Simple Chemical Transformation of Lignocellulosic Biomass into Furans for Fuels and Chemicals

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Calculations of Energy Yields

Relevant enthalpies of combustion[1]

glucose	669.9 kcal/mol
xylose	559.0 kcal/mol
ethanol	326.7 kcal/mol
HMF[2]	664.8 kcal/mol
furfural	559.5 kcal/mol

Note: Below, the mannose and galactose enthalpies of combustion are approximated by that of glucose (which is also a hexose); the arabinose enthalpy of combustion is approximated by that of xylose (which is also a pentose).

Energy yield for cellulosic ethanol production

Corn stover starting material (100 g) in previous work contains:[3,4]

cellulose	37.4 g
xylan	21.1 g
arabinan	2.9 g
galactan	2.0 g
mannan	1.6 g

$$\frac{37.4\text{ g}+2.0\text{ g}+1.6\text{ g}}{162.14\text{ g/mol hexose units}}=0.253\text{ mol hexose units}$$

$$\frac{21.1\text{ g}+1.9\text{ g}}{132.12\text{ g/mol pentose units}}=0.182\text{ mol pentose units}$$

Theoretical combustion energy available from sugar content:

$$(0.253\text{ mol}\times 669.9\text{ kcal/mol})+(0.182\text{ mol}\times 559.0\text{ kcal/mol})=271.2\text{ kcal}$$

Ethanol yield is 72 gal/dry ton stover:[3,4] 0.237 g/g stover

Actual combustion energy attainable from ethanol product:

$$100\text{ g stover}\times(0.237\text{ g ethanol/g stover})\times(\text{mol}/46.07\text{ g ethanol})\times 326.7\text{ kcal/mol}=168.1\text{ kcal}$$

Combustion-energy yield = 168.1 kcal/271.2 kcal = **62%**

Energy yield for furan production

Corn stover starting material (100 g) in this work contains:

cellulose	34.4 g
xylan	22.8 g

$$\frac{34.4\ \text{g}}{162.14\ \text{g/mol hexose units}} = 0.212\ \text{mol glucose}$$

$$\frac{22.8\ \text{g}}{162.14\ \text{g/mol hexose units}} = 0.173\ \text{mol xylose}$$

Theoretical combustion energy available from glucose and xylose:

$$(0.212\ \text{mol} \times 669.9\ \text{kcal/mol}) + (0.173\ \text{mol} \times 559.0\ \text{kcal/mol}) = 238.7\ \text{kcal}$$

Actual combustion energy attainable from furanic products (HMF and furfural):

$$47.2\%\ \text{yield} \times (0.212\ \text{mol} \times 664.8\ \text{kcal/mol}) + 36.6\%\ \text{yield} \times (0.173\ \text{mol} \times 559.5\ \text{kcal/mol}) = 101.9\ \text{kcal}$$

Combustion-energy yield = 102.4 kcal/238.7 kcal = **43%**

References

(1) *CRC Handbook of Chemistry and Physics*, 65th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, 1984.
(2) Middendorp, J.A. *Recl. Trav. Chim. Pays-Bas* **1919**, *38*, 1–71.
(3) Aden, A. *Biochemical Production of Ethanol from Corn Stover: 2007 State of Technology Model*; Report No. NREL/TP-510-43205; National Renewable Energy Laboratory: Golden, CO, 2008; http://www.nrel.gov/docs/fy08osti/43205.pdf.
(4) Aden, A.; Ruth, M.; Ibsen, K.; Jechura, J.; Neeves, K.; Sheehan, J.; Wallace, B.; Montague, L.; Slayton, A.; Lukas, J. *Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover*; Report No. NREL/TP-510-32438; National Renewable Energy Laboratory: Golden, CO, 2002; http://www.nrel.gov/docs/fy02osti/32438.pdf.

