Selective Production of Formic Acid by Wet Oxidation of Aqueous-Phase Bio-Oil

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Supporting information

GC/MS analysis I (levoglucosan quantification)

Samples were prepared by dissolving 0.4 g bio-oil in acetone, adding 1 mL of internal standard fluoranthene (1 mg/mL) and completing 10 mL with acetone. A sample of 200 uL were injected in a HP 6890 Series gas chromatograph equipped with Combi PAL CTC-G6500 auto sampler, a split/split less injector and a HP 5973 mass-selective detector. The chromatographic separation was performed using a VF-1701 (14% cyanopropyl/phenyl, 86% polydimethylsiloxane) column (Varian) of 60 m × 0.25 mm I.D., 0.25 µm film thickness, with electronic helium grade 6.0 at 2 mL min^{-1}. The GC/MS transfer line was kept at 280 °C and the detection was carried out in scan mode with electron energy of 70 eV. The ionization source was set at 230 °C and analyzer temperature at 150 °C. The initial temperature was 80 °C, with an increase of 3 °C min^{-1} up to 150 °C (ramp 1), 40 °C min^{-1} up to 280 °C (ramp 2), and a final clean-up at 280 °C for 5 min. The injection port temperature was 260 °C.

GC/MS analysis II (Figure 1)

The GC front inlet temperature was kept at 250 °C. The temperature of the GC oven was programmed as follows: 4 min at 45 °C, heating to 60 °C at 1 °C/min, hold time 4 min; heating to 150°C at 3°C/min, hold time 10 min; heating to 230°C at 3°C/min, hold time 10 min, and finally heating to 280°C at 3°C/min and hold time of 30 min. A split ratio of 50:1 was set for injection, and the gas flow rate was maintained at 2.00 mL/min. Compounds were identified using the National Institute of Standards and Technology (NIST) mass spectral library. Compounds reported appeared consistently with high probability.

Table S1. Literature Data for Formic Acid (FA) Yields from Wet Oxidation of Glycolaldehyde (GA)

system	T (°C)	O_2 (MPa)[c]	time	GA conversion (%)	FA yield (%)	reference
$H_5PV_2Mo_{10}O_{40}$	90	3.0	24 h	100	80	[1]
$H_8PV_5Mo_7O_{40}$	90	2.0	5 h	98	77	[2]
$H_4PVMo_{11}O_{40}$	150	2.0	3 h	100	71	[3]
$H_5PV_2Mo_{10}O_{40}$	90	3.0	5 h	68	50	[2]
$H_5PV_2Mo_{10}O_{40}$	100	3.0	3 h	90	56	[4]
$NaVO_3$, H_2SO_4 0.7 wt %	160	3.0	1 m	100	63	[5]
$VOSO_4$	140	2.0	1 h	>99	53	[6]
H_2SO_4 5 wt % [a]	170	3.0	20 m	79	54	this study
Bio-oil, FA 4 wt %[b]	170	3.0	20 m	95	59	this study

[a] 1 wt % GA; [b] 5 wt % GA with aqueous-phase bio-oil I3 (GA content corresponding to 80% mol-C substrate). [c] initial O_2 pressure at room temperature.

Table S2. Literature Data for Formic Acid (FA) Yields from Wet Oxidation of Glucose

system	glucose (wt %)	T (°C)	O_2 (MPa)	time	conversion (%)	FA yield (%)	reference
no catalyst	10	190	1.6	30 m	>98	24	[7]
$Fe_2(SO_4)_3$ 0.67 wt %	10	190	1.6	30 m	-	26	[7]
$Fe_2(SO_4)_3$ 0.67 wt %	10	190	3.3	30 m	-	35	[7]
$H_5PV_2Mo_{10}O_{40}$	3.0	90	3.0	3 h	>98	48	[1]
$H_8PV_5Mo_7O_{40}$	4.5	90	2.0	24 h	>99	66	[2]
$H_5PV_2Mo_{10}O_{40}$	2.5	100	2.0	2 h	90	36	[4]
$H_5PV_2Mo_{10}O_{40}$	2.5	150	1.0	3 h	100	29	[4]
$H_5PV_2Mo_{10}O_{40}$	1.0	100	2.0	3 h	100	55	[4]
$NaVO_3$, H_2SO_4 2 wt %	0.8	160	3.0	1 m	94	44	[8]
$NaVO_3$, H_2SO_4 0.7 wt %	1.6	160	3.0	1 m	97	43	[5]
$VOSO_4$ 0.076 wt %	5.1	140	2.0	1 h	>99	45	[6]
$H_4PVMo_{11}O_{40}$	1.0	180	2.0	3 h	100	54	[3]

