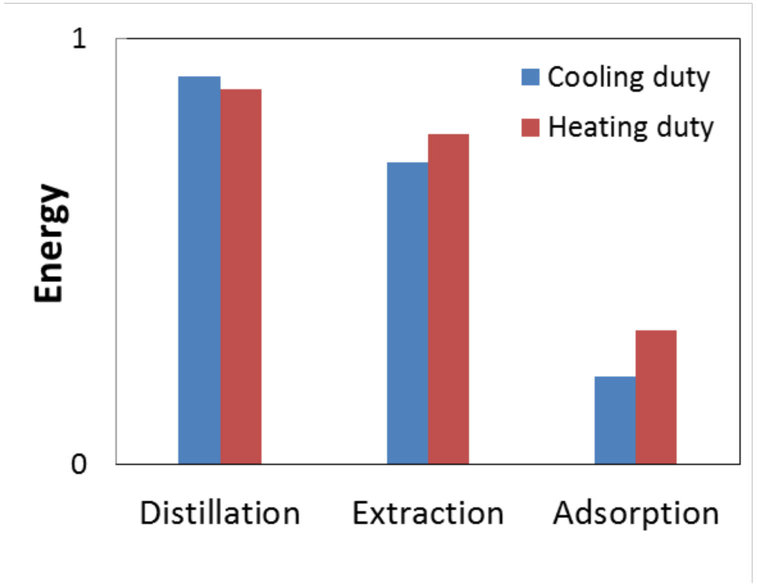


Mixture Isotherms

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

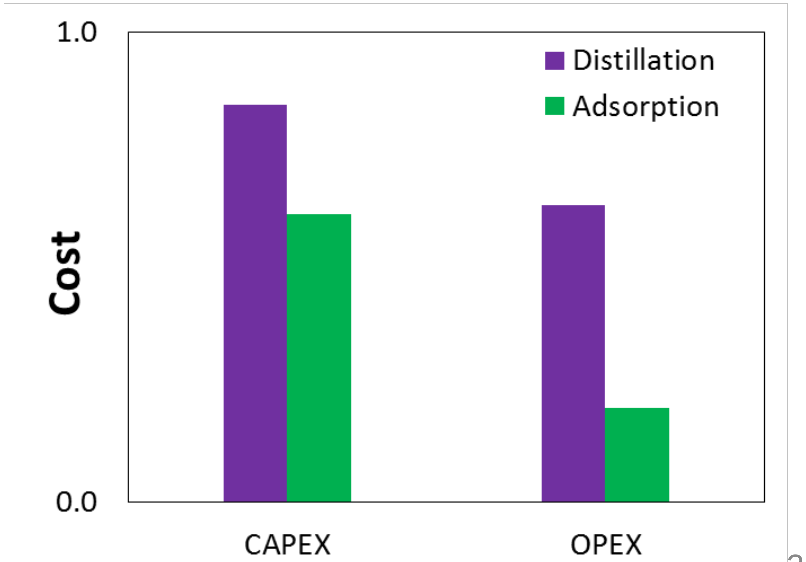
Energy Savings:

