

SUPPORTING INFORMATION

One-pot production of oxygenated monomers and modified lignin from biomass based on plasma electrolysis

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Table S1. Proximate, ultimate, and compositional analyses of red oak

<i>Ultimate Analysis [wt%]</i>	
Carbon	46.13
Hydrogen	6.38
Oxygen	47.34
Nitrogen	0.15
<i>Proximate Analysis [wt%]</i>	
Moisture	7.74
Volatiles	80.39
Fixed carbon	11.46
Ash	0.64
<i>Compositional Analysis [wt%]</i>	
Cellulose	41
Hemicellulose	16
Lignin	23
Other	20

Table S2. Molecular weight and polydispersity of MWL and PELs produced using different reaction conditions. $f = 6$ kHz.

	MWL	PEL 300 mg 10.5 mM 6 kV 20 min	PEL 300 mg 10.5 mM 7 kV 20 min	PEL 100 mg 10.5 mM 7 kV 20 min	PEL 300 mg 10.5 mM 7 kV 10 min	PEL 300 mg 7 mM 7 kV 20 min	PEL 300 mg 14 mM 7 kV 20 min
Number Average M_n	1566	955	955	973	996	1121	876
Weight Average M_w	3853	1919	2013	2194	2282	3098	2023
Polydispersity PD	2.46	2.01	2.11	2.25	2.29	2.76	2.31

Table S3. The list of phenolic monomers and their yields produced from pyrolysis of MWL, PELs, and the thermally-based lignin. Reaction conditions for PELs: 10.5 mM acid, V = 7 kV and f = 6 kHz. The reaction condition for the thermally-based lignin: 10.5 mM acid, 165 °C, and 30 min.

		Monomer Yield [wt%]				Thermally-based lignin
		MWL	PEL 10 min	PEL 15 min	PEL 20 min	
1	Phenol	0.06±0.00	0.33±0.05	0.52±0.08	0.52±0.07	0.11±0.01
2	Guaiacol	0.35±0.01	1.05±0.19	1.19±0.09	1.18±0.11	0.60±0.00
3	o-Cresol	0.07±0.00	0.13±0.10	0.20±0.07	0.28±0.04	0.05±0.03
4	p-cresol	0.08±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
5	p-Methyl Guaiacol	0.05±0.00	0.43±0.13	0.58±0.05	0.64±0.06	0.10±0.03
6	o-Methyl Guaiacol	0.01±0.00	1.15±0.18	1.16±0.07	1.38±0.04	0.57±0.02
7	phenol, 2,5-dimethyl-	0.07±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
8	3,4-dimethyl-2-methoxy Phenol	0.84±0.03	0.21±0.09	0.20±0.07	0.29±0.07	0.03±0.01
9	4-Ethyl Phenol	0.00±0.00	0.69±0.36	1.13±0.10	1.32±0.09	0.17±0.01
10	4-Ethyl Guaiacol	0.20±0.00	1.08±0.29	1.44±0.17	1.88±0.20	0.46±0.03
11	4-Vinyl Phenol	0.52±0.00	1.30±0.58	1.98±0.13	2.09±0.43	0.35±0.02
12	4-Vinyl Guaiacol	0.14±0.01	2.14±0.55	2.20±0.13	2.35±0.03	0.90±0.03
13	Syringol	0.63±0.03	1.91±0.45	1.98±0.12	1.86±0.10	0.97±0.02
14	2-methoxy-4-propyl-phenol	0.10±0.01	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
15	4-Hydroxy-3-Methoxybenzoic Acid	0.00±0.00	1.86±0.34	2.12±0.04	2.15±0.11	1.08±0.04
16	1,2,4-Trimethoxytoluene	1.43±0.09	0.26±0.09	0.42±0.08	0.33±0.12	0.13±0.01
17	Trans-isoeugenol	0.34±0.02	0.19±0.03	0.20±0.03	0.22±0.01	0.00±0.00
18	Vanillin	0.21±0.01	0.68±0.32	1.21±0.27	0.84±0.10	0.22±0.01
19	1,2,3-trimethoxy-5-methyl-benzene	0.39±0.04	0.03±0.01	0.02±0.00	0.02±0.01	0.09±0.02
20	Apocynin	0.21±0.01	0.21±0.03	0.21±0.01	0.24±0.01	0.00±0.00
21	3',5'-Dimethoxyacetophenone	0.65±0.01	0.54±0.10	0.70±0.10	0.51±0.05	0.25±0.02
22	2,6-Dimethoxy-4-allylphenol	0.90±0.06	0.49±0.13	0.64±0.08	0.47±0.02	0.20±0.01
23	4-hydroxy-3,5-dimethoxy-benzaldehyde	0.38±0.04	0.27±0.03	0.28±0.02	0.28±0.01	0.11±0.01
24	2,6-Dimethoxy-4-allylphenol	0.00±0.00	0.40±0.10	0.70±0.10	0.61±0.07	0.20±0.01
25	3,5-dimethoxy-4-hydroxyphenylacetic acid	0.13±0.04	0.30±0.01	0.30±0.04	0.27±0.04	0.14±0.02
26	3,4,5-trimethoxyphenylacetic acid	0.08±0.01	0.30±0.10	0.26±0.03	0.23±0.01	0.12±0.02
27	1-(4-hydroxy-3-methoxyphenyl)- 2-propanone	0.07±0.02	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
28	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone	0.30±0.04	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
29	2-oxo-2-phenylethyl benzoate	0.00±0.00	0.32±0.04	0.34±0.04	0.24±0.01	0.09±0.02
30	Methyl 3-(4-hydroxy-3,5-dimethoxyphenyl)-3-oxopropanoate	0.00±0.00	0.26±0.07	0.37±0.00	0.30±0.01	0.00±0.00
31	2-oxo-2-phenylethyl acetate	0.00±0.00	0.14±0.03	0.21±0.03	0.15±0.01	0.05±0.01
32	1-(2,4,6-trihydroxyphenyl) desaspidinol/2-pentanone	0.10±0.02	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
33	(E)-3-(4-hydroxy-3,5-dimethoxyphenyl) acrylaldehyde	0.00±0.00	0.12±0.03	0.12±0.02	0.11±0.01	0.00±0.00
34	3,5-dimethoxy-4-hydroxycinnamaldehyde	0.30±0.04	0.11±0.06	0.16±0.01	0.14±0.01	0.00±0.00
	Sum	8.61	16.92	20.86	20.91	6.96