FA yield on a mol-C basis; O_2 pressure at room temperature;

Table S3. Literature Data for Formic Acid (FA) Yields from Wet Oxidation of Cellulose

system	cellulose (wt %)	T (°C)	O_2 (MPa)	time	conversion (%)	FA yield (%)	acetic acid yield (%)	reference
no catalyst	5.0	227	1.6	30 m	50	5	-	[7]
$Fe_2(SO_4)_3$ 0.67 wt %	5.0	227	1.6	30 m	-	13	7	[7]
$H_5PV_2Mo_{10}O_{40}$ +TS	2.9	90	3.0	66 h	-	29	-	[1]
$H_8PV_5Mo_7O_{40}$ +TS	2.8	90	3.0	24 h	-	28	-	[2]
H_2SO_4 2 wt %	1.6	150	3.0	10 m	-	2	n.d.	[8]
H_2SO_4 0.7 wt %	1.6	160	3.0	2 h	95	21	-	[5]
H_2SO_4 2 wt %	1.6	170	3.0	10 m	-	45	-	[8]
$H_5PV_2Mo_{10}O_{40}$	<1	170	1.0	9 h	100	3	-	[4]
$H_5PV_2Mo_{10}O_{40}$ H_2SO_4 0.1wt %	<1	170	1.0	9 h	100	28	-	[4]
$H_5PV_2Mo_{10}O_{40}$	<1	170	5.0*	9 h	100	35	-	[4]
$NaVO_3$, H_2SO_4 2 wt %	1.6	160	3.0	10 m	-	58	1	[8]
$NaVO_3$, H_2SO_4 2 wt %	1.6	170	3.0	10 m	-	48	5	[8]
$NaVO_3$, H_2SO_4 0.7 wt %	1.6	160	3.0	2 h	100	65	-	[5]
$VOSO_4$ 0.16 wt %	0.9	180	2.0	2 h	-	39	-	[6]
$H_4PVMo_{11}O_{40}$	1.0	180	0.6	3 h	100	68	12	[3]

TS: p-toluene sulfonic acid; O_2 pressure at room temperature; * air; n.d.: not detected; - not reported.

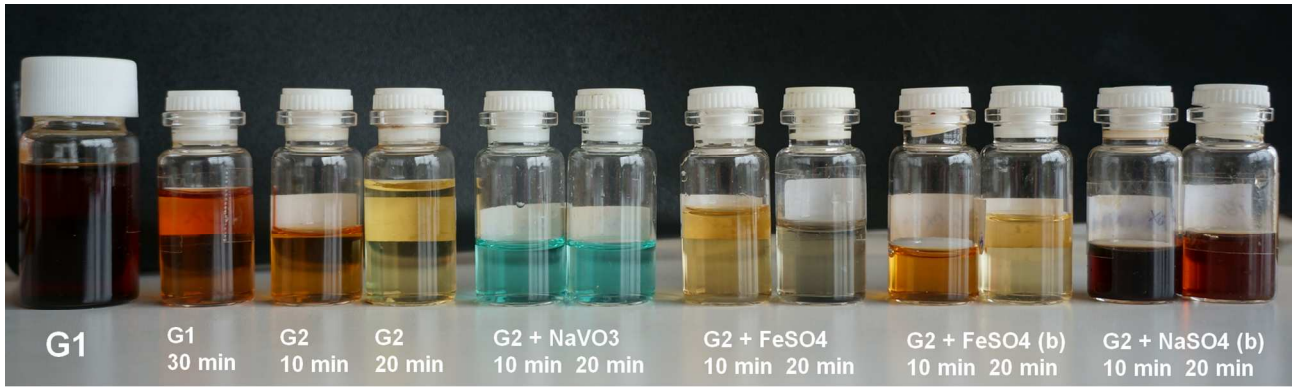


Figure S1. Photographs of bio-oil G1 and solutions obtained after wet oxidation (Figure 2) (b) without H_2SO_4.

