Electronic Supplementary Material (ESI) for Green Chemistry.
This journal is © The Royal Society of Chemistry 2017

Supporting information

One-pot Integrated Processing of Biopolymers to Furfurals in Molten Salt Hydrate: Understanding Synergy in Acidity

Sunitha Sadula, Owen Oesterling, Andrew Nardone, Brian Dinkerlacker, Basudeb Saha*

Catalysis Center for Energy Innovation and Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716, USA

Corresponding author's email: bsaha@udel.edu

Table S1. Retention times of various xylo-oligosaccharides.

Oligosaccharides	RT (min)
Xylobiose	37.55
Xylotriose	32.26
Xylotetraose	28.23
Xylopentaose	22.86
Xylohexaose	25.18

Table S2. Hammett function (H_0), EP and pH values of MSH solutions containing fixed amount of LiBr (59 wt%) and varying amount of acid additive.

Acid additive, mM	H_0	pH	EP (mV)
0	-4.83	5.9	82.6
0.001	-3.84	4.5	152
0.002	-4.01	3	228
0.005	-4.42	1.4	334
0.05	-5.01	-2	618

Table S3. Hammett acidity values of salt solutions with varying amount of LiBr at fixed acid additive (0.05 M).

LiBr wt%)	Hammett value (H_0)
10	-4.17
20	-4.43
30	-4.57
40	-4.77
50	-4.72
55	-5.45
59	-5.52

Table S4. Partition coefficients of furfural in EA/MSH and MIBK/MSH solvents. Reaction conditions: 1.5 mL of 59 wt% LiBr in 0.05M aqueous acid additive solution, 4.5 mL organic solvents and 19 mg furfural. 21.4 mg $AlCl_3$ was dissolved in the aqueous MSH phase in experiments using $AlCl_3$.

Solvents	**$AlCl_3.6H_2O$**	**T (°C)**	**$P_{Furfural}$**
EA	-	120	2.2 ± 0.1
EA	+	120	2.2 ± 0.1
EA	-	60	0.7 ± 0.1
EA	+	60	0.6 ± 0.1
MIBK	-	120	2.1 ± 0.1
MIBK	+	120	1.9 ± 0.1
MIBK	-	60	0.5
MIBK	+	60	0.5

EA = ethylacetate; MIBK = methylisobutylketone.

Table S5: Cellulose hydrolysate dehydration in dimethylfuran/MSH at 120 °C. Reaction conditions: 1. 5 mL hydrolysate containing 33 mg glucose, 50 mol% $AlCl_3$, 4.5 mL DMF, 120 °C.

Time (min)	Glucose conversion (%)	HMF Yield (%)
30	76.3	11
60	99.5	25
90	99.6	23.9
120	99.6	23.9

