Supporting Information

Biotransformation of Furanic and Phenolic Compounds with Hydrogen Gas Production in a Microbial Electrolysis Cell

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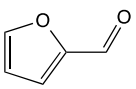
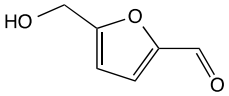
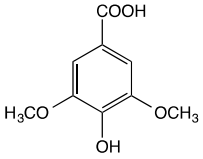
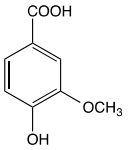
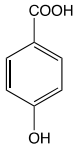
Table S1. Furanic and phenolic compounds used in the present study

Property	Furfural (FF)	5-hydroxymethyl furfural (HMF)	Syringic acid (SA)	Vanillic acid (VA)	4-hydroxy benzoic acid (HBA)
CAS number	98-01-1	67-47-0	530-57-4	121-34-6	99-96-7
Structure					
Molecular formula	$C_5H_4O_2$	$C_6H_6O_3$	$C_9H_{10}O_5$	$C_8H_8O_4$	$C_7H_6O_3$
Molecular Weight	96.08	126.11	198.17	168.15	138.12
log K_{ow}	0.41[a]	-0.09[b]	1.04[a]	1.43[a]	1.58[a]
Henry's law constant (atm-m^3/mol, 25°C) [b]	3.8×10^{-6}	5.4×10^{-10}	4.0×10^{-14}	4.6×10^{-12}	5.6×10^{-12}
Water solubility (g/L, 25°C)	74[c]	364 [b]	1.5[b]	1.5[d]	5.0[d]
pK_a	NA[e]	13.65[f]	3.93[f]	4.16[f]	4.38[f]
G_f^0 (kJ/mol)	-102.87[g]	-260.41[h]	-583.95[h]	-494.08[g]	-416.5[g]
$E^{0\prime}$(V)[i]	-0.386	-0.388	-0.367	-0.341	-0.303
ThOD (g O_2/g)[j]	1.67	1.57	1.45	1.52	1.62
Electron equivalents (eeq/g)	0.21	0.20	0.18	0.19	0.20

[a] Data from Hansch et al.[1]; [b] Predicted by EPISuite[2]; [c] Data from Yalkowsky and He[3]; [d] Data from Yalkowsky and Dannenfelser[4]; [e] NA, not available; [f] Predicted by ChemAxon[5]; [g] Data from Yaws [6]; [h] Values calculated based on the group contribution method[7]; [i] Half reactions with HCO_3^- as the oxidized species at pH 7.0, equations listed in Table S2; [j] ThOD, theoretical oxygen demand

Table S2. Half reduction reactions and standard potentials of the five compounds.

Reduced compound	Reaction	$E^{0\prime}$, V
Furfural	$5\ HCO_3^- + 25\ H^+ + 20\ e^- \rightarrow C_5H_4O_2 + 13\ H_2O$	-0.386
5-Hydroxymethylfurfural	$6\ HCO_3^- + 30\ H^+ + 24\ e^- \rightarrow C_6H_6O_3 + 15\ H_2O$	-0.388
Syringic acid	$9\ HCO_3^- + 45\ H^+ + 36\ e^- \rightarrow C_9H_{10}O_5 + 22\ H_2O$	-0.367
Vanillic acid	$8\ HCO_3^- + 40\ H^+ + 32\ e^- \rightarrow C_8H_8O_4 + 20\ H_2O$	-0.341
4-Hydroxybenzoic acid	$7\ HCO_3^- + 35\ H^+ + 28\ e^- \rightarrow C_7H_6O_3 + 18\ H_2O$	-0.303

Table S3. Volumetric transformation rate of the furanic and phenolic compounds tested at various initial concentrations in the MEC bioanode.