Table S1. Synthesis of HMF from Fructose[a,b]

sugar	solvent	catalyst (mol%)	additives (wt%)	*T* (°C)	time (h)	molar yield (%)
fructose	DMA–LiCl (10%)	—	—	80	5	58
fructose	DMA–LiCl (10%)	—	—	100	4	62
fructose	DMA–LiCl (10%)	—	—	120	2	65
fructose	DMA–LiCl (10%)	—	—	140	0.5	55
fructose	DMA–LiCl (10%)	H_2SO_4, 6	—	80	4	66
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	—	80	4	66
fructose	DMA–LiCl (10%)	$RuCl_3$, 6	—	80	4	58
fructose	DMA–LiCl (10%)	$PdCl_2$, 6	—	80	5	60
fructose	DMA–LiCl (10%)	CuCl, 6	—	80	5	62
fructose	DMA–LiCl (1%)	H_2SO_4, 6	—	80	1	57
fructose	DMA	H_2SO_4, 6	—	80	1	16
fructose	DMA–LiCl (10%)	H_2SO_4, 6	—	100	5	63
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	—	100	4	55
fructose	DMA–LiCl (10%)	$RuCl_3$, 6	—	100	5	65
fructose	DMA–LiCl (10%)	$PdCl_2$, 6	—	100	4	62
fructose	DMA–LiCl (10%)	CuCl, 6	—	100	5	62
fructose	DMA–LiCl (10%)	$CrCl_2$, 6	—	100	5	66
fructose	DMA–LiCl (10%)	H_2SO_4, 6	—	120	1	68
fructose	DMA–LiCl (10%)	CuCl, 6	—	120	3	71
fructose	DMA–LiCl (10%)	$RuCl_3$, 6	—	120	1.5	61
fructose	DMA–LiCl (10%)	$PtCl_2$, 6	—	120	3	66
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	—	120	3	65
fructose	DMA–LiCl (10%)	H_2SO_4, 6	—	140	0.5	66
fructose	DMA–LiCl (10%)	CuCl, 6	—	140	0.5	58
fructose	DMA–LiCl (10%)	$PtCl_2$, 6	—	140	0.5	58
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	—	140	0.5	62

[a]Fructose was reacted at a concentration of 10 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the total mass of the reaction mixture. Catalyst loading is relative to fructose. Yields are based on HPLC analysis.

[b]Some of the data in this table are also listed in Table 1.

Table S2. Synthesis of HMF from Fructose with Additives[a,b]

sugar	solvent	catalyst (mol%)	additives (wt%)	*T* (°C)	time (h)	molar yield (%)
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 5	80	5	74
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 10	80	5	64
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 20	80	5	74
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 40	80	5	78
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 5	80	4	70
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 10	80	4	72
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 20	80	4	78
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 40	80	4	75
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 5	120	1	62
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 10	120	1.5	68
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 20	120	1	64
fructose	DMA–LiCl (10%)	$CuCl_2$, 6	[EMIM]Cl, 40	120	1	67
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 5	120	1	61
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 10	120	1	67
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 20	120	1	69
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]Cl, 40	120	1	75
fructose	DMA–LiCl (10%)	CuCl, 6	[EMIM]Cl, 5	120	1.5	62
fructose	DMA–LiCl (10%)	CuCl, 6	[EMIM]Cl, 10	120	1.5	70
fructose	DMA–LiCl (10%)	CuCl, 6	[EMIM]Cl, 20	120	1	67
fructose	DMA–LiCl (10%)	CuCl, 6	[EMIM]Cl, 40	120	1.5	83
fructose	DMA	H_2SO_4, 6	LiF, 10	80	2	0
fructose	DMA	$CuCl_2$, 6	LiF, 10	80	2	0
fructose	DMA	H_2SO_4, 6	NaCl, 10	80	1	71
fructose	DMA	H_2SO_4, 6	NaI, 10	80	1	80
fructose	DMA	H_2SO_4, 6	CsF, 10	80	2	0
fructose	DMA	$CuCl_2$, 6	CsF, 10	80	2	0
fructose	DMA	H_2SO_4, 6	KCl, 1.5; 18-crown-6, 5.6	80	2	63
fructose	DMA	H_2SO_4, 6	KCl, 1.5	80	2	56
fructose	DMA	H_2SO_4, 6	KI, 10	100	5	92
fructose	DMA	H_2SO_4, 6	NaI, 10	100	5	91
fructose	DMA	H_2SO_4, 6	LiI, 10	100	6	89
fructose	DMA	H_2SO_4, 6	KBr, 10	100	2	92
fructose	DMA	H_2SO_4, 6	NaBr, 10	100	2	93
fructose	DMA	H_2SO_4, 6	LiBr, 10	100	4	92
fructose	DMA	H_2SO_4, 6	NaI, 8	120	0.2	84
fructose	DMA	H_2SO_4, 6	NaI, 0.5	120	0.2	52
fructose	DMA	H_2SO_4, 6	LiI, 8	120	0.2	85
fructose	DMA	H_2SO_4, 6	LiI, 0.5	120	0.2	62
fructose	DMA	H_2SO_4, 6	LiBr, 10	120	0.25	85
fructose	DMA	—	LiI, 10	120	3	16
fructose	DMA	—	LiBr, 10	120	3	63
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]BF_4, 20	100	2	71
fructose	DMA	H_2SO_4, 6	[EMIM]BF_4, 20	100	4	59
fructose	DMA–LiCl (10%)	H_2SO_4, 6	[EMIM]OTf, 20	100	1	71
fructose	DMA	H_2SO_4, 6	[EMIM]OTf, 20	100	2	48
fructose	DMA	H_2SO_4, 6	[EMIM]Cl, 20	100	2	84
fructose	DMA	H_2SO_4, 6	[EMIM]Br, 20	100	1	94
fructose	DMA	H_2SO_4, 6	[PMIM]I, 20	100	2	81
fructose	DMA	H_2SO_4, 6	[EtPy]Cl, 20	100	2	81
fructose	DMA	H_2SO_4, 6	[MBPy]Cl, 20	100	2	78
fructose	DMA	H_2SO_4, 6	[MMEIM]Cl, 20	100	2	79

