Supplementary Information

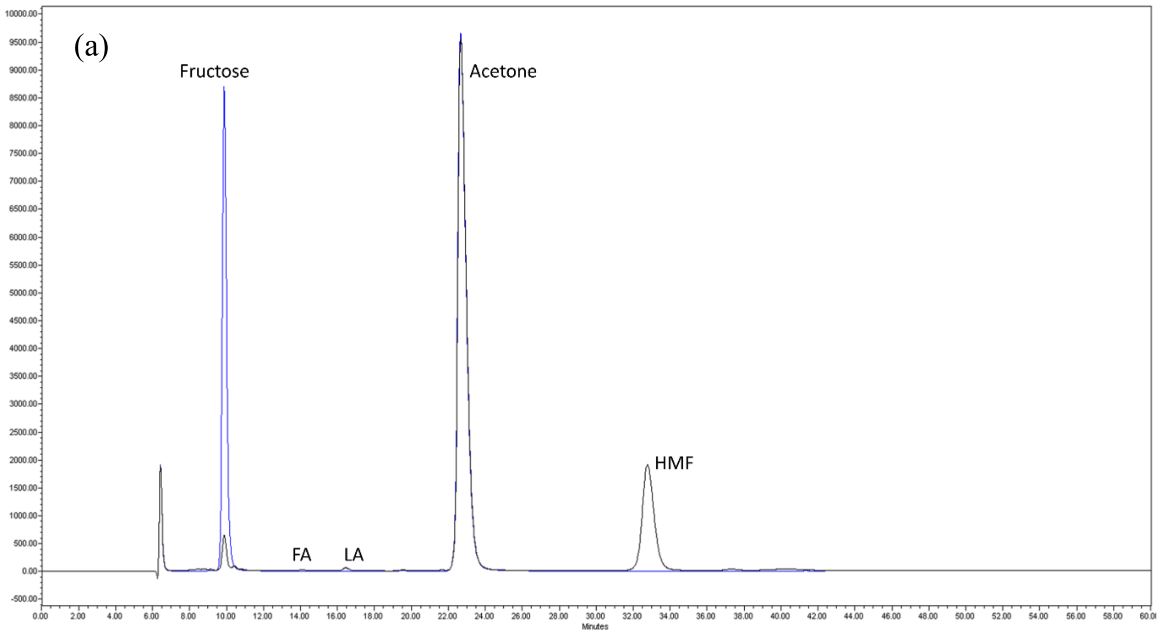
Solvent System for Effective Near-term Production of Hydroxymethylfurfural (HMF) with Potential for Long-term Process Improvement

Ali Hussain Motagamwala,[a,b] Kefeng Huang [a,b], Christos T. Maravelias [a,b] and James A. Dumesic [a,b]

[a] Department of Chemical and Biological Engineering, University of Wisconsin-Madison, Madison, WI 53706, USA.

[b] DOE Great Lakes Bioenergy Research Center, University of Wisconsin-Madison, 1552 University Ave, Madison, WI 53726, USA .

[*] Corresponding author: James A. Dumesic (jdumesic@wisc.edu)



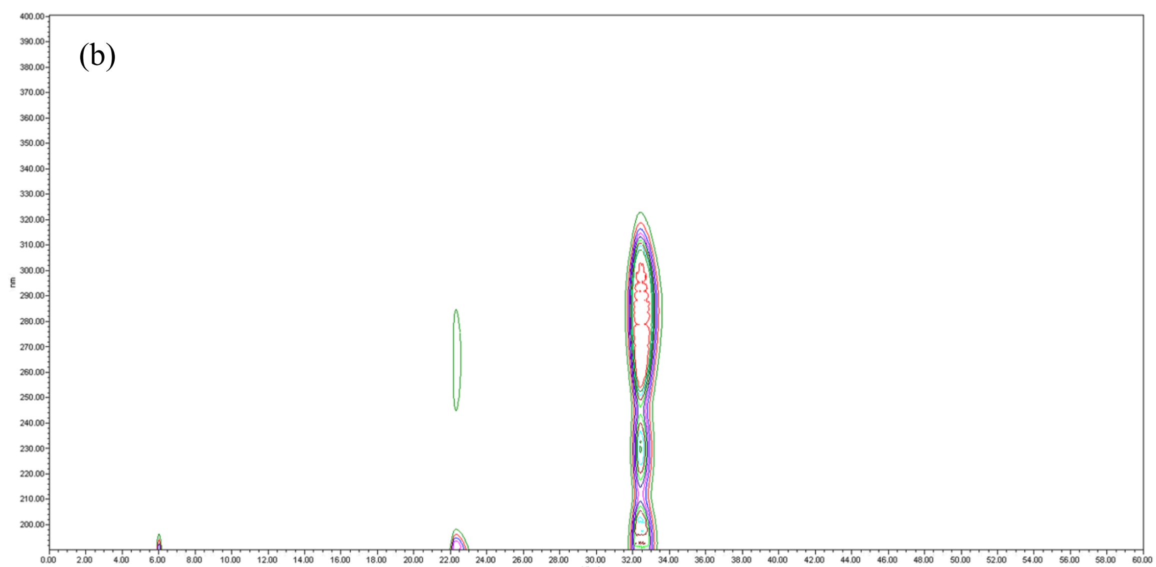


Fig. S1. HPLC chromatogram of product solution obtained during fructose dehydration. Reaction condition: Feed – 25 wt% fructose (aqueous basis); solvent – acetone:H_2O = 80:20; reaction temperature – 393 K; acid concentration – 0.050 M HCl; reaction time – 30 min. (a) Chromatogram using refractive index detector, fructose (9.9 min), formic acid (14.1 min), Acetone (22.7 min), HMF (32.8 min). (b) Chromatogram using PDA detector, Acetone (22.3 min), HMF (32.4 min).