Compound	**Initial Conc. (mg/L)**		**Rate[a]**		**R^2**	**P Value**
	Mixture	**Individual Compound**	**mg/L-d**	**mM/d**		
Furfural (FF)	200	33.6	32.0 ± 4.9[b]	0.333 ± 0.051	0.768	0.0072
	400	65.9	64.5 ± 1.3	0.671 ± 0.014	0.997	<0.0001
	800	113.4	78.7 ± 1.0	0.819 ±0.010	0.999	<0.0001
	1,200	191.5	225.1 ± 3.4	2.343 ± 0.035	0.999	0.0002
5-hydroxymethyl furfural (HMF)	200	27.5	24.8 ± 2.1	0.197 ± 0.017	0.976	0.0123
	400	57.5	28.3 ± 1.9	0.224 ± 0.015	0.981	0.0001
	800	102.6	46.8 ± 5.3	0.371 ± 0.042	0.963	0.0030
	1,200	178.9	129.8 ± 19.9	1.029 ± 0.158	0.837	0.0073
Syringic acid (SA)	200	42.9	9.4 ± 0.2	0.047 ± 0.001	0.994	<0.0001
	400	86.7	24.2 ± 1.0	0.122 ± 0.005	0.975	<0.0001
	800	180.0	47.0 ± 2.2	0.237 ± 0.011	0.969	<0.0001
	1,200	292.9	181.7 ± 18.4	0.917 ± 0.093	0.961	0.0101
Vanillic acid (VA)	200	39.6	8.8 ± 0.5	0.052 ± 0.003	0.955	<0.0001
	400	81.4	20.0 ± 0.8	0.119 ± 0.005	0.972	<0.0001
	800	166.8	39.0 ± 1.7	0.232 ± 0.010	0.967	<0.0001
	1,200	270.0	143.6 ± 8.5	0.854 ± 0.051	0.963	<0.0001
4-hydroxybenzoic acid (HBA)	200	33.9	11.8 ± 0.8	0.085 ± 0.006	0.948	0.0001
	400	69.8	14.8 ± 0.6	0.107 ± 0.004	0.970	<0.0001
	800	133.4	34.1 ± 1.5	0.247 ± 0.011	0.969	<0.0001
	1,200	212.4	133.3 ± 15.9	0.965 ± 0.115	0.885	0.0036

[a] Rates estimated by linear regression; [b] Mean ± standard error ($n \geq 5$)

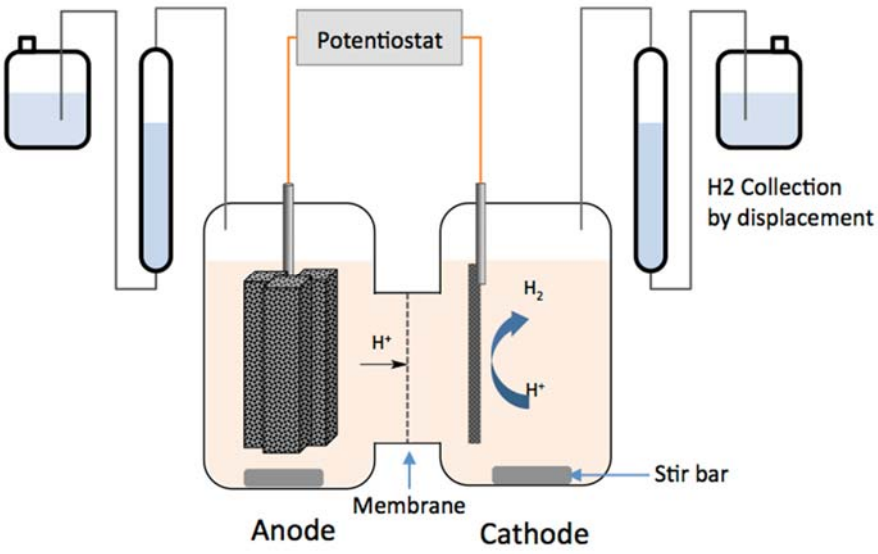


Figure S1. MEC setup.