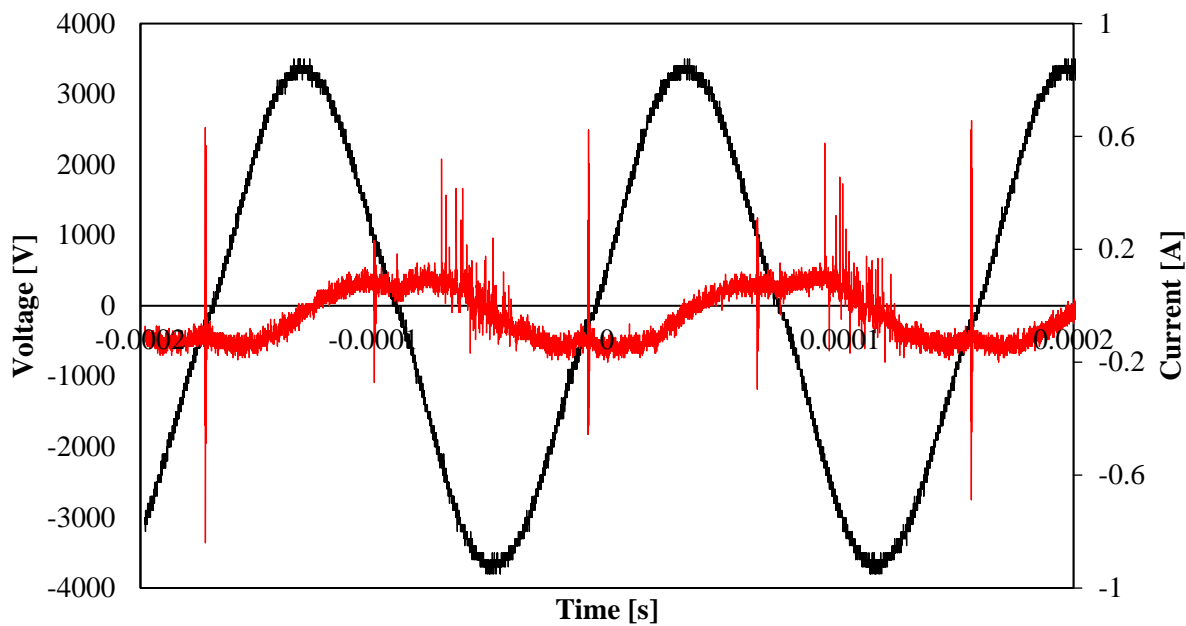


Figure S1. Current and voltage waveform. The current spikes are due to dielectric breakdown and microdischarge.