Fig. S2. Picture showing the formation of humins during fructose dehydration in water. Black tarry (sticky) material is formed during dehydration of fructose in water.

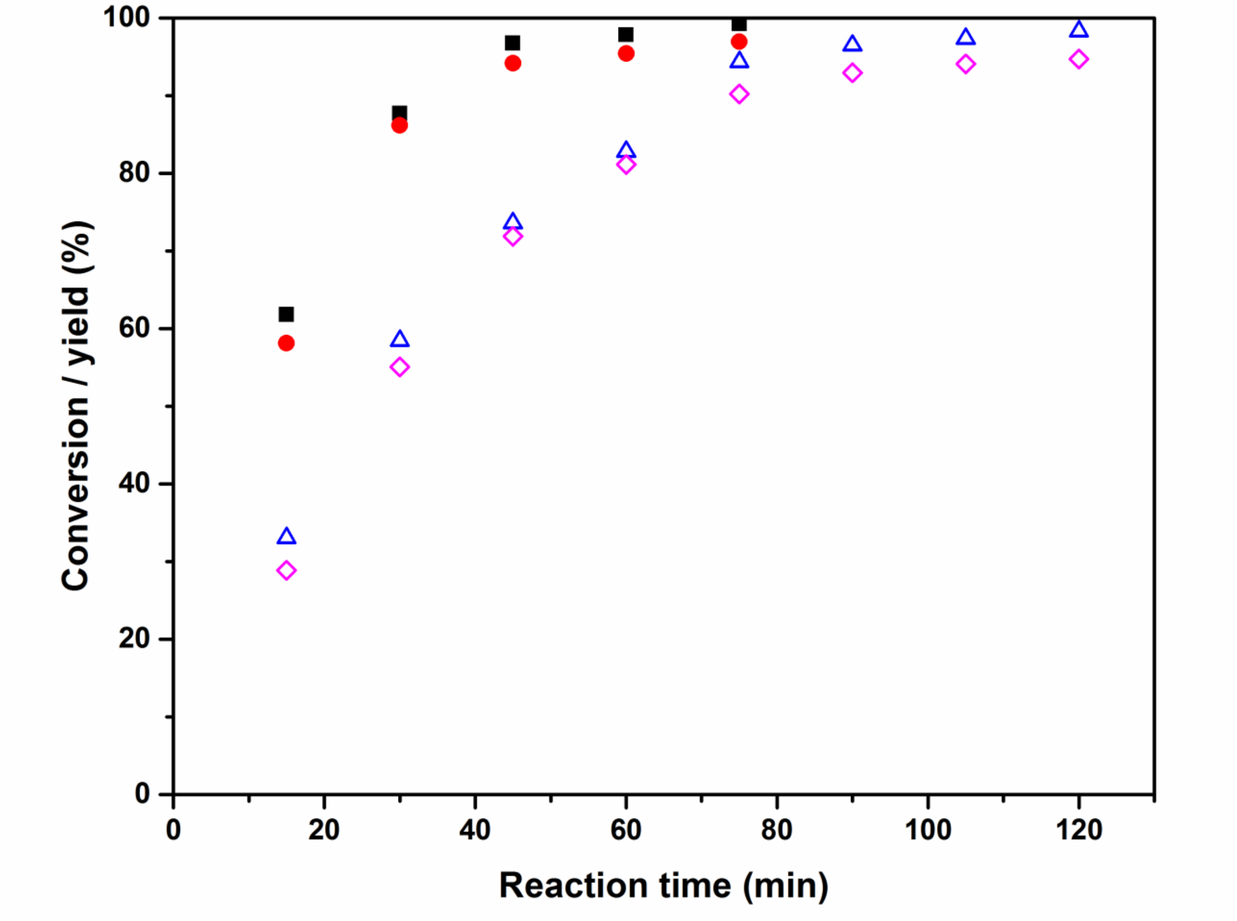
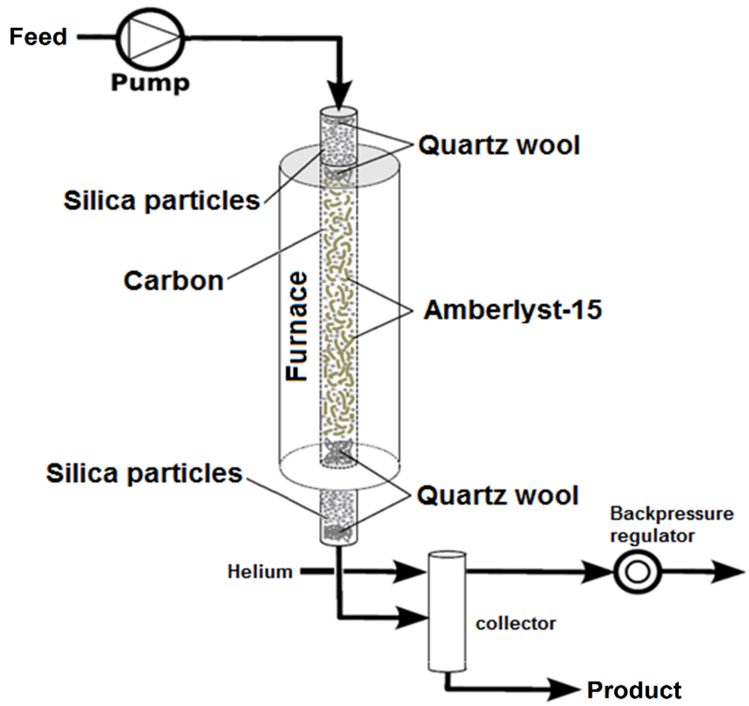