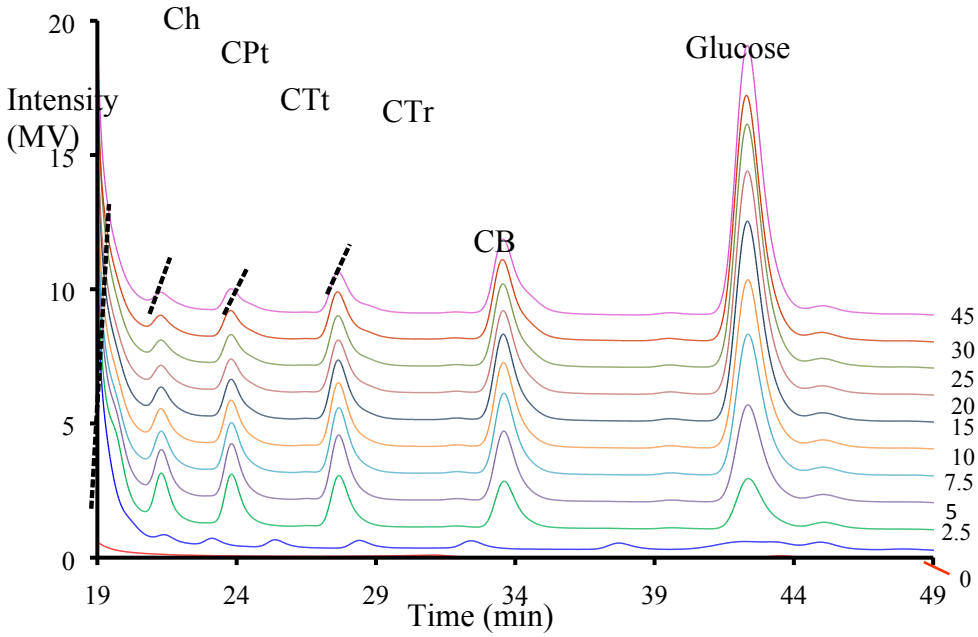

Figure S1. HPLC chromatogram of hydrolysate obtained from crystalline cellulose saccharification showing formation of gluco-oligosaccharides of DP ≤6. (Ch = Cellohexose, CPt = Cellopentaose, CTt = Cellotetraose, CTr = Cellotriose, CB = Cellobiose). Reaction conditions: crystalline cellulose = 1.58 wt%, H_2O/LiBr = 3.25, LiBr = 59 wt%, H_2SO_4 = 0.05 M, 85 ˚C.

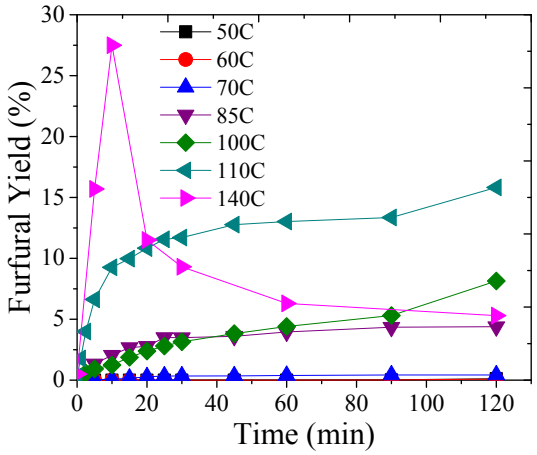

Figure S2: Xylan saccharification results at different temperatures showing xylose degradation to furfural occurs at high temperatures. Reaction conditions: 1.3 wt% xylan, 0.05 M H_2SO_4, water/salt molar ratio = 3.25, 59 wt% LiBr.

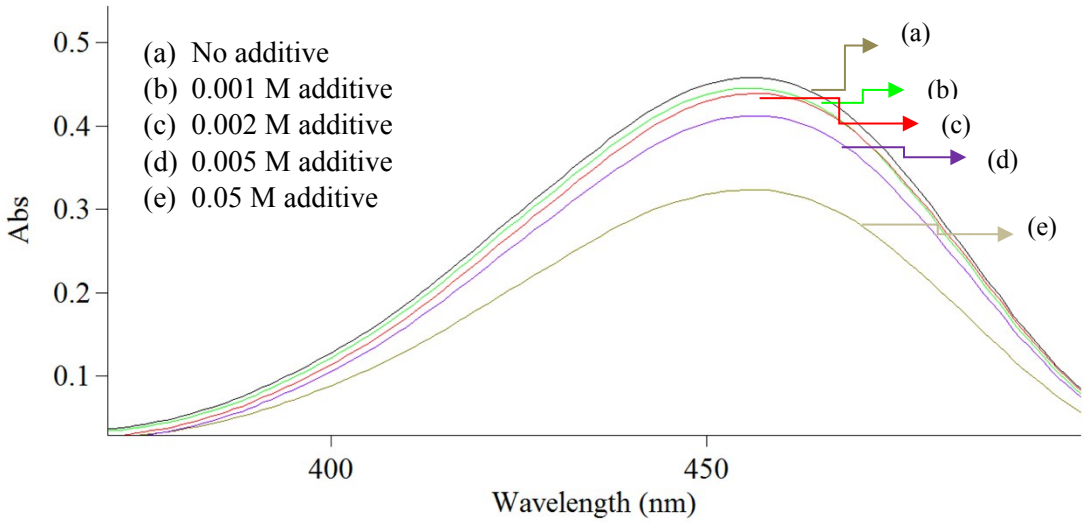

Figure S3. Absorption spectra of 2,6-dinitroaniline in the presence of 59 wt% LiBr and varying acid additive concentrations.