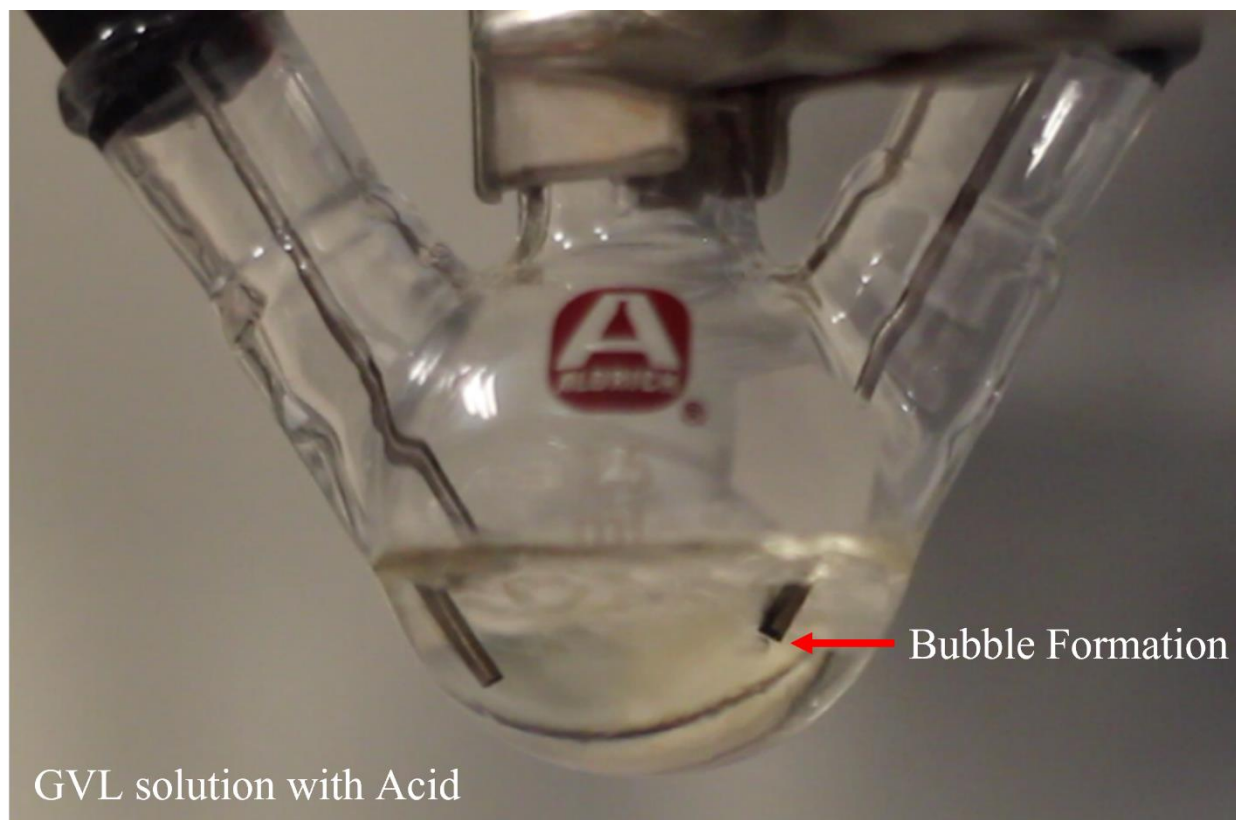


Figure S2. Bubble formation inside the solvent near the electrode prior to the plasma generation.