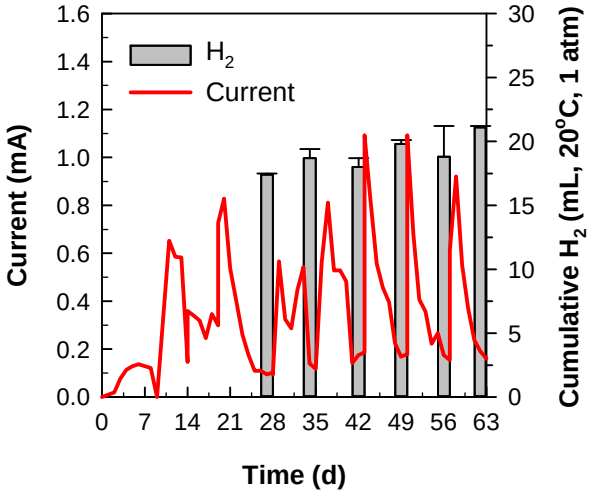


Figure S2. Current and cumulative H_2 production during the MEC startup.

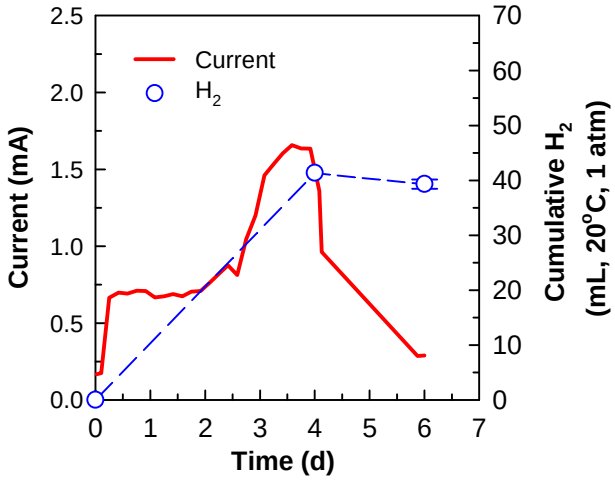


Figure S3. Current and H_2 production at 200 mg/L initial substrate concentration after the observed inhibition during the 1,200 mg/L feeding cycle.

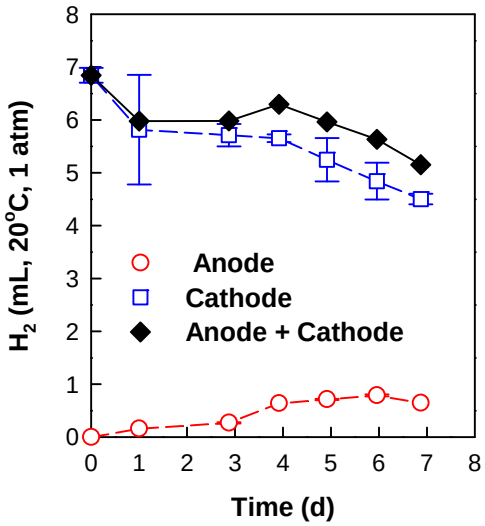


Figure S4. H_2 diffusion from the cathode to the anode headspace in a biomass-free MEC with an open circuit.