Fig. S3. Effect of salt on dehydration rate during fructose dehydration. Reaction condition: Feed – 1 wt% fructose; solvent – acetone:H_2O = 80:20; reaction temperature – 393 K; acid concentration – 15 mM CH_3SO_3H. Black squares represent fructose conversion in presence of salt. Blue triangles represent fructose conversion in the absence of salt. Red circles represent HMF yield in the presence of salt. Pink diamonds represents HMF yield in the absence of salt.

a



b

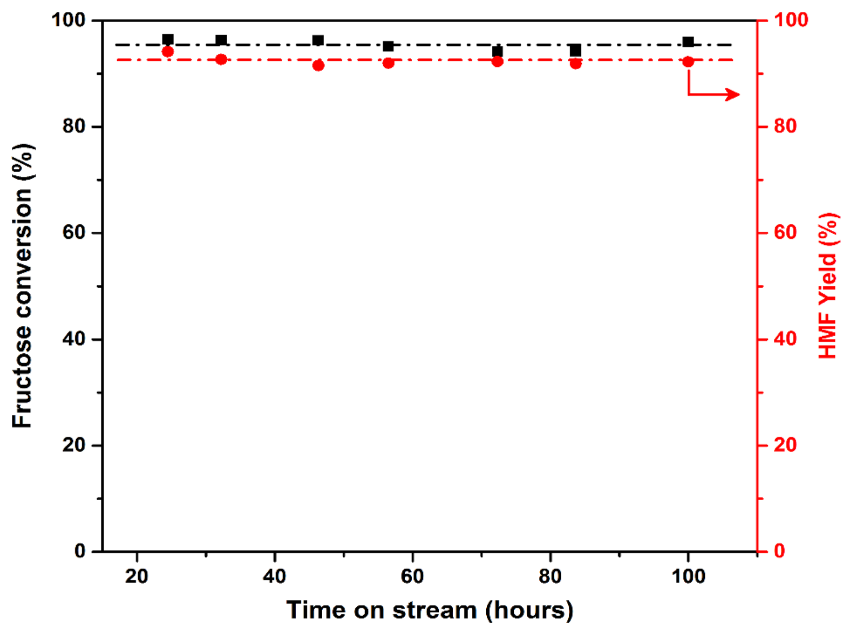


Fig. S4. Stability of solid dehydration catalyst. (a) Schematic diagram of the reactor setup used to study the stability of Amberlyst-15® for fructose dehydration. (b) HMF yield and fructose conversion over solid acid catalyst (Amberlyst-15) as a function of time on stream. Reaction condition: Feed – 1 wt% fructose; solvent – acetone:H_2O = 80:20; reaction temperature – 383 K; Amberlyst-15® – 250 mg. Black squares represent fructose conversion. Red circles represent HMF yield.