[a]Fructose was reacted at a concentration of 10 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the total mass of the reaction mixture. Catalyst loading is relative to fructose. Yields are based on HPLC analysis.
[b]Some of the data in this table are also listed in Table 1.

Table S3. Synthesis of HMF from Glucose[a,b]

sugar	solvent	catalyst (mol%)	additives (wt%)	*T* (°C)	time (h)	molar yield (%)
glucose	DMA–LiCl (10%)	—	—	100	6	<1
glucose	DMA–LiCl (10%)	—	[EMIM]Cl, 20	100	6	<1
glucose	DMA	$CrCl_2$, 6	—	100	4	60
glucose	DMA	$CrCl_2$, 6	—	120	3	47
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 8	120	3	57
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 5	100	6	64
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 10	100	6	67
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 20	100	6	67
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	—	100	5	60
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	—	120	3	53
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	TMEDA, 1	120	3	28
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	pyridine, 1	120	3	43
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 5	100	6	58
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 10	100	6	61
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 20	100	6	62
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 5	120	5	67
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 10	120	3	62
glucose	DMA	$CrCl_2$, 6	[EMIM]Cl, 20	120	3	63
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 5	120	3	64
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 10	120	5	70
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 20	120	5	66
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	—	120	2	55
glucose	DMA	$CrCl_3$, 6	[EMIM]Cl, 5	100	6	59
glucose	DMA	$CrCl_3$, 6	[EMIM]Cl, 10	100	6	63
glucose	DMA	$CrCl_3$, 6	[EMIM]Cl, 20	100	6	67
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	[EMIM]Cl, 5	100	6	57
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	[EMIM]Cl, 10	100	6	69
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	[EMIM]Cl, 20	100	3	65
glucose	DMA	$CrCl_3$, 6	[EMIM]Cl, 5	120	3	62
glucose	DMA	$CrCl_3$, 6	[EMIM]Cl, 10	120	4	60
glucose	DMA	$CrCl_3$, 6	[EMIM]Cl, 20	120	3	64
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	[EMIM]Cl, 5	120	3	61
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	[EMIM]Cl, 10	120	3	61
glucose	DMA–LiCl (10%)	$CrCl_3$, 6	[EMIM]Cl, 20	120	2	62
glucose, 45% in water	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]Cl, 20	100	6	62
glucose	DMA–LiCl (10%)	$CrCl_2$, 6	[EMIM]OTf, 20	100	2	59
glucose	DMA	$CrCl_2$, 6	[EMIM]OTf, 20	100	4	54
glucose	DMA	$CrCl_2$, 6	[EMIM]Br, 20	100	2	78
glucose	DMA	$CrCl_2$, 6	[PMIM]I, 20	100	1	55
glucose	DMA	$CrCl_2$, 6	[EtPy]Cl, 20	100	1	64
glucose	DMA	$CrCl_2$, 6	[MBPy]Cl, 20	100	2	63
glucose	DMA	$CrCl_2$, 6	[MMEIM]Cl, 20	100	1	76
glucose	DMA	$CrCl_2$, 6	LiBr, 10	100	4	79
glucose	DMA–LiCl (5%)	$CrCl_2$, 6	LiBr, 5	100	4	56
glucose	DMA	$CrCl_2$, 6	LiI, 10	100	4	54
glucose	DMA	$CrCl_3$, 6	LiBr, 10	100	6	79
glucose	DMA	$CrBr_3$, 6	LiBr, 10	100	6	80
glucose	DMA	$CrBr_3$, 2	LiBr, 10	100	6	76
glucose	DMA	$CrBr_3$, 1	LiBr, 10	100	6	66
glucose	DMA	$CrCl_2$, 6	NaBr, 10	100	5	77
glucose	DMA	$CrCl_3$, 6	NaBr, 10	100	5	81
glucose	DMA	$CrCl_2$, 6	[EMIM]Br, 20	100	5	78