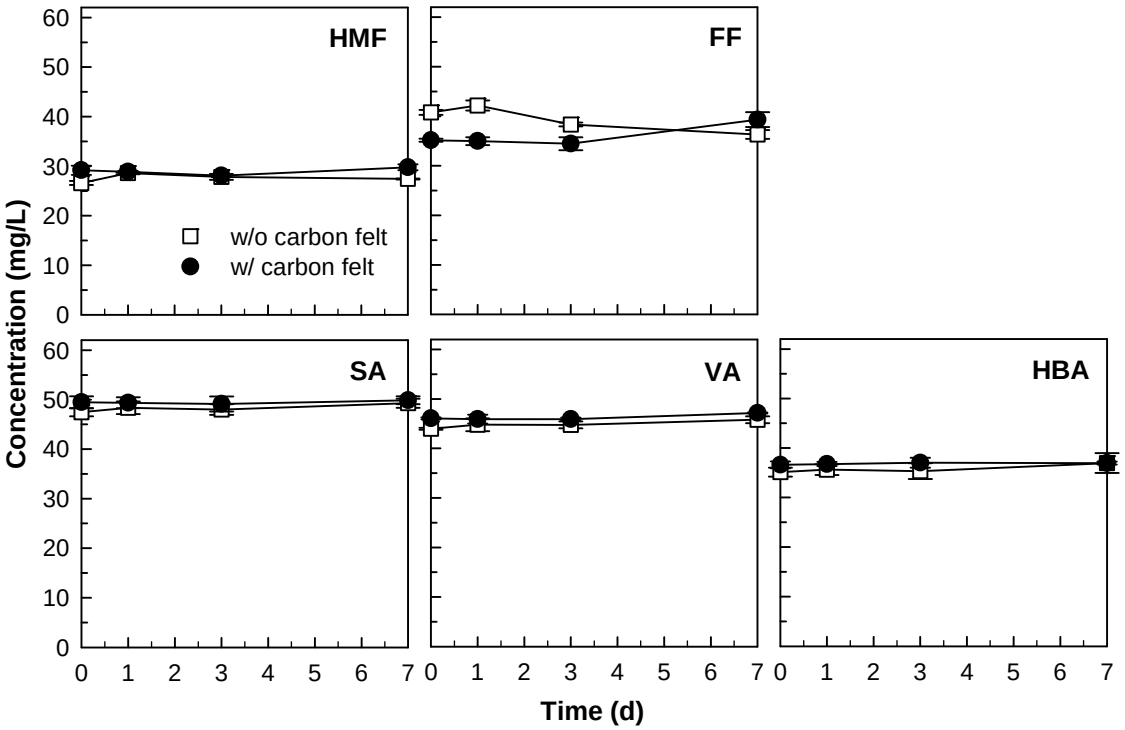


Figure S5. Stability of the five compounds in the presence and absence of carbon felt under N_2 atmosphere.