- 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

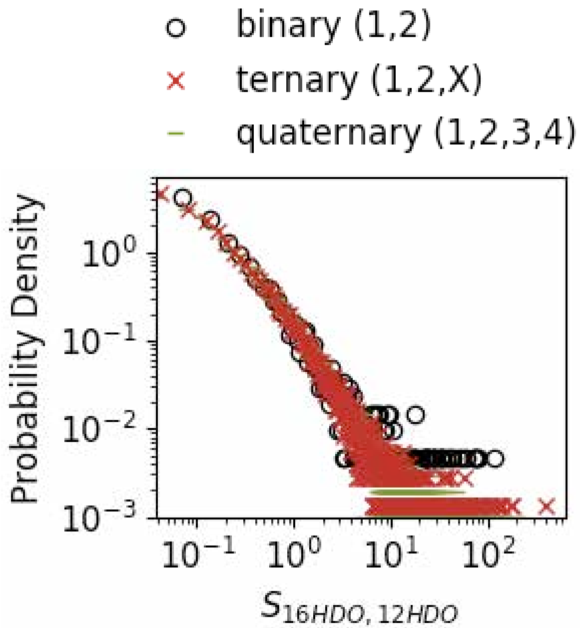


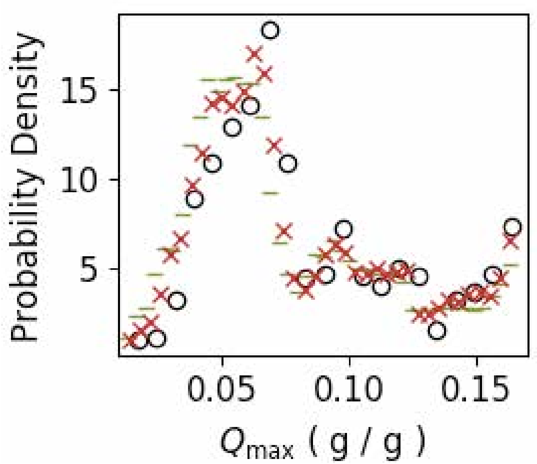
Economic Analysis:

- 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



Multi-step Separation of C6 Product Mixture





Found zeolites with high 16HDO/12HDO selectivity (S >> 1) and inverse selectivity (S << 1)

Screening of Zeolites considering 3 Product Mixtures

Reaction Condition	Major Products	Minor Products
1	**1,6-HDO (1)** **1,2-HDO (2)**	**1,5-PDO (3)** **1,5-HDO (4)**
2	1,6-HDO/1-hexanol	1,5-HDO/1,2-HDO
3	THFDM/1,2,6-HTO/1,6-HDO	1-hexanol/1,5-HDO/1,2-HDO

If 1-hexanol is present in significant concentration, then liquid–liquid extraction with high-boiling solvent yields high selectivity for 1-hexanol versus 1,6-HDO (S ≈ 1500)

Compound	$10^3\ x_{aq}$	$10^3\ x_{org}$
water	990 ± 5	5 ± 3
1-hexanol	1.2 ± 0.7	20 ± 10
1,6-HDO	9 ± 5	0.10 ± 0.05

Subsequent Adsorptive Separation of 1,6-HDO from intermediates and other side products

Results from project are being published in peer reviewed journals and at conferences

5 Publications already published:

1. Fei Cao, Thomas J. Schwartz, Daniel J. McClelland, Siddarth H. Krishna, James A. Dumesic, and George W. Huber, Dehydration of cellulose to levoglucosenone using polar aprotic solvents, Energy Environ. Sci., 2015, 8, 1808—1815.

2. Siddarth Krishna, Theodore Walker, James A. Dumesic, George W. Huber, Kinetics of levoglucosenone isomerization, *ChemSusChem,* in press.

3. Siddarth H. Krishna, Daniel J. McClelland, Quinn A. Rashke, James A. Dumesic and George W. Huber, "Hydrogenation of levoglucosenone to renewable chemicals," *Green Chemistry*, 2017.

4. Zachary J. Brentzel, Kevin J. Barnett, Kefeng Huang, Christos T. Maravelias, George W. Huber, James A. Dumesic . Synthesis of 1,5-pentanediol from furfural combining hydrogenation and ring-opening reactions. *ChemSusChem,* 2017.

5. Samuel P. Burt, Kevin J. Barnett, Daniel J. McClelland, Patrick Wolf, James A. Dumesic, George W. Huber, Ive Hermans, Production of 1,6 Hexanediol from Tetrahydropyran-2-methanol by Dehydration-Hydration and Hydrogenation, *Green Chemistry*, 2017.