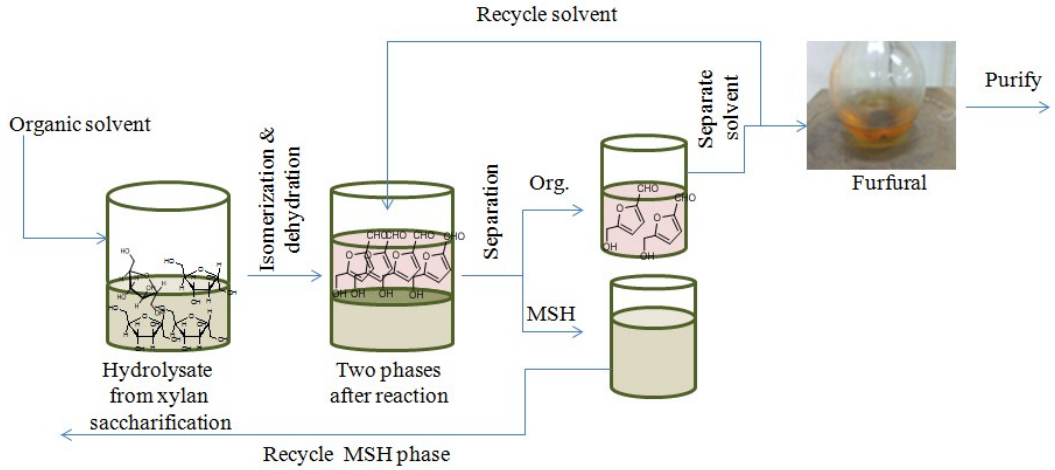

Figure S4. Integrated process for xylan saccharification and product separation in the MSH.

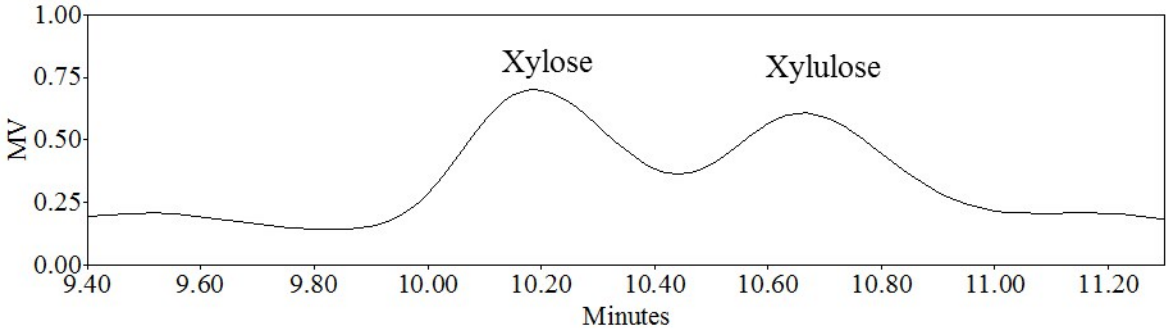

Figure S5. HPLC chromatogram of the MSH phase obtained from dehydration of xylose hydrolysate in biphasic solvent (EA/MSH) showing formation of xylulose as an intermediate.