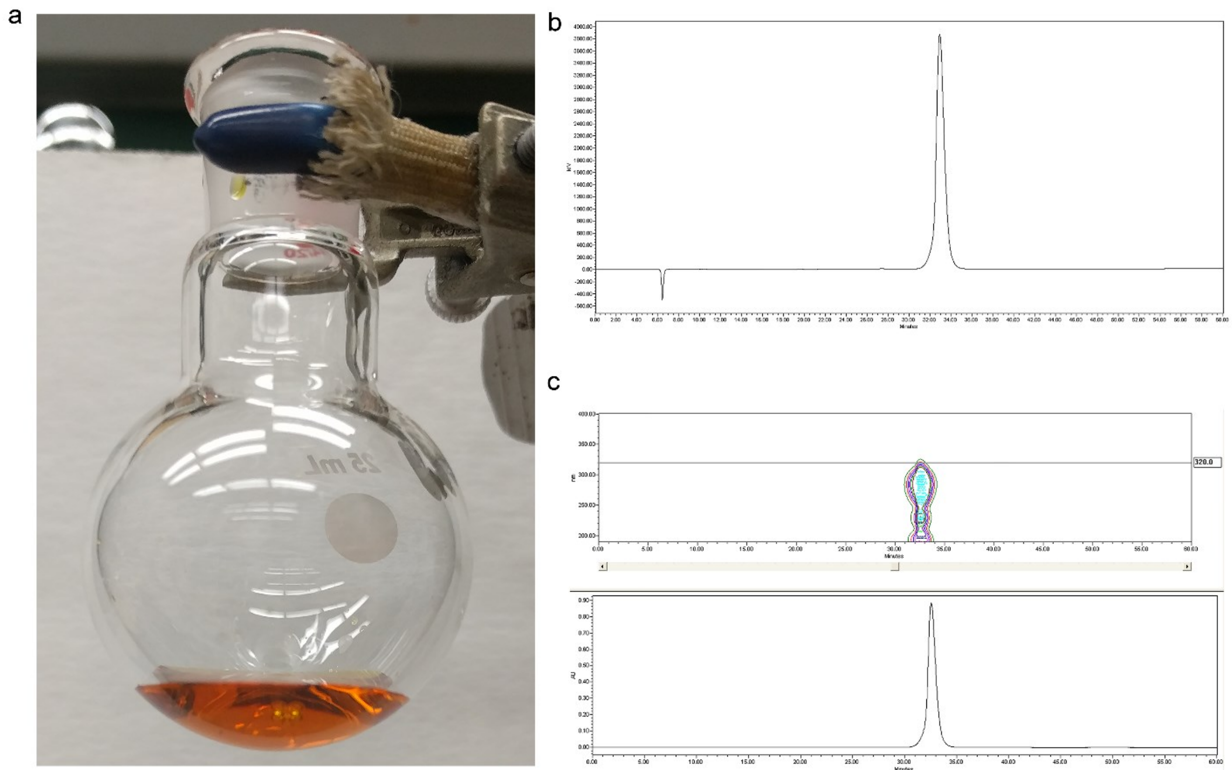


Fig. S5. HMF recovery and purity. (a) Picture of product obtained after separation from MIBK under reduced pressure (50 mbar) and at 313 K. (b-c) HPLC chromatogram of product obtained after separation under reduced pressure. (b) Chromatogram using refractive index detector. (c) Chromatogram using PDA detector (extracted at 320 nm). HMF purity is >99%.

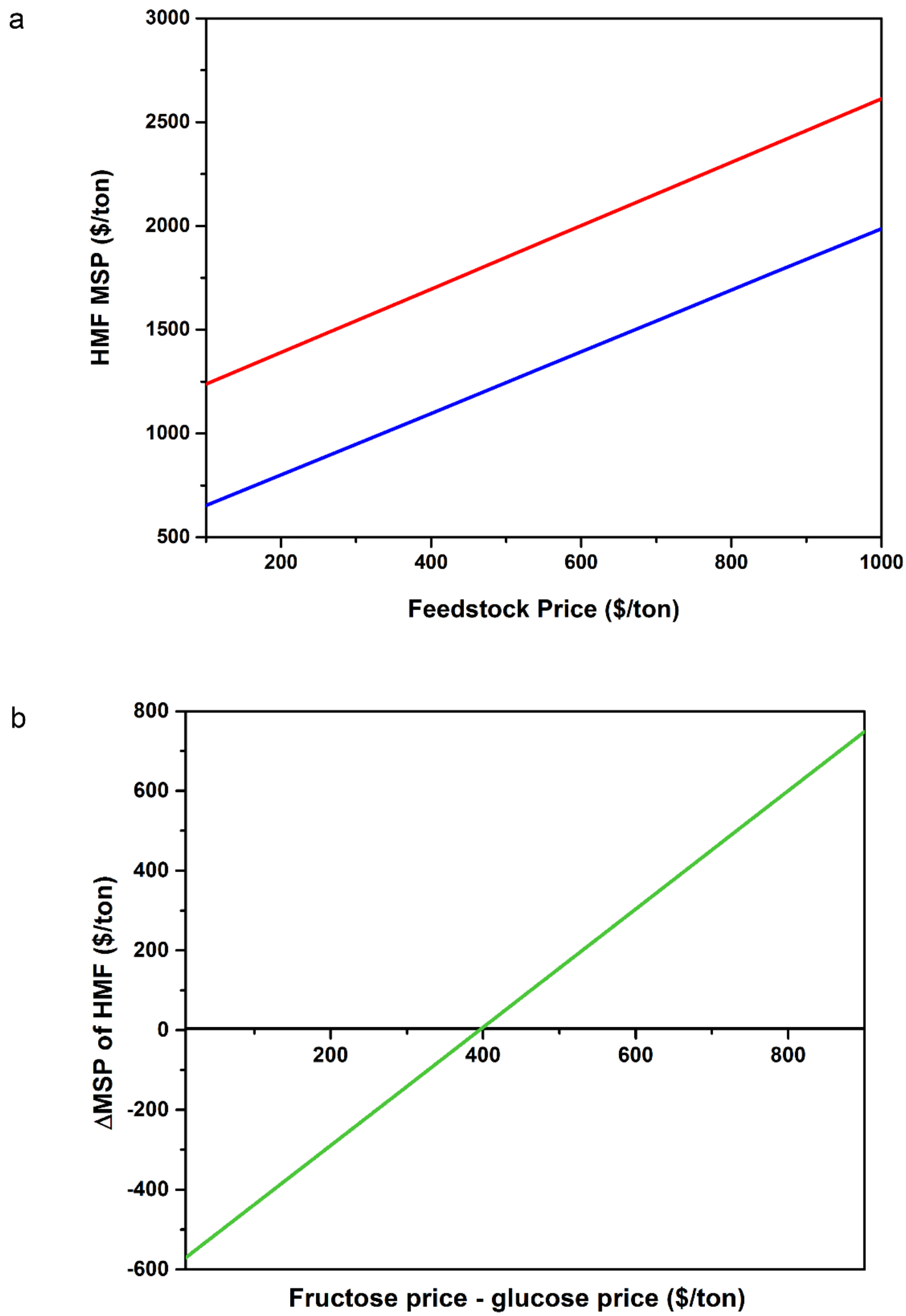


Fig. S6. Techno-economic comparison between glucose and fructose feedstock (a) HMF minimum selling price (MSP) as a function of the fructose and glucose feedstock prices. Red line represents glucose as feedstock. Blue represents fructose as feedstock. (b) Difference of HMF minimum selling price (ΔMSP) as a function of the difference between the fructose and glucose feedstock prices.