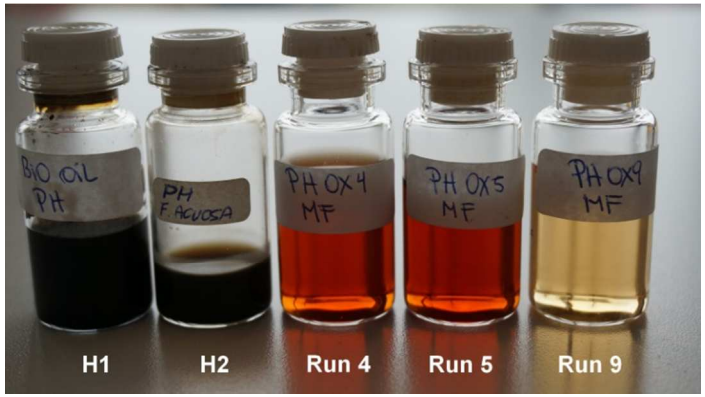
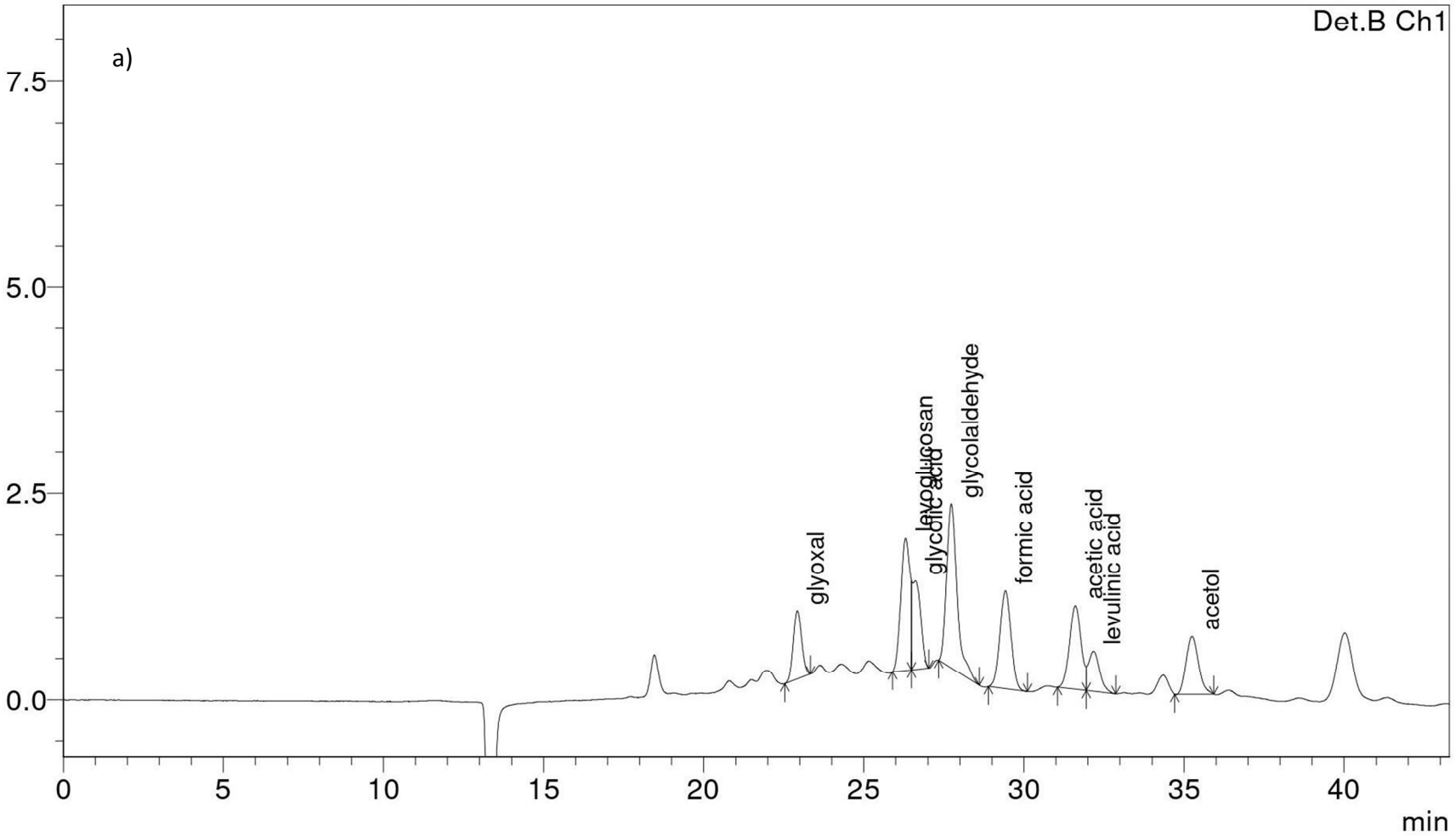