2 Submitted Publications under review

1. Jiayue He, Kefeng Huang, Kevin Barnett, Siddarth Krishna, Samuel P. Burt, Ive Hermans, Christos T. Maravelias, James A. Dumesic, George W. Huber New catalytic strategy for alfa-omega diol production from lignocellulose biomass, Faraday Discussion, *submitted.*

2. Kefeng Huang, Kevin J. Barnett, Zachary J. Brentzel, George W. Huber, James A. Dumesic, Christos T. Maravelias, Process Synthesis and Analysis for Conversion of Furfural to 1,5-Pentanediol. *Submitted*

9 Manuscripts in Preparation

1 granted US Patent, several more patent applications and invention disclosures

3 Plenary Keynotes Talks at: 1) International Symposium on Catalytic Conversion of Biomass (ISCCB 2016), Taipei, Taiwan; 2) New York Catalysis Club; 3) Symposium on Thermal and Catalytic Sciences for Biofuels and Biobased Products (TCS 2016), Chapel Hill, NC

7 Talks at Technical Meetings: 4 at AICHE Annual Meeting in 2016

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

Phase 2 Plans

- Process integration: start with white birch as feedstock and integrate process at laboratory scale
- Move reactions from batch to continuous flow reactors
- Obtain required laboratory data that for design of a pilot plant
- Continual improvement by integration between experiments and technoeconomic model to reduce costs
- For 1,5-PDO, i) integration of the separate dehydration-hydration-hydrogenation (DHH) reaction pathway reaction steps in continuous flow reactors ii) Starting from real biomass-derived feeds iii) studying catalyst regeneration and stability.
- For 1,6-HDO, i) integration of the process from cellulose to 1,6-HDO in continuous flow reactor ii) develop more advanced catalysts (zeolites, bimetallics, etc) to improve activity, selectivity, or stability iii) Study effect of impurities present in cellulose-derived feed on catalyst stability, with the ultimate goal of upgrading a crude cellulose-derived mixture.
- Test adsorption with real feedstock
- Find partner for pilot plant

Risks and Mitigation Plan for Phase 2

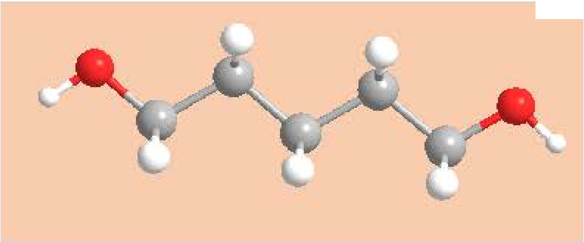
- Market for 1,5 pentanediol small
  - Continue to discuss with licensees of technology and industry to learn more about this market
- Economics not attractive to industry
  - Continue to optimize process, reduce catalyst cost by understanding chemistry
  - Look at other products that could be made from this process (cyrene, THFDM, LGO, etc)
- Catalyst poisons for 1,6 hexanediol pathway
  - Identify cause and separation approaches
- Catalysts deactivate due to leaching, sintering
  - Measure catalyst concentrations with ICP
  - Identify catalyst composition early on
- Solvents decompose/reactive
  - Have other backup solvents, work at conditions where solvent doesn't decompose
- DOE delays contract approval
  - DOE working to make sure this doesn't happen

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

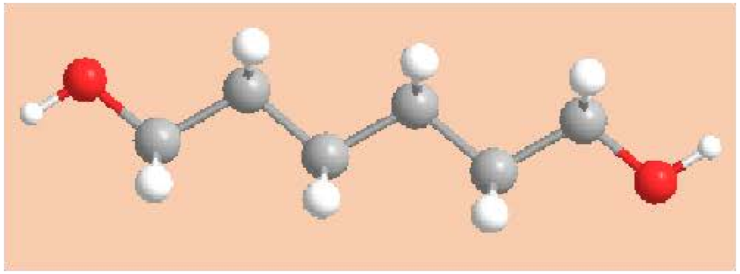
GlucanBio

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, corn stover) into 1,5 pentanediol and 1,6 hexanediol.

Argonne NATIONAL LABORATORY