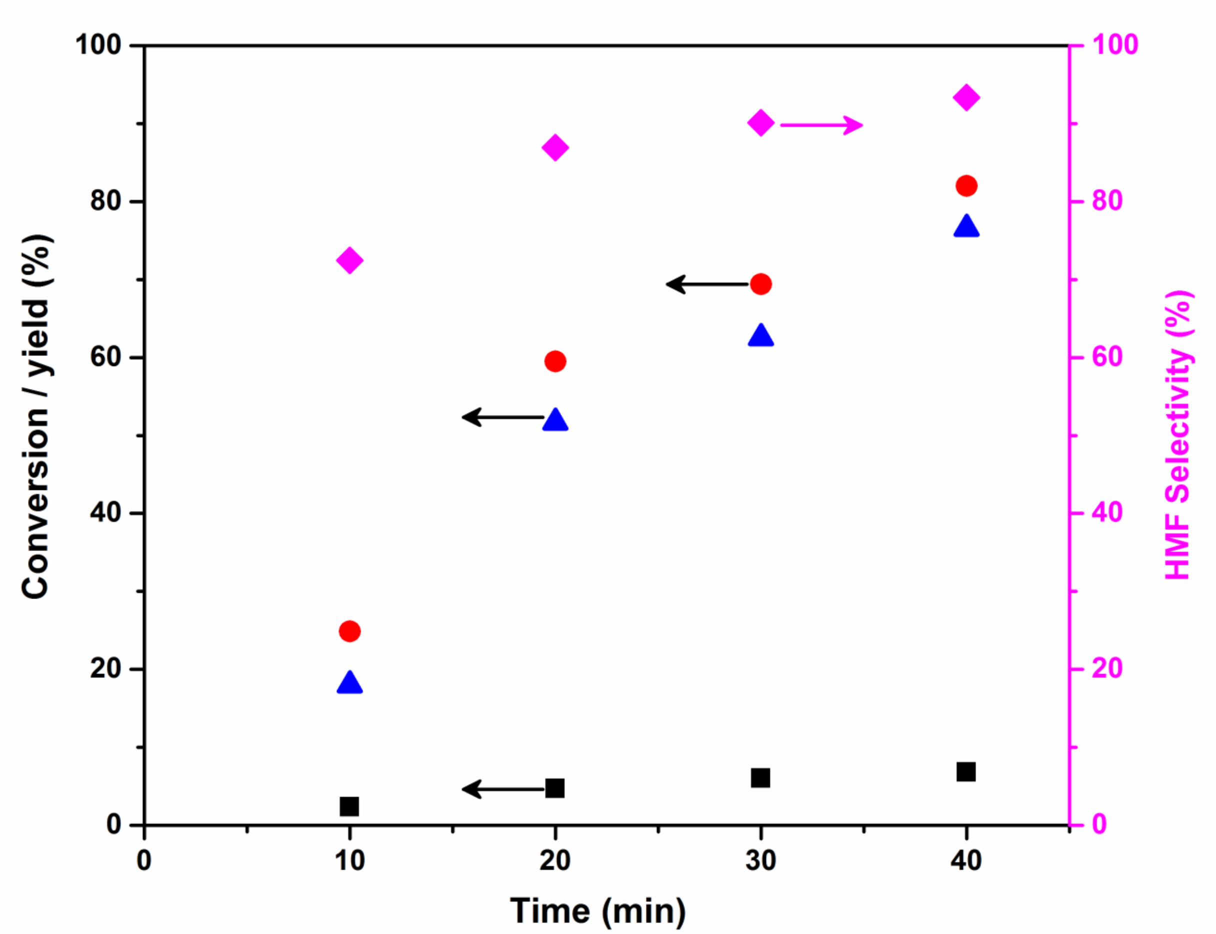


Fig. S7. Dehydration of simulated feed from enzymatic isomerization process. Reaction condition: Feed – 14.5 wt% glucose (aqueous basis); 10.5 wt% glucose (aqueous basis); solvent – acetone:H_2O = 80:20; reaction temperature – 393 K; Amberlyst-15® – 625 mg. Black squares represent glucose conversion. Red circles represent fructose conversion. Blue triangles represent HMF yield. Pink diamonds represent HMF selectivity