Figure S2. Photographs of aqueous-phase bio-oil H1, H2 (H1 extracted), and solutions obtained after wet oxidation (Table 2).


Det.B Ch1
a)
7.5
5.0
2.5
0.0
0
5
10
15
20
25
30
35
40
min
glyoxal
levoglucosan
glycolic acid
glycolaldehyde
formic acid
acetic acid
levulinic acid
acetol

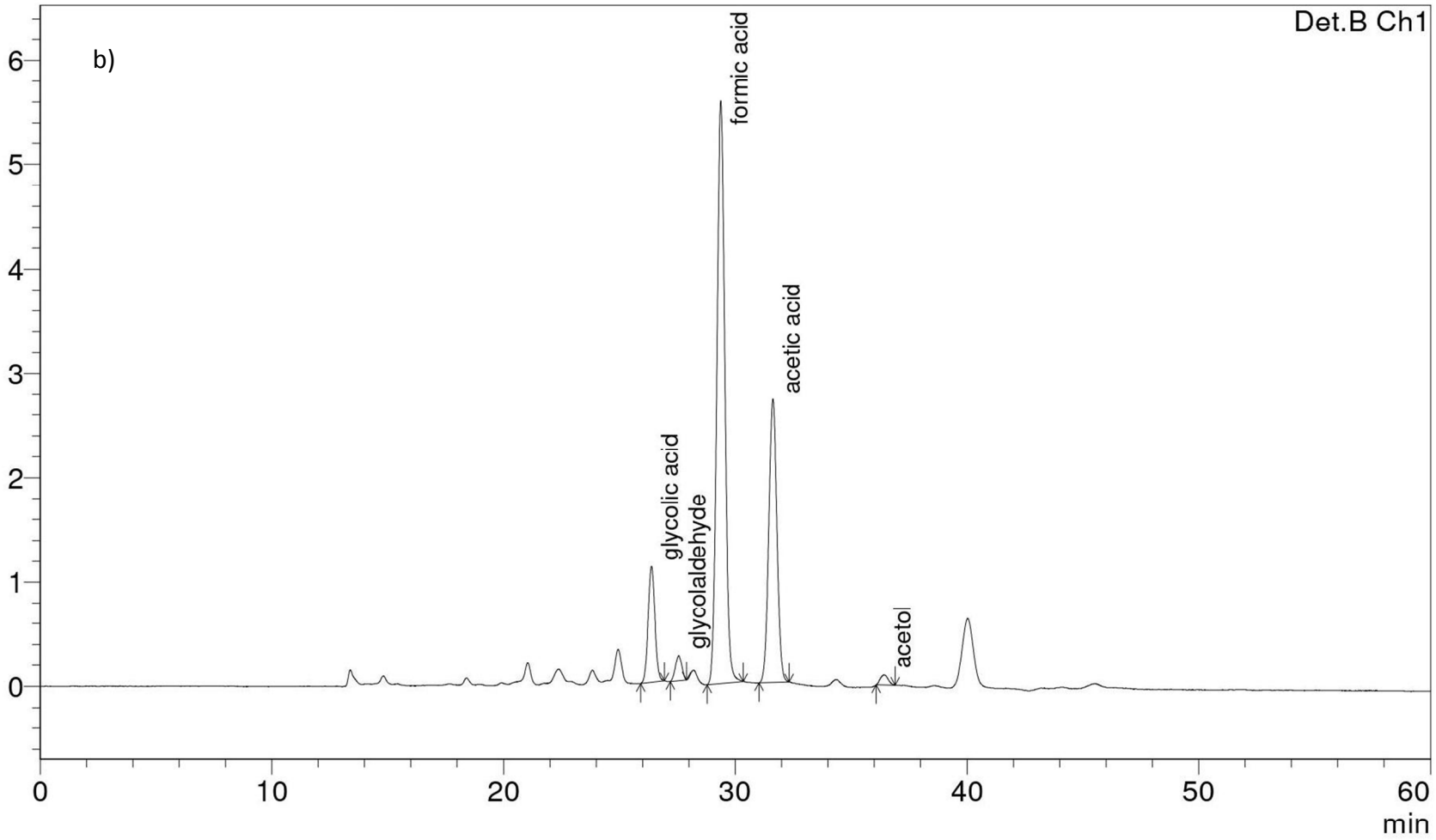


