Supplementary information to "Effect of different Brønsted acids on the hydrothermal conversion of fructose to HMF"

Computational determination of the proton concentration at elevated temperature

In order to determine the pK_a at 140°C ($pK_{a140°C}$), we used the model developed by Helgeson[34], in which the pK_a is calculated from the free energy of dissociation. Helgeson also provides a set of parameters for different acids. The selection that is used here is listed in Table 1. Where no data was available, $pK_{a25°C}$ was taken from literature and $pK_{a140°C}$ was estimated by assuming that pK_a values that are similar at 25°C would also be similar at 140°C.

$$\mathrm{pK}_a\,(T) = \frac{\Delta S_e^{\circ}(T_r)}{2.303RT}\left[T_r - T - \frac{\theta}{\omega}\left(1 - \exp\left[\exp\,(b + aT) - c + \frac{(T - T_r)}{\theta}\right]\right)\right] - \frac{\Delta H_r^{\circ}(T_r)}{2.303RT} + \frac{\Delta S_r^{\circ}(T_r)}{2.303R} + \frac{\alpha}{2.303R}\left(\ln\frac{T}{T_r} - 1 + \frac{T}{T_r}\right) + \frac{\beta(T - T_r)^2}{4.606RT}$$

Table 1: Parameters for the calculation of pK_a values at 140°C as provided by Helgeson[34].

Parameter	Symbol	pK_{a1} (H_2O)	pK_{a1} (H_3PO_4)	pK_a (HNO_3)	pK_{a2} (H_2SO_4)	pK_a (AcOH)	pK_a (HCl)
Reference temperature	T_r (K)	298.15					
Temperature	T (K)	413.15					
Gas constant	R (cal/molK)	1.987					
Solvent-dependent constant	a	0.01875					
Solvent-dependent constant	b	-12.741					
Solvent-dependent constant	θ	219					
Solvent-dependent constant	c	0.000784					
Electrostatic contribution to ΔS_r°	ΔS_e° (cal/molK)	-13.4482	-60.1485	3.7356	-39.8978	-3.9504	-15.525
Entropy of dissociation	ΔS_r° (cal/molK)	-19.31	-16.0	-7.2	-22.0	-22.1	-34,4
Enthalpy of dissociation	ΔH_r° (cal/mol)	13,335	-1,840	-4,100	-3,850	-112	-18,630
Reaction-dependent coefficient	α	-135.070	-300.614	10.434	-424.825	-30.199	-685.62
Reaction-dependent coefficient	β	3,479.41	11,613.89	-1,875.98	12,657.02	-88.49	1.9054

From these $pKa_{140°C}$ values $[H]_{140°C}$ was calculated as

$$[H] = \left[H_2A^-\right]_c + 2\left[HA^{2-}\right]_c + 3\left[A^{3-}\right]_c$$

where $\left[H_2A^-\right]$, $\left[HA^{2-}\right]$ and $\left[A^{3-}\right]$ are the concentrations of the different rest ions. The index c is attributed to the necessity of corrections, which are: $\left[H_2A^-\right]_c = \left[H_2A^-\right] - \left[HA^{2-}\right]$

$$\left[HA^{2-}\right]_c = \left[HA^{2-}\right] - \left[A^{3-}\right]$$

$$\left[A^{3-}\right]_c = \left[A^{3-}\right]$$

$$\left[H_2A^-\right] = -\frac{K_{a1}}{2} + \sqrt{\frac{K_{a1}^2}{4} + K_{a1}c_0 + K_W}$$

$$\left[HA^{2-}\right] = \frac{K_{a2}}{2} + \sqrt{\frac{K_{a2}^2}{4} + K_{a2}\left[H_2A^-\right] + K_W}$$

$$\left[A^{3-}\right] = -\frac{K_{a3}}{2} + \sqrt{\frac{K_{a3}^2}{4} + K_{a3}\left[HA^{2-}\right] + K_W}$$

c_0 is the initial concentration of the acid and K_W is the dissociation constant of water.

If necessary, K_{a3} and K_{a2} were zero in the case that the acid was not triprotic.

c_0 was determined by the reverse calculation using $[H]_{RT}$ and $pKa_{25°C}$ values which are known from the measurements and the literature, respectively.

Experimental yields, conversion and selectivities

Table 2: Conversion of fructose (C(Frc)), yield of HMF and LA (Y(HMF/LA)) and selectivity, depending on reaction time and acid. n.d. not determined [a] 22 h