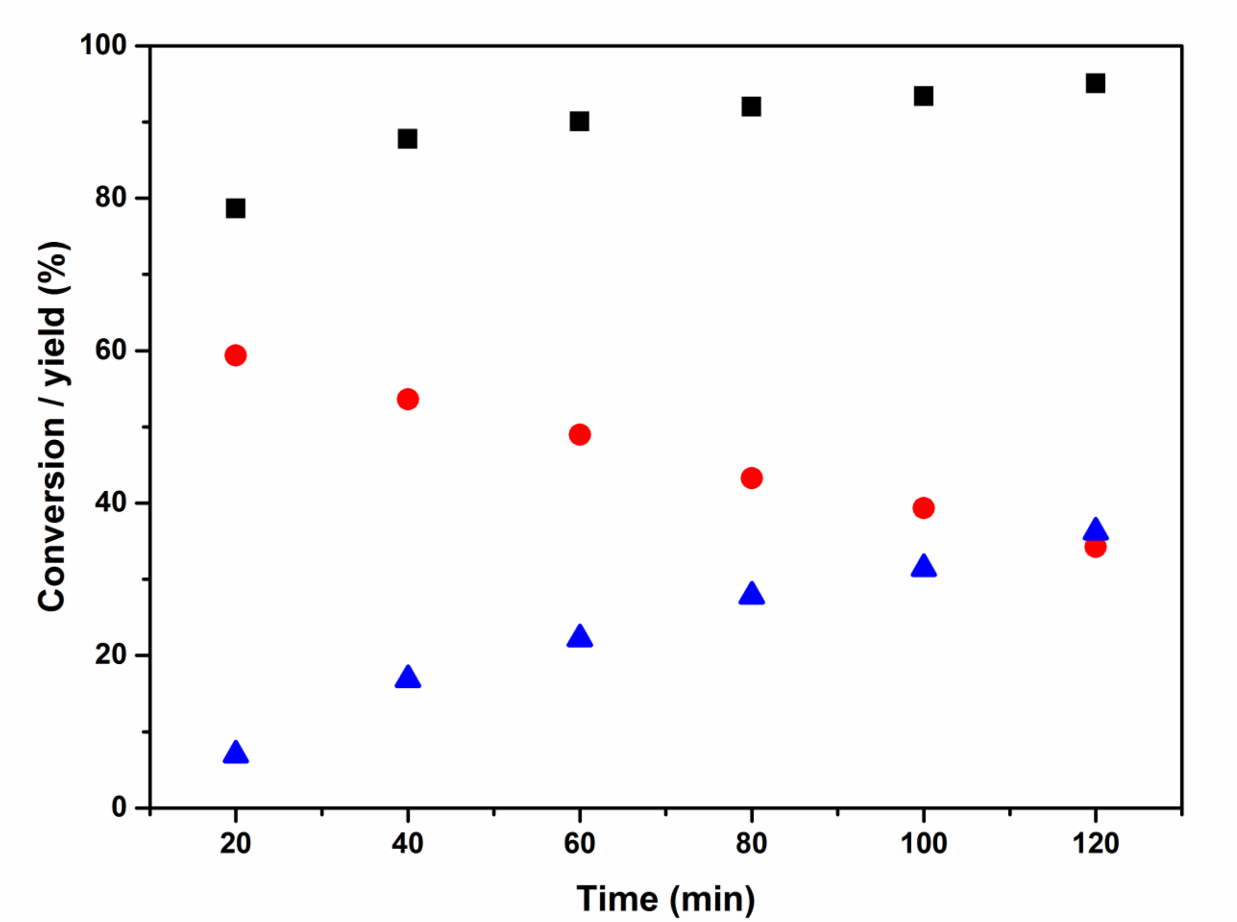


Fig. S8. One-pot glucose conversion to HMF. Reaction condition: Feed – 1 wt% glucose; solvent – acetone:H_2O = 80:20; reaction temperature – 393 K; Amberlyst-15® – 50 mg, Sn-β – 50 mg. Black squares represent glucose conversion. Red circles represent fructose yield. Blue triangles represent HMF yield.

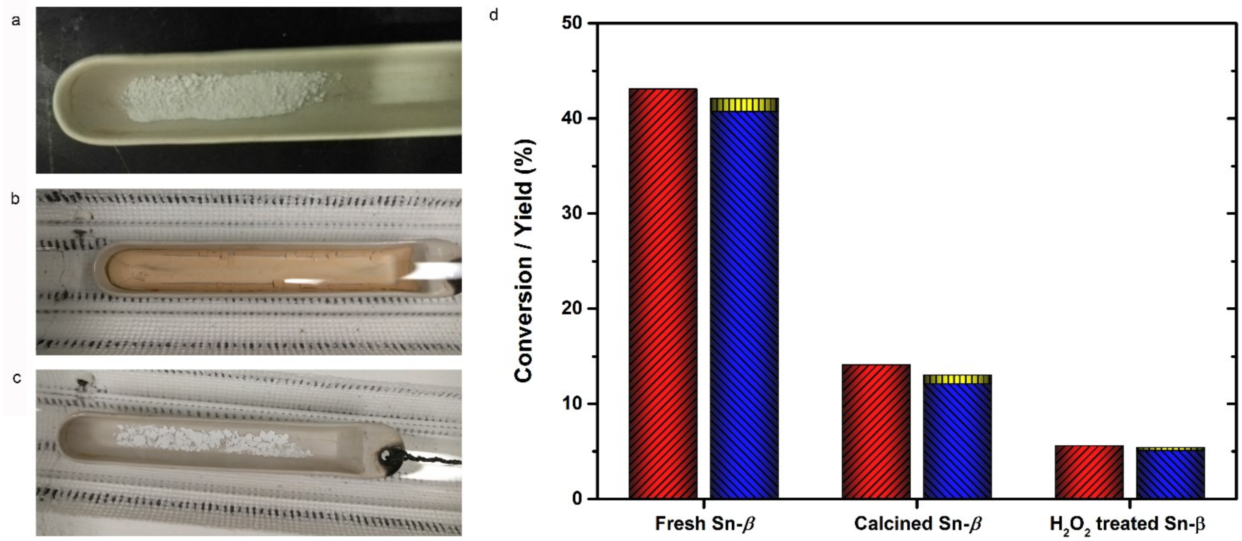


Fig. S9. Regeneration of isomerization catalyst. Pictures of isomerization catalyst. (a) Fresh catalyst. (b) Catalyst after one complete cycle (i.e., glucose isomerization followed by selective fructose dehydration). (c) Catalyst after calcination at 773 K. (d) Glucose isomerization over Sn-β. Reaction condition: Feed – 1 wt% glucose; solvent – acetone:H_2O – 80:20; reaction temperature – 353 K. Red bars represent glucose conversion, blue bars represent fructose yield and yellow bars represent mannose yield.