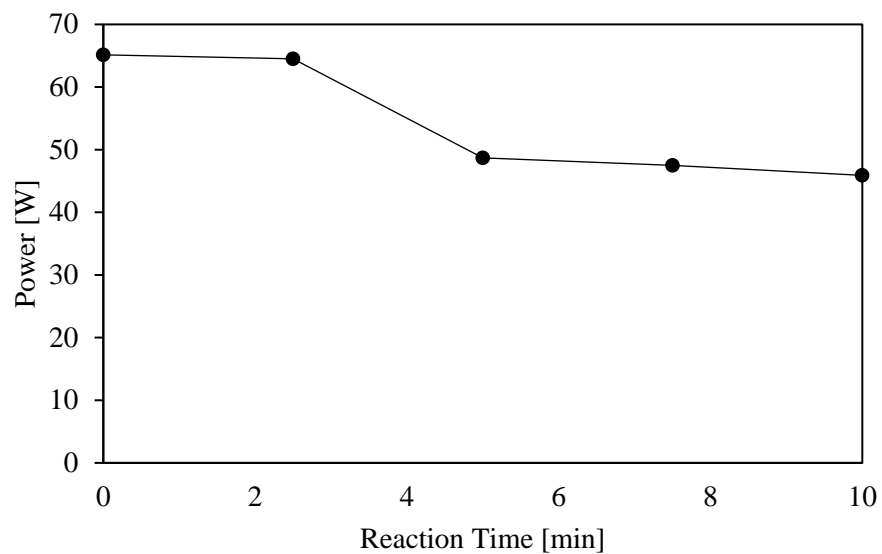


Figure S3. The measured power input during plasma electrolysis of red oak. Reaction conditions: biomass loading: 4 wt%; $V = 7$ kV; $f = 6$ kHz; 10.5 mM acid.

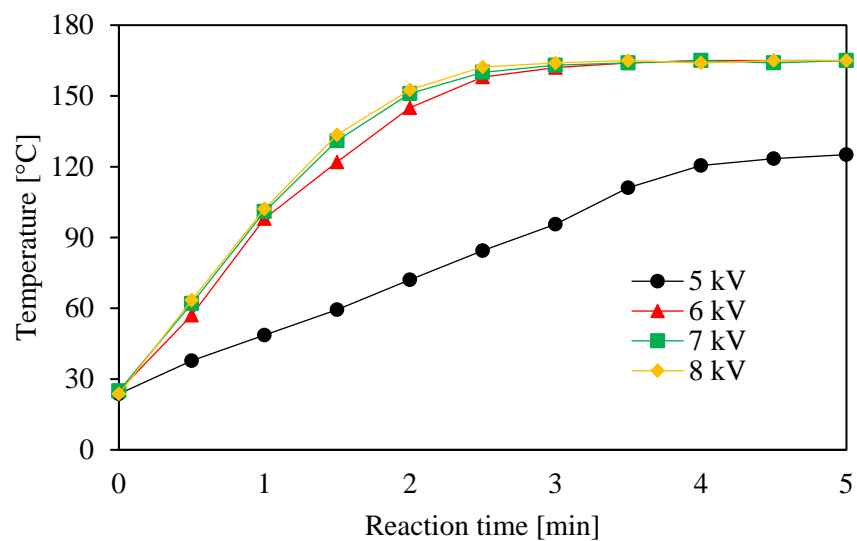


Figure S4. The effect of electric voltage on the temperature profiles of the solvent. Reaction conditions: $f = 6$ kHz; 10.5 mM acid.

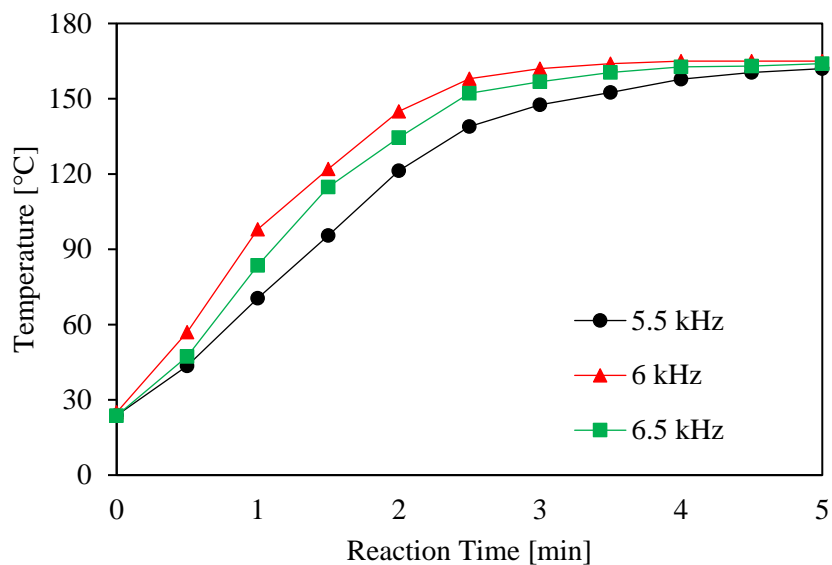


Figure S5. The effect of electric frequency on the temperature profiles of the solvent. Biomass loading: 4 wt%. Other reaction conditions: $V = 6$ kV; acid concentration = 10.5 mM.