Figure S3. Sample HPLC chromatograms of aqueous-phase bio-oil H1 before (a) and after wet oxidation (b) (Table 2 run 4).

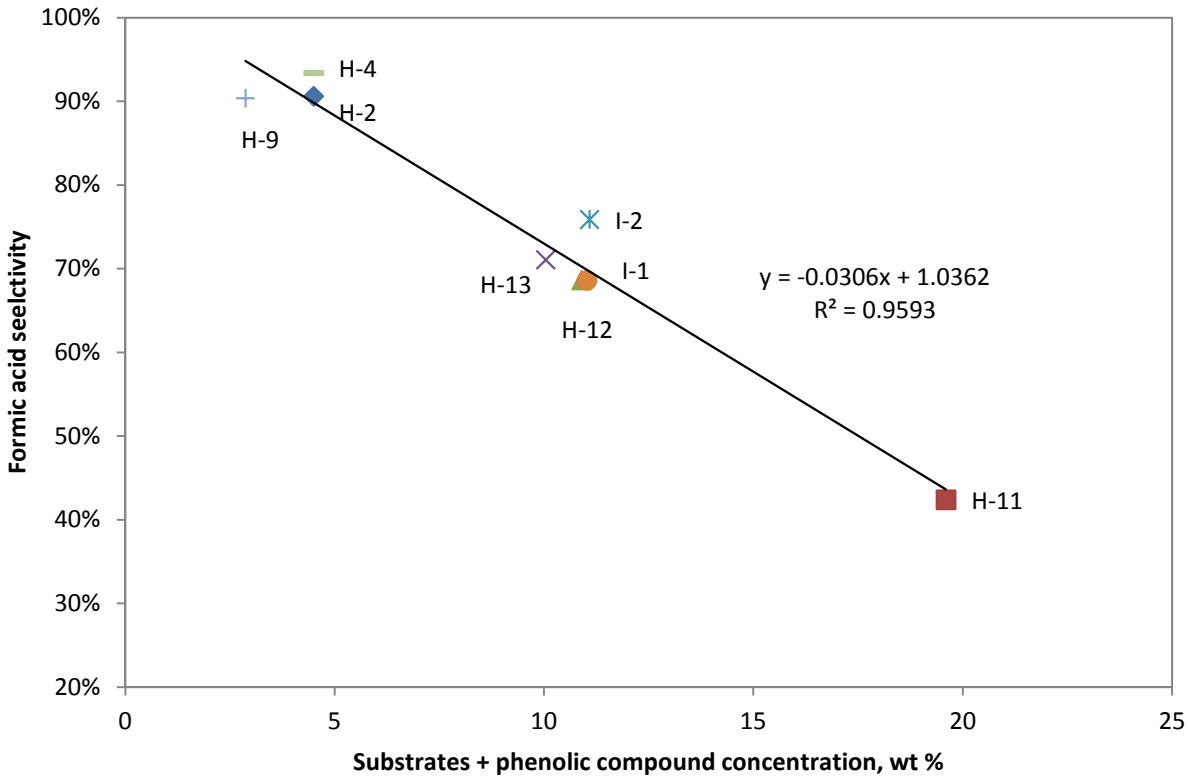


Figure S4. Effect of concentration of substrates and phenolic compounds on the relative yield (wt % dry basis) of formic (FA) to acetic acid (AA), FA / (FA+AA).

References

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