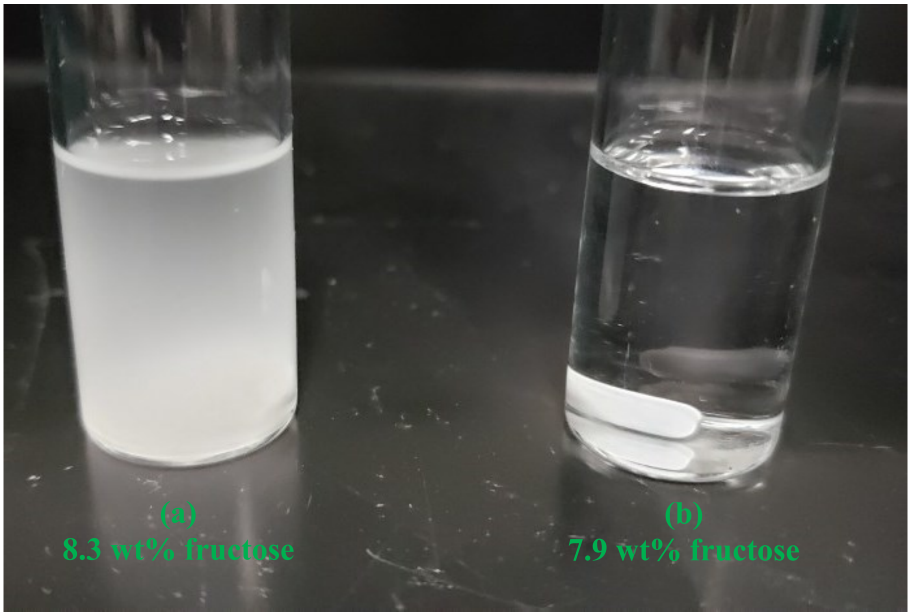


Fig. S10. Fructose solubility in acetone water. Pictures of fructose solution in 80 vol% acetone solution at 303 K. (a) 8.3 wt% fructose. (b) 7.9 wt% fructose.

Table S1. Acid sites in fresh and used Amberlyst-15® catalyst.

	Fresh catalyst	Used catalyst
Sample weight (mg)	250	250
Saturated NaCl solution (mL)	4.0	4.0
100 mM NaOH (mL)	11.1	10.9
% loss in H^+ ions	--	2%

Table S2. Product concentration before and after activated carbon treatment.

Compound	Concentration (mM)	
	Before	After
Glucose	128.7	129.7
Fructose	31	31.2
Oligomers	4.9	4.8
HMF	77	76

Table S3. Process operating data.

	Fructose feedstock	Glucose feedstock
Reactions	*Molar yield (%)*	
Glucose to fructose	–	42.9
Fructose to HMF	85.8	66.1
HMF Recovery	*Recovery (%) & purity (wt%)*	
HMF recovery from reaction effluent	99.7 & 99.1	99.1 & 98.7

Table S4. Mass and energy balances (basis: 11 kilotons of HMF production per year)

Process section	Stream number	Mass flow (kg/hr)	Pressure (bar)	Temperature (C)	Energy requirement (kW)
Fructose feedstock					
HMF production	1	1,943	1.0	25.0	Heating: 1,814
	2	58	1.0	25.0	Electricity: 15
	3	48	1.0	25.0	
	4	29,334	10.0	125.0	
	5	27,046	1.0	59.5	
	11	239	1.0	16.9	
Acetone/H_2O recovery	6	662	2.0	58.9	Heating: 6,241
	7	64	1.0	125.0	Cooling water: 3,773
	8	1,562	0.01	60.0	Refrigeration: 4,261
					Electricity: 2
HMF purification	9	19	1.0	25.0	Heating: 557
	10	18	1.5	-3.1	Refrigeration: 581
	12	1,322	1.5	33.0	Electricity: 1
Glucose feedstock					
HMF production	1	2,000	1.0	25.0	Heating: 5,572
	2	54	1.0	25.0	Cooling water: 3
	3	96,555	3.0	80.0	Electricity: 32
	4	96,555	8.0	120.0	
	5	90,238	1.5	60.0	
	11	4,261	1.0	40.9	
Acetone/H_2O recovery	6	596	1.5	45.0	Heating: 11,392
	7	114	8.0	120.0	Cooling water: 12,908
	8	5,608	0.01	60.0	Refrigeration: 12,965
					Electricity: 3
HMF purification	9	69	1.0	25.0	Heating: 444
	10	88	1.5	-7.0	Refrigeration: 520
	12	1,328	1.5	33.0	Electricity: 1

Table S5. Energy requirement of each process before and after heat integration

Energy required (kW)	Before	After
Fructose feedstock		
Heating	8,780	8,628
Cooling water	3,773	3,774
Refrigeration 1	4,379	4,275
Refrigeration 2	632	581
Glucose feedstock		
Heating	18,978	17,407
Cooling water	14,150	12,911
Refrigeration 1	13,255	12,965
Refrigeration 2	563	520