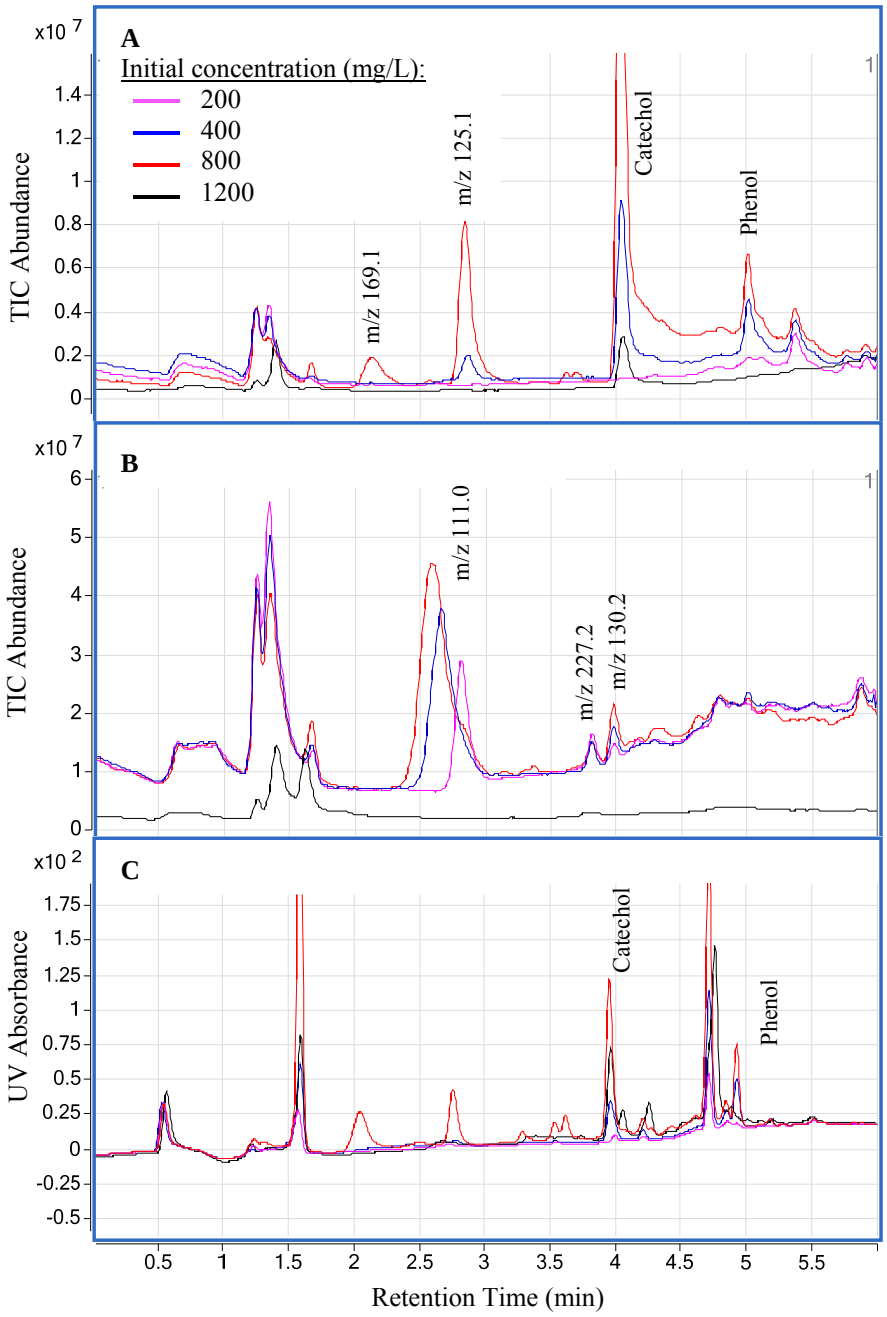


Figure S6. LC/MS chromatograms at the end of four batch assays revealing un-identified metabolites. (A) MS scan in negative mode; (B) MS scan in positive mode; (C) UV absorbance at 254 nm.

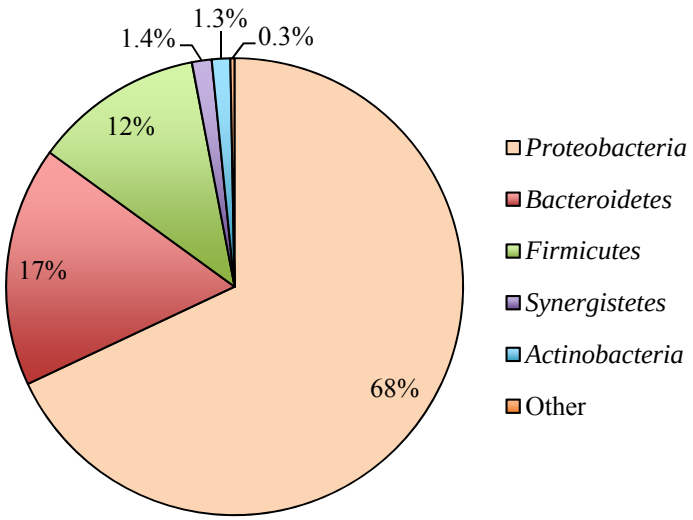


Figure S7. Composition of the MEC anode microbial community at phylum level.