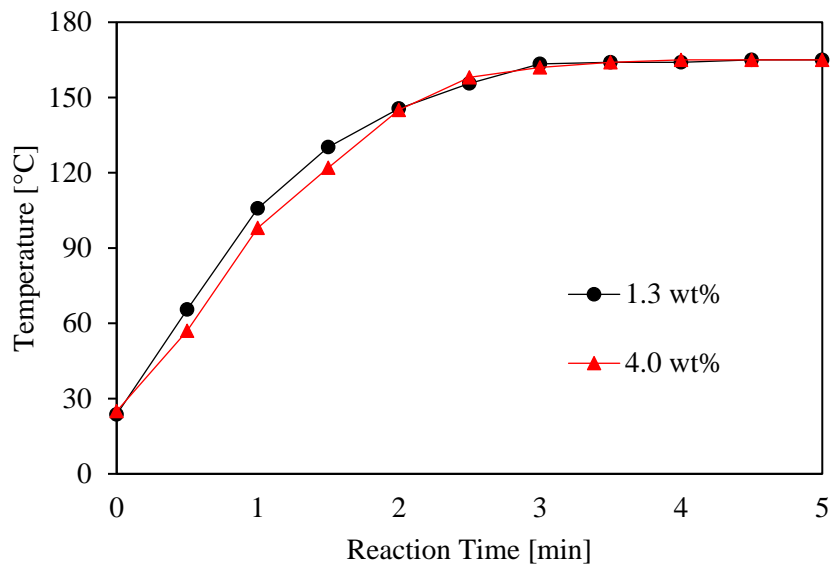


Figure S6. The effect of biomass loading on the temperature profiles of the solvent. Other reaction conditions: $V = 6$ kV; $f = 6$ kHz; acid concentration = 7.0 mM.