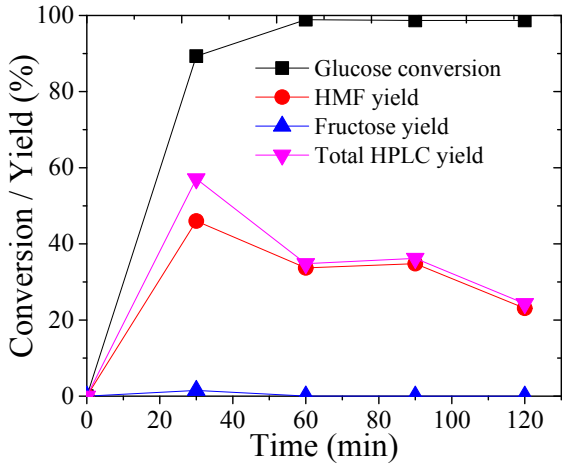

Figure S6. Glucose hydrolysate (obtained from crystalline cellulose saccharification in MSH) dehydration. Reaction conditions: 1.5 mL hydrolysate, 50 mol% $AlCl_3$, 4.5 mL EA, 140 °C

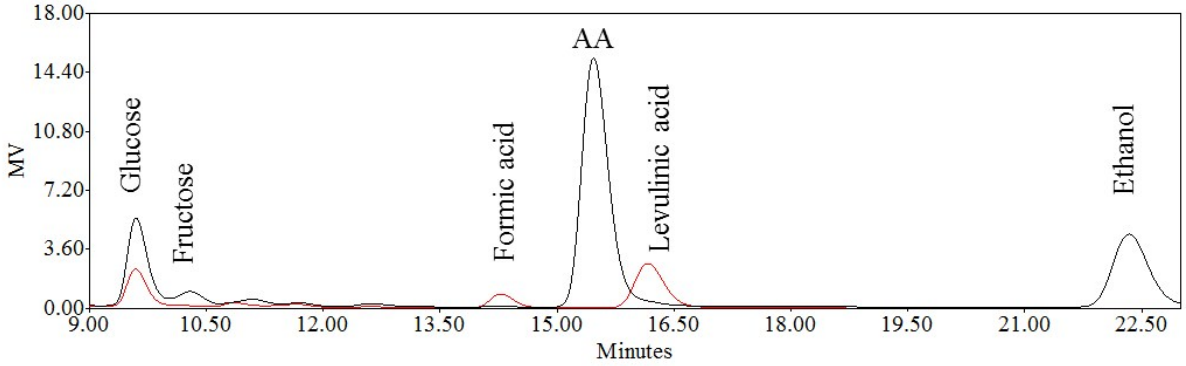

Figure S7. HPLC chromatogram of the product solution obtained from dehydration of glucose hydrolysate in MSH (red color). It shows formation of levulinic acid and formic acid. HPLC chromatogram of the MSH phase (black line), obtained from dehydration of glucose hydrolysate in EA/MSH biphasic solvent, shows no peaks for levulinic acid and formic acid. This suggests that HMF rehydration takes place in monophasic MSH but not in biphasic solvent. Acetic acid (AA) and ethanol in the biphasic reaction could form from decomposition of EA.

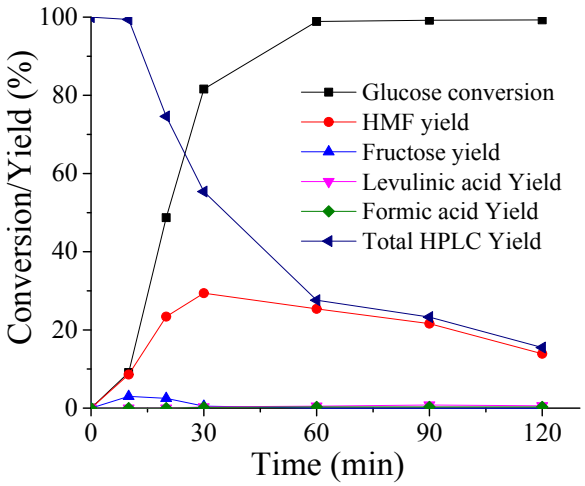

Figure S8: Glucose hydrolysate dehydration with 50 mol% $AlCl_3$ in MIBK/MSH biphasic solvent at 120 °C. MIBK to MSH ratio is 1:3 (v/v).