[a]Glucose was reacted at a concentration of 10 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the total mass of the reaction mixture. Catalyst loading is relative to glucose. Yields are based on HPLC analysis.

[b]Some of the data in this table are also listed in Table 2.

Table S4. Synthesis of HMF from Glucose in Various Solvents[a]

sugar	solvent	catalyst (mol%)	additives (wt%)	T (°C)	time (h)	molar yield (%)[b]
glucose	DMA	$CrCl_2$, 6	—	120	3.25	45
glucose	*N,N*-dimethylformamide	$CrCl_2$, 6	—	120	3.25	36
glucose	*N*-methylpyrrolidone	$CrCl_2$, 6	—	120	3.25	45
glucose	sulfolane	$CrCl_2$, 6	—	120	3.25	35
glucose	dimethylsulfoxide	$CrCl_2$, 6	—	120	3.25	46
glucose	acetonitrile	$CrCl_2$, 6	—	120	3.25	0
glucose	dioxane	$CrCl_2$, 6	—	120	3.25	13
glucose	1-butanol	$CrCl_2$, 6	—	120	3.25	4
glucose	pyridine	$CrCl_2$, 6	—	120	3.25	0
glucose	1-ethyl-2-pyrrolidinone	$CrCl_2$, 6	—	120	3.25	32
glucose	*N*-methylcaprolactam	$CrCl_2$, 6	—	120	3.25	38
glucose	*N,N*-diethylacetamide	$CrCl_2$, 6	—	120	3.25	28
glucose	1-formylpyrrolidine	$CrCl_2$, 6	—	120	3.25	33
glucose	*N,N*-dimethylpropionamide	$CrCl_2$, 6	—	120	3.25	29

[a]Glucose was reacted at a concentration of 10 wt% relative to the total mass of the reaction mixture. Catalyst loading is relative to glucose. Yields are based on HPLC analysis.
[b]Average of two trials.