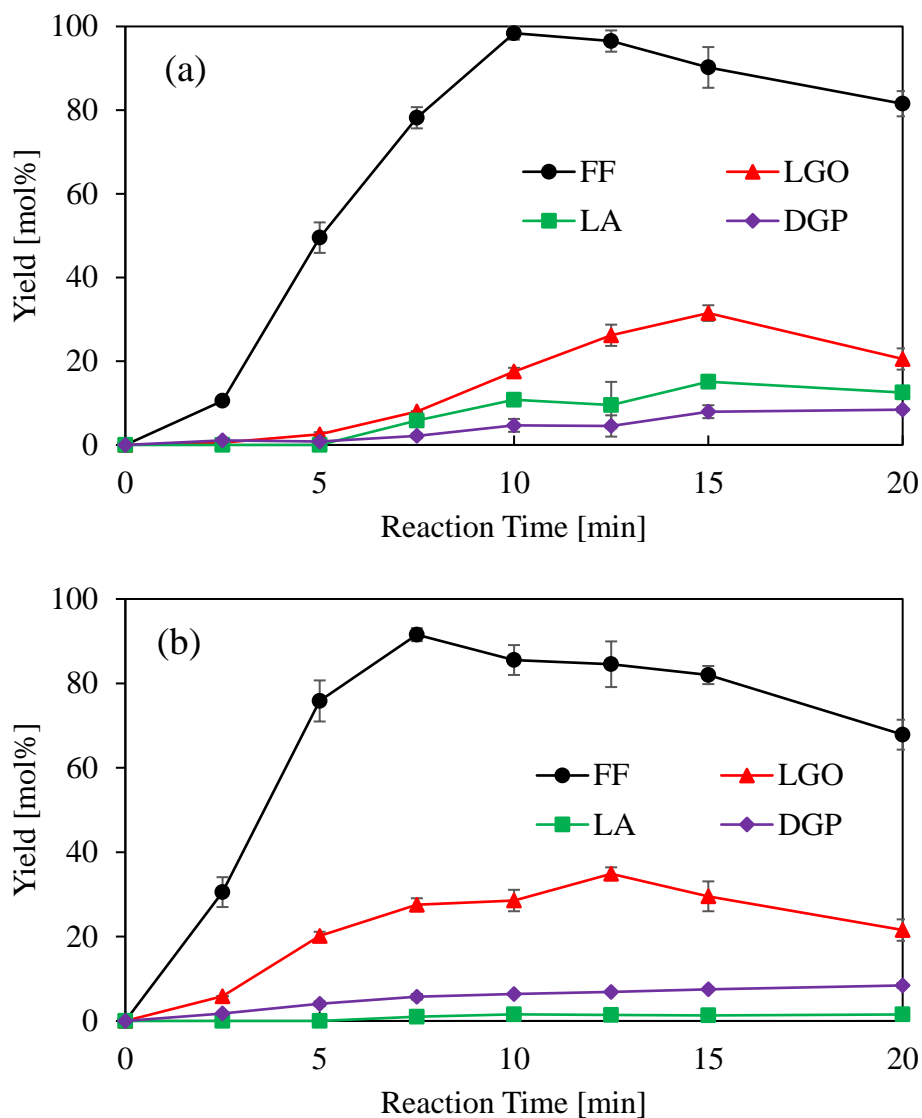


Figure S7. Monomer production during plasma electrolysis with 1 wt.% water in solvent. (a) $V = 6$ kV; (b) $V = 7$ kV. Biomass loading: 4 wt%. Other reaction conditions: 10.5 mM acid and $f = 6$ kHz.

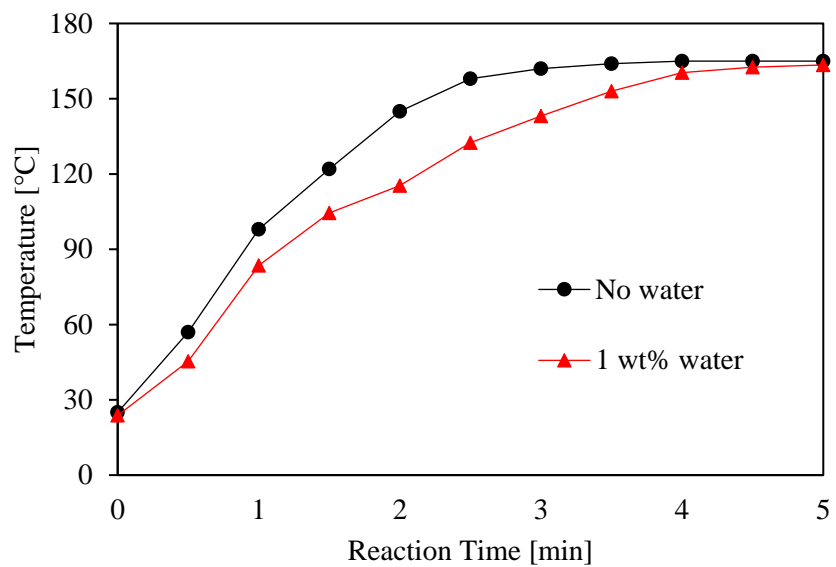


Figure S8. The effect of water addition on the temperature profiles of the solvent. Biomass loading: 4 wt%. Other reaction conditions: $V = 6$ kV; $f = 6$ kHz; acid concentration = 10.5 mM.