	Time (min):	0	10	20	40	60	120	180	240	300
H_3PO_4 pH.1.0	C(Frc)	33%	82%	98%	100%	n.d.	n.d.	n.d.	n.d.	n.d.
	Y(HMF)	15%	45%	42%	25%	n.d.	n.d.	n.d.	n.d.	n.d.
	Y(LA)	0%	11%	24%	40%	n.d.	n.d.	n.d.	n.d.	n.d.
	S(HMF)	46%	55%	42%	25%	n.d.	n.d.	n.d.	n.d.	n.d.
	S(HMF+LA)	47%	68%	67%	65%	n.d.	n.d.	n.d.	n.d.	n.d.
H_2SO_4 pH.1.1	C(Frc)	24%	n.d.	73%	n.d.	91%	100%	n.d.	n.d.	n.d.
	Y(HMF)	12%	n.d.	37%	n.d.	32%	16%	n.d.	n.d.	n.d.
	Y(LA)	1%	n.d.	10%	n.d.	29%	51%	n.d.	n.d.	n.d.
	S(HMF)	53%	n.d.	50%	n.d.	36%	16%	n.d.	n.d.	n.d.
	S(HMF+LA)	55%	n.d.	64%	n.d.	68%	68%	n.d.	n.d.	n.d.
HCl pH.1.2	C(Frc)	33%	57%	73%	86%	n.d.	n.d.	n.d.	n.d.	n.d.
	Y(HMF)	20%	37%	41%	35%	n.d.	n.d.	n.d.	n.d.	n.d.
	Y(LA)	1%	10%	18%	35%	n.d.	n.d.	n.d.	n.d.	n.d.
	S(HMF)	61%	66%	56%	40%	n.d.	n.d.	n.d.	n.d.	n.d.
	S(HMF+LA)	65%	82%	80%	81%	n.d.	n.d.	n.d.	n.d.	n.d.

HNO_3 pH.1.2	C(Frc)	43%	n.d.	81%	n.d.	91%	97%	n.d.	n.d.	n.d.
	Y(HMF)	26%	n.d.	40%	n.d.	22%	6%	n.d.	n.d.	n.d.
	Y(LA)	3%	n.d.	22%	n.d.	51%	68%	n.d.	n.d.	n.d.
	S(HMF)	60%	n.d.	50%	n.d.	24%	6%	n.d.	n.d.	n.d.
	S(HMF+LA)	67%	n.d.	77%	n.d.	80%	77%	n.d.	n.d.	n.d.
Citric acid pH.1.4	C(Frc)	8%	n.d.	40%	n.d.	86%	100%	n.d.	n.d.	n.d.
	Y(HMF)	5%	n.d.	30%	n.d.	42%	30%	n.d.	n.d.	n.d.
	Y(LA)	0%	n.d.	2%	n.d.	11%	27%	n.d.	n.d.	n.d.
	S(HMF)	63%	n.d.	75%	n.d.	49%	30%	n.d.	n.d.	n.d.
	S(HMF+LA)	63%	n.d.	80%	n.d.	62%	57%	n.d.	n.d.	n.d.
Glycolic acid pH.1.8	C(Frc)	6%	n.d.	22%	n.d.	44%	71%	n.d.	n.d.	n.d.
	Y(HMF)	1%	n.d.	9%	n.d.	25%	37%	n.d.	n.d.	n.d.
	Y(LA)	0%	n.d.	0%	n.d.	1%	3%	n.d.	n.d.	n.d.
	S(HMF)	12%	n.d.	42%	n.d.	57%	53%	n.d.	n.d.	n.d.
	S(HMF+LA)	12%	n.d.	42%	n.d.	59%	57%	n.d.	n.d.	n.d.
Citric acid pH.2.0	C(Frc)	15%	n.d.	29%	n.d.	46%	62%	81%	90%	98%
	Y(HMF)	7%	n.d.	16%	n.d.	27%	40%	42%	42%	37%
	Y(LA)	0%	n.d.	0%	n.d.	1%	5%	9%	12%	19%
	S(HMF)	47%	n.d.	56%	n.d.	60%	64%	52%	47%	38%
	S(HMF+LA)	47%	n.d.	57%	n.d.	63%	72%	62%	60%	57%
H_3PO_4 pH.2.0	C(Frc)	7%	n.d.	17%	n.d.	32%	48%	62%	74%	88%
	Y(HMF)	1%	n.d.	7%	n.d.	16%	29%	39%	43%	43%
	Y(LA)	0%	n.d.	0%	n.d.	0%	2%	5%	8%	15%
	S(HMF)	17%	n.d.	44%	n.d.	50%	61%	63%	58%	49%
	S(HMF+LA)	17%	n.d.	44%	n.d.	50%	65%	71%	69%	66%
Acetic acid pH.2.0	C(Frc)	19%	n.d.	n.d.	n.d.	n.d.	79%	n.d.	96%	100%[a]
	Y(HMF)	0%	n.d.	n.d.	n.d.	n.d.	37%	n.d.	45%	19%[a]
	Y(LA)	0%	n.d.	n.d.	n.d.	n.d.	0%	n.d.	2%	7%[a]
	S(HMF)	0%	n.d.	n.d.	n.d.	n.d.	47%	n.d.	47%	19%[a]
	S(HMF+LA)	0%	n.d.	n.d.	n.d.	n.d.	48%	n.d.	49%	26%[a]

Reaction rate constants

Table 3: reaction rate constants determined at 140°C

	k_1 (10^{-3} min^{-1})	k_2 (10^{-3} min^{-1})	k_3 (10^{-3} min^{-1})	k_4 (10^{-3} min^{-1})
H_3PO_4 pH.1.0	102,00	30,00	24,00	0,00
H_2SO_4 pH.1.1	33,50	14,50	13,30	0,00
HCl pH.1.2	43,60	23,50	0,00	3,50
HNO_3 pH.1.2	45,32	24,16	0,56	2,99
Citric acid pH.1.4	20,80	6,00	5,70	5,70
Glycolic acid pH.1.8	6,00	0,90	3,20	0,80
Citric acid pH.2.0	7,20	1,50	0,70	2,30
H_3PO_4 pH.2.0	3,92	1,35	1,38	0,06
Acetic acid pH.2.0	7,60	0,17	3,80	0,70