Table S5. Synthesis of HMF from Cellulose[a,b]

biomass	solvent	catalyst (mol%)	additives (wt%)	temp. (°C)	time (h)	molar yield (%)
cellulose	DMA–LiCl (10%)	—	[EMIM]Cl, 40	140	2	4
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25; HCl, 10	—	140	2	22
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 10	—	140	2	33
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25	—	140	6	15
cellulose	DMA–LiCl (15%)	$CrCl_3$, 36	—	140	6	17
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25	[EMIM]Cl, 10	140	4	18
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25	[EMIM]Cl, 20	140	4	24
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25	[EMIM]Cl, 40	140	4	33
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25; HCl, 6	[EMIM]Cl, 10	140	4	21
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25; HCl, 6	[EMIM]Cl, 20	140	4	33
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25; HCl, 6	[EMIM]Cl, 40	140	1	43
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25; HCl, 6	[EMIM]Cl, 60	140	2	54
cellulose	DMA–LiCl (10%)	$CrCl_2$, 25; HCl, 6	[EMIM]Cl, 80	140	2	47
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 6	[EMIM]Cl, 10	140	4	22
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 6	[EMIM]Cl, 20	140	4	30
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 6	[EMIM]Cl, 40	140	4	38
cellulose	[EMIM]Cl	$CrCl_2$, 25; HCl, 6	—	140	1	53
cellulose	DMA	$CrCl_2$, 25; HCl, 10	LiI, 10	140	3	<1
cellulose	DMA	$CrCl_2$, 25; HCl, 10	LiBr, 10	140	3	<1
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 10	LiI, 2	140	1	27
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 10	LiBr, 1	140	2	34
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 10	LiI, 5	140	1	23
cellulose	DMA–LiCl (10%)	$CrCl_3$, 25; HCl, 10	LiBr, 3	140	2	37

[a]Cellulose was reacted at a concentration of 4 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the total mass of the reaction mixture. Catalyst loading and yield are relative to moles of glucose monomers contained in the cellulose. Yields are based on HPLC analysis.

[b]Some of the data in this table are also listed in Table 3.

Table S6. Synthesis of HMF and Furfural from Corn Stover and Pine Sawdust[a,b]

biomass	solvent	catalyst (mol%)	additives (wt%)	*T* (°C)	time (h)	HMF yield (%)[c]
pine sawdust	DMA–LiCl (10%)	$CrCl_2$, 33	[EMIM]Cl, 15	140	5	19
pine sawdust	DMA–LiCl (10%)	$CrCl_3$, 33	[EMIM]Cl, 15	140	5	17
corn stover	DMA–LiCl (10%)	$CrCl_2$, 19	[EMIM]Cl, 10	140	6	8
corn stover	DMA–LiCl (10%)	$CrCl_2$, 38	[EMIM]Cl, 10	140	6	16
AFEX corn stover	DMA–LiCl (10%)	$CrCl_2$, 19	[EMIM]Cl, 10	140	6	10
AFEX corn stover	DMA–LiCl (10%)	$CrCl_2$, 38	[EMIM]Cl, 10	140	6	16
corn stover	DMA–LiCl (10%)	$CrCl_3$, 19	[EMIM]Cl, 10	140	6	10
AFEX corn stover	DMA–LiCl (10%)	$CrCl_3$, 19	[EMIM]Cl, 10	140	6	11
corn stover	DMA–LiCl (10%)	$CrCl_2$, 10; HCl, 10	[EMIM]Cl, 20	140	3	23
corn stover	DMA–LiCl (10%)	$CrCl_2$, 10; HCl, 10	[EMIM]Cl, 40	140	3	24
corn stover	DMA–LiCl (10%)	$CrCl_2$, 10; HCl, 10	[EMIM]Cl, 60	140	3	36
corn stover	DMA–LiCl (10%)	$CrCl_2$, 10; HCl, 10	[EMIM]Cl, 80	140	3	31
corn stover	[EMIM]Cl	$CrCl_2$, 10; HCl, 10	—	140	3	29
corn stover	DMA–LiCl (10%)	$CrCl_3$, 10; HCl, 10	[EMIM]Cl, 20	140	3	26
corn stover	DMA–LiCl (10%)	$CrCl_3$, 10; HCl, 10	[EMIM]Cl, 40	140	1	39
corn stover	DMA–LiCl (10%)	$CrCl_3$, 10; HCl, 10	[EMIM]Cl, 60	140	2	48
corn stover	DMA–LiCl (10%)	$CrCl_3$, 10; HCl, 10	[EMIM]Cl, 80	140	2	47
corn stover	[EMIM]Cl	$CrCl_3$, 10; HCl, 10	—	140	1	42

[a]Biomass was reacted at a concentration of 10 wt% relative to the total mass of the reaction mixture. The solvent composition is indicated by the wt% of LiCl relative to DMA with additive concentrations relative to the mass of the reaction mixture. Catalyst loading and yield are relative to moles of glucose monomers contained in the cellulose in the biomass. Yields are based on HPLC analysis.