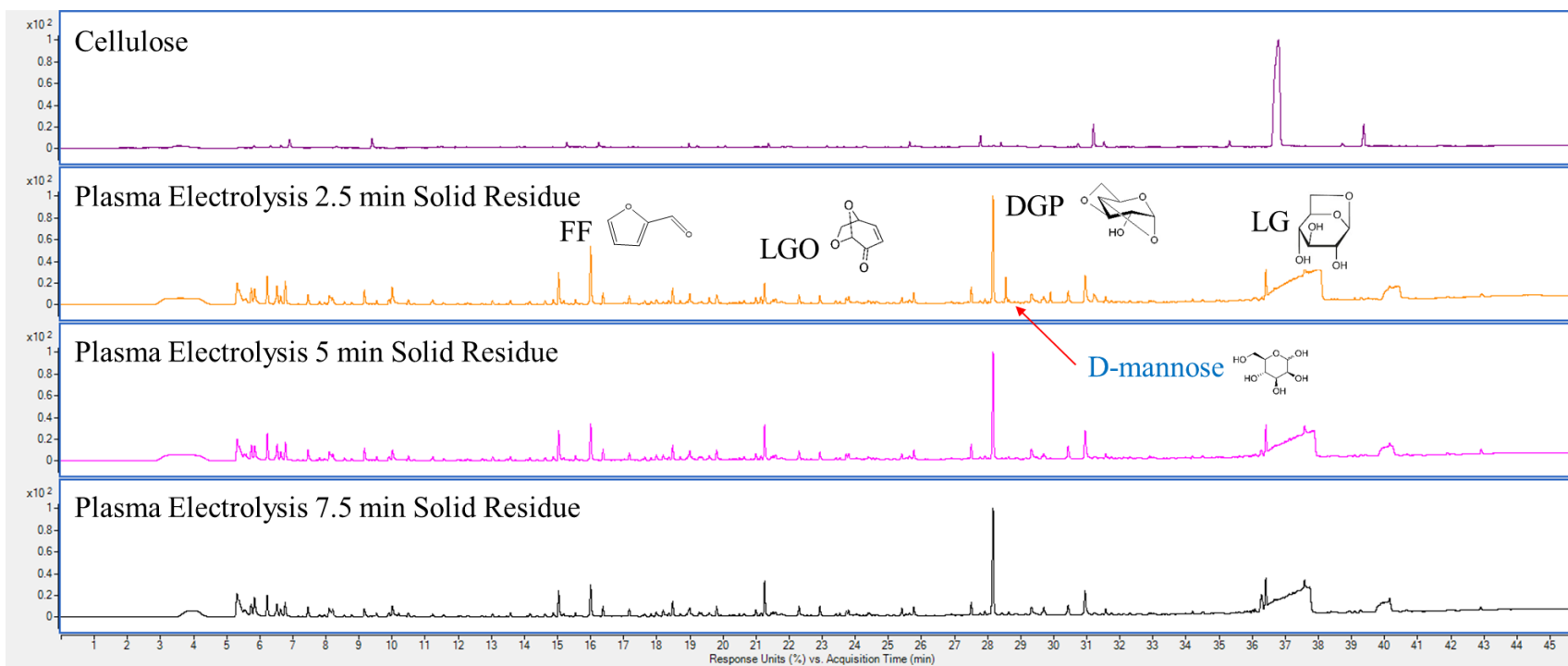


Figure S9. Pyrolysis GC/MS chromatograms of cellulose or the solid residues recovered during plasma electrolysis of red oak with different conversion times. Plasma electrolysis condition: 10.5 mM acid, $V = 7$ kV and $f = 6$ kHz.