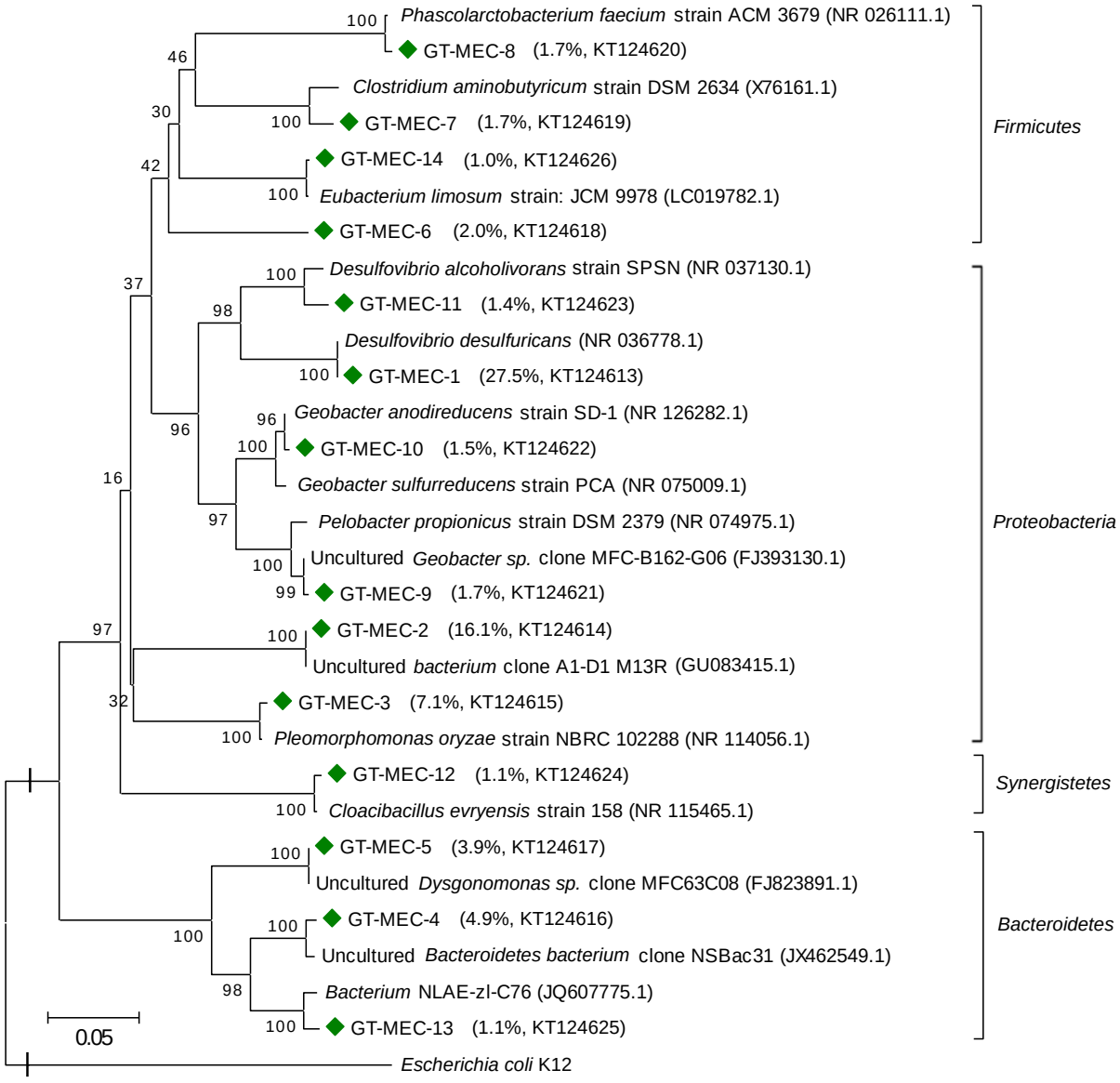


Figure S8. Phylogenetic tree of the dominant bacteria identified in the MEC anode. Fraction of bacterial population and GenBank accession numbers shown in parentheses. *Escherichia coli* K12 was used as the outgroup.

REFERENCES

(1) Hansch, C.; Leo, A.; Hoekman, D. H., *Exploring QSAR.: Hydrophobic, electronic, and steric constants*. American Chemical Society: Washington DC, 1995; Vol. 2.

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(4) Yalkowsky, S. H.; Dannenfelser, R. M., Aquasol database of aqueous solubility. *College of Pharmacy, University of Arizona, Tucson, AZ* **1992**.

(5) ChemAxon *Calculator plugins*, ChemAxon (http://www.chemaxon.com).