[b]Some of the data in this table are also listed in Table 3.

[c]Yield from pine sawdust assumes a typical cellulose content of 40%; yields from corn stover are based on cellulose analysis of 34.4% for both AFEX-treated and untreated stover and xylan analysis of 22.8% for untreated stover.

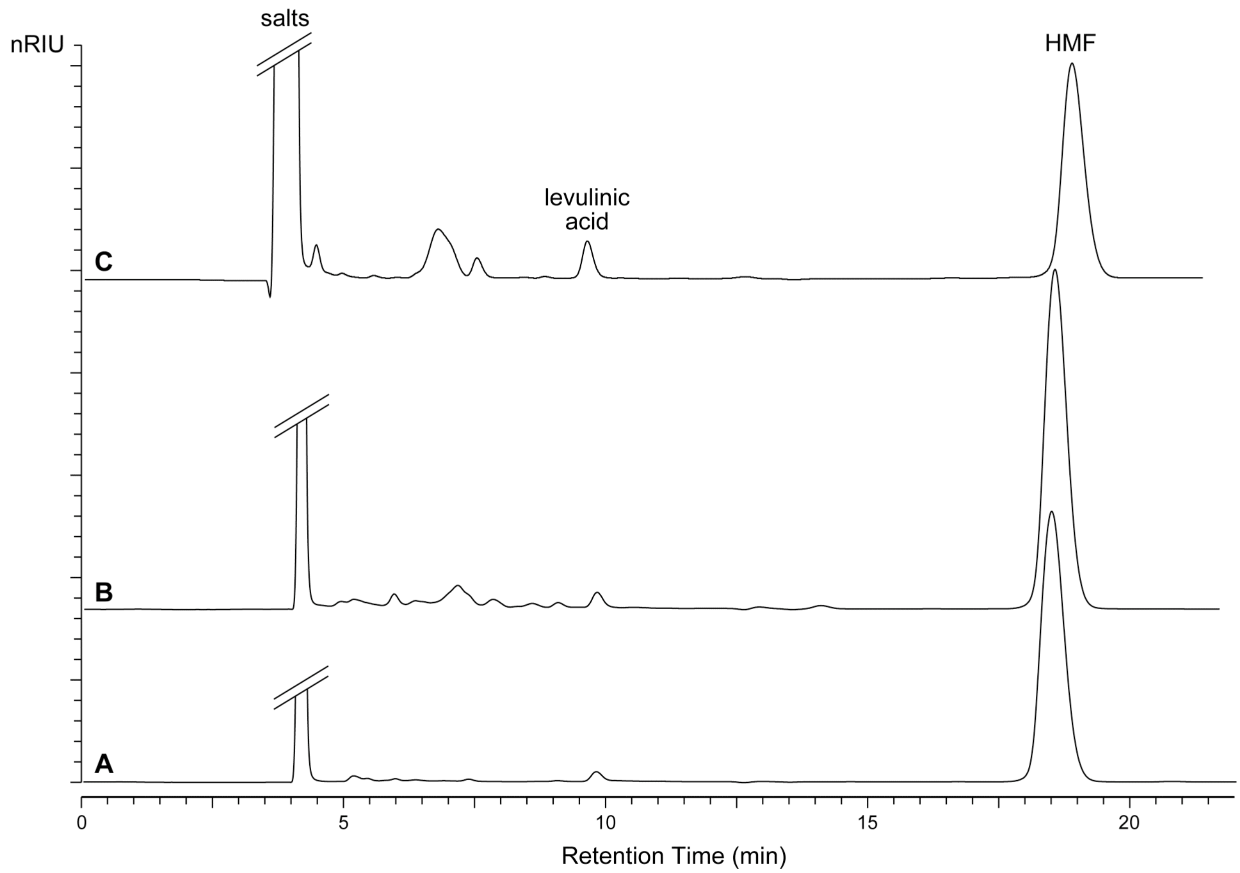

Figure S1. Refractive index HPLC traces of representative reaction mixtures. Analyses were performed with a Bio-Rad Aminex® HPX-87H column and a flow rate of 0.9 mL/min. (A) Synthesis of HMF from fructose with halide additives in DMA. (B) Synthesis of HMF from glucose with lithium bromide in DMA. (C) Synthesis of HMF from cellulose.