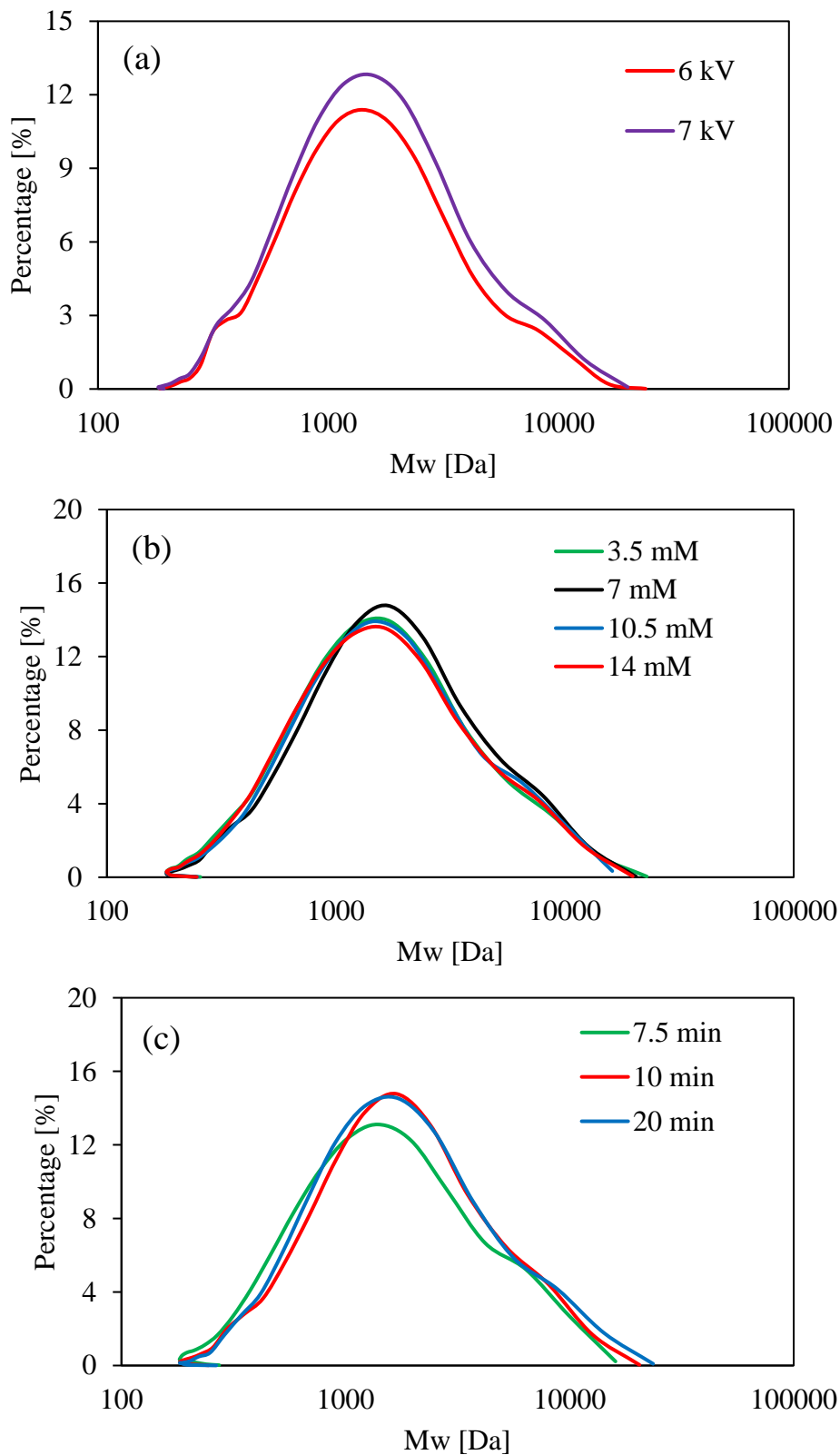


Figure S10. Molecular weight distribution of PELs with different plasma electrolysis conditions. (a) different voltage; (b) different acid concentration; (c) different treatment time. Other reaction conditions other than changing parameter: 10.5 mM acid, $V = 7$ kV, and $f = 6$ kHz.

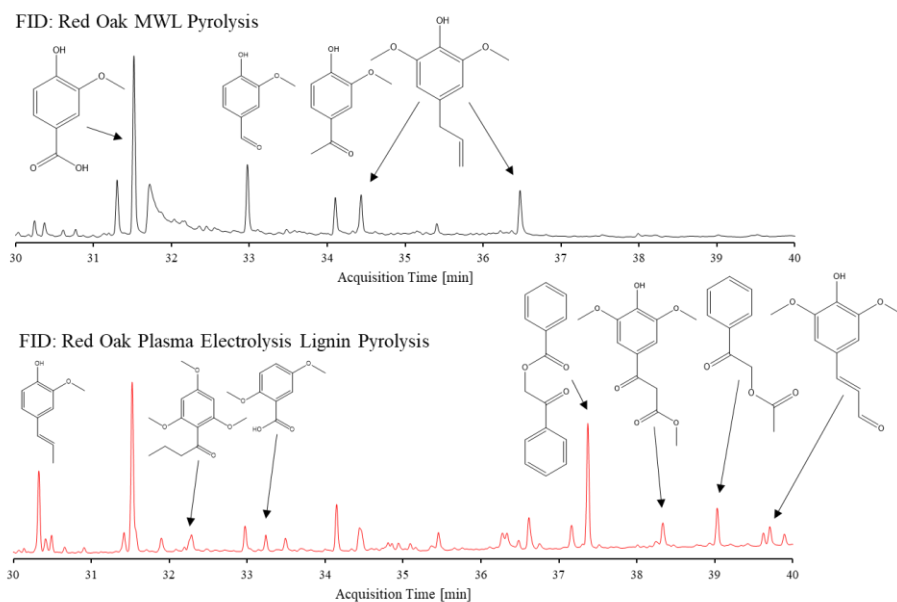


Figure S11. Pyrolysis-GC/MS chromatograms of MWL and PEL. Shown retention time between 30 and 40 mins. Plasma electrolysis condition for obtaining the PEL: 10.5 mM acid, $V = 7$ kV, $f = 6$ kHz, and 20 min.