Table S6. Capital costs and operating costs

	Fructose feedstock	**Glucose feedstock**
Process section	*Capital costs (MM$)*	
HMF production	0.4	2.3
Acetone/H_2O recovery	3.8	6.6
HMF purification	0.9	1.0
OSBL†	2.1	3.9
Total installed cost	7.2	13.8
Total capital investment	16.2	31.0
Raw material	*Operating costs (MM$/yr)*	
Feedstock	13.8	4.1
Refrigeration	1.2	3.1
Solvent makeup	0.7	1.3
Steam	0.8	1.6
Catalysts‡	0.04	0.4
Cooling water	0.02	0.1
Electricity	0.01	0.02
Wastewater disposal	0.02	0.2
Total variable operating costs	16.5	10.8
Total fixed operating costs	1.0	1.8

† OSBL (outside battery limits of the plant) includes infrastructure costs for waste disposal, on-site storage, and utilities.

‡ 20% Catalyst (both Amberlyst-15® and Sn-β) is refurbished every 3 months.

Table S7. List of economic parameters and assumptions

Fructose price ($/ton) [a]	816
Glucose price ($/ton) [a]	236
Acetone price ($/ton) [b]	800
MIBK price ($/ton) [b]	1400
0.5 M HCl price ($/ton) [c]	97.86
Sn-β catalyst ($/kg) [a]	30
Amberlyst-15 catalyst ($/kg) [a]	21
Activated carbon ($/kg) [d]	1.44
Wastewater treatment cost ($/ton) [e]	0.57
Low pressure steam ($/kJ) [f]	3.26e-06
Cooling water ($/kJ) [g]	2.12e-07
-25 °C refrigerant ($/kJ) [g]	7.89e-06
-40 °C refrigerant ($/kJ) [g]	1.31e-05
Electricity price ($/kWh) [c]	0.0572
Plant operating hours per year (hours) [c]	7,884
Plant life (year) [c]	30
Discount rate (%) [c]	10
Plant depreciation (year) [c]	7
Federal tax rate (%)	21
Financing (% of equity) [c]	40
Loan terms [c]	10-year loan at 8% APR
Construction period (year) [c]	3
First 12 months' expenditures (%) [c]	8
Next 12 months' expenditures (%) [c]	60
Last 12 months' expenditures (%) [c]	32
Start-up time (month) [c]	6
Revenue during startup (%) [c]	50
Variable costs incurred during startup (%) [c]	75
Fixed costs incurred during startup (%) [c]	100

[a] Taken from reference prices by ZAUBA (*1-4*)
[b] Taken from reference prices by ICIS News (*5,6*)
[c] Taken from a study by NREL (*7*)
[d] Taken from a report by ProcurementIQ (*8*)
[e] Estimated from value reported by IWW (*9*)
[f] Estimated from a report by DOE (*10*)
[g] Estimated using Aspen Process Economic Analyzer (V8.8 Aspen Technology)

Assumptions

- The outside-battery-limits (OSBL) equipment costs for raw materials storage and etc. are 40% of the inside-battery-limits equipment costs (ISBL).
- Additional direct costs including warehouse, site development, and additional piping are 4%, 9%, and 4.5% of ISBL, respectively.

- Indirect costs including prorateable costs, field expenses, home office and construction project contingency, and other costs are 10%, 10%, 20%, 40%, and 10% of total direct cost, respectively.
- Land and working capital is 5% of the fixed capital investment.
- Labor and supervision costs in the fixed operating costs are estimated as 4.5% of the fixed capital investment.
- Other overhead in the fixed operating costs, such as annual maintenance materials are estimated as 3% of the installed ISBL capital cost, and property insurance and local property tax are estimated as 0.7% of the fixed capital investment.

Supplementary References

1. Zauba. Import data of fructose crystalline. (2018). https://www.zauba.com/import-fructose-crystalline-hs-code.html
2. Zauba. Import data of glucose syrup. (2018). https://www.zauba.com/import-glucose-syrup-hs-code.html
3. Zauba. Import data of h beta zeolite. (2018). https://www.zauba.com/import-h+beta+zeolite-hs-code.html
4. Zauba. Import data of amberlyst 15. (2018). https://www.zauba.com/import-amberlyst+15-hs-code.html
5. ICIS News. OUTLOOK '18: US acetone set to tighten on production cutback. (2017). https://www.icis.com/resources/news/2017/12/29/10173016/outlook-18-us-acetone-set-to-tighten-on-production-cutback/?redirect=english
6. ICIS News. US MIBK spot delivered price holds steady. (2016). https://www.icis.com/resources/news/2016/06/10/10007091/us-mibk-spot-delivered-price-holds-steady/
7. R. Davis *et al.*, "Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons: dilute-acid and enzymatic deconstruction of biomass to sugars and catalytic conversion of sugars to hydrocarbons," (NREL/TP-5100-62498, 2015).
8. Purchasing Activated Carbon - Procurement Research Report (2018). https://www.procurementiq.com/procurement-research-reports/chemicals-fuels-wood-products/activated-carbon.html
9. Industrial water world survey examines wastewater treatment costs. (2016). http://www.waterworld.com/articles/iww/print/volume-11/issue-1/feature-editorial/survey-examines-wastewater-treatment-costs.html
10. U.S. Department of Energy. Benchmark the Fuel Cost of Steam Generation. (2012). https://www.energy.gov/sites/prod/files/2014/05/f16/steam15_benchmark.pdf