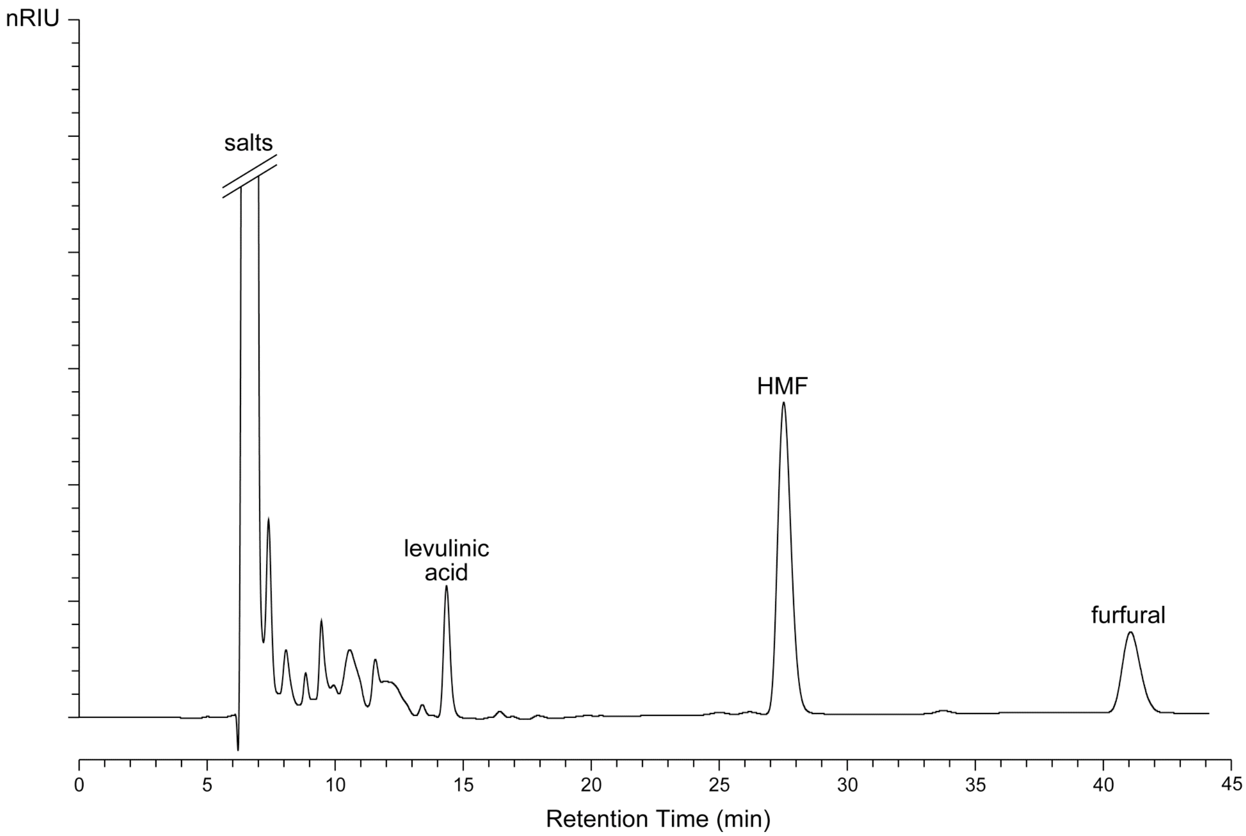

Figure S2. Refractive index HPLC trace of corn stover reaction mixture. Analyses were performed with a Bio-Rad Aminex HPX-87H column and a flow rate of 0.6 mL/min. Major components are indicated.