Impact of bentonite clay on in situ pyrolysis vs. hydrothermal carbonization of avocado pit biomass

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Supplemental Information (*for online publication only*)

Contents

Table S1: Complete compound species breakdown for bio-oils as detected by GC-MS. Reporting mg compound / kg biomass informs how much biomass you require to produce the various compounds detected in the bio-oil. Percent of each compound type out of detectable compounds. Total concentrations of detectable compounds ranged 30,000 -50,000 mg compound / kg biomass.

Group	Pyrolysis @ 600°C		HTC @ 250°C	
	Avocado	Avocado + Bentonite Clay	Avocado	Avocado + Bentonite Clay
Compound	mg compound / kg bio-oil			
Alcohol				
Cyclopropyl carbinol	19366.32 ± 9916.49	3819.7 ± 61.1		
% Total Conc.	*10.89%*	*9.71%*		
Aldehyde				
Pentanal		1518.18 ± 698.2		
% Total Conc.		*3.86%*		
Alkane				
Dodecane		181.18 ± 113.96		
Undecane		44.47 ± 62.89		
Octadecane, 1-chloro-	2245.31 ± 3175.35			
% Total Conc.	*1.26%*	*0.57%*		
Alkene				
1-Tetradecene		216.67 ± 40.5		
% Total Conc.		*0.55%*		
Ester				
1,2-Benzenediol, 4-methyl-	325.27 ± 81.12	168.2 ± 11.59		
1,2-Ethanediol, dipropanoate	400.18 ± 79.37			
% Total Conc.	*0.41%*	*0.43%*		
Furan				
2(3H)-Furanone, 5-methyl-	1729.05 ± 735.79	840.91 ± 33.65		
2(5H)-Furanone		1004.71 ± 1420.88		
2-Furanmethanol, acetate	4064.4 ± 5747.94			
2-Furanmethanol, tetrahydro-	5719.99 ± 203.13			
5-Methylfurfural	1439.83 ± 998.5	456.43 ± 206.42	598.35 ± 329.08	597.7 ± 328.73
Benzofuran		748.74 ± 912.36		
Ethanone, 1-(2-furanyl)-	12835.71 ± 5275.7	950.66 ± 277.77	119.67 ± 41.88	206.74 ± 72.44
% Total Conc.	*14.50%*	*10.17%*	*100.00%*	*73.95%*

Ketone								
1,2-Cyclopentanedione	6714.16	±	4072.06	907.47	±	420.91		
1H-Inden-1-one, 2,3-dihydro-	9598.5	±	3297.08	1680.86	±	269.39		
2-Butanone	979.76	±	1385.59					
2-Butanone, 1-(acetyloxy)-	2272.02	±	3213.11	1036.32	±	1465.58		
2-Cyclopenten-1-one	5046.57	±	333.88	698.65	±	988.04		
Ketone (cont.)								
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	13950	±	5135.66	1764.52	±	342.81		
2-Cyclopenten-1-one, 2-methyl-	3744.04	±	1172.93	1000.65	±	608.2		283.43 ± 130.41
2-Hydroxy-gamma-butyrolactone	3344.8	±	1826.6					
% Total Conc.	*25.67%*			*18.01%*				*26.05%*
Phenol								
Naphthalene	5704.62	±	804.14	1687.48	±	2386.46		
Naphthalene, 2-methyl-	8311.26	±	1171.96	2373.09	±	3356.06		
o-Xylene	485.13	±	686.08	284.66	±	110.34		
Phenol	10329.89	±	1053.39	4460.03	±	545.94		
Phenol, 2,3,6-trimethyl-				2831.89	±	229.28		
Phenol, 2,3-dimethyl-				196.75	±	170.58		
Phenol, 2,5-dimethyl-				152.32	±	100.16		
Phenol, 2,6-dimethoxy-	8524.59	±	682.11					
Phenol, 2-methyl-	7170.58	±	953.9	1997.31	±	1678.1		
Phenol, 3,4-dimethyl-	124.58	±	176.19	65.91	±	93.21		
Phenol, 3,5-dimethyl-	400.52	±	43.06	107.2	±	151.6		
Phenol, 3-ethyl-	128.86	±	182.2	53.25	±	75.3		
Phenol, 3-methyl-	10384.53	±	4761.75	3394.65	±	4800.75		
Styrene				152.46	±	215.61		
2-Propenal, 3-phenyl-				1514.91	±	635.97		
Benzene, 1-butynyl-	2783.37	±	3936.28					
Benzene, 1-propynyl-	1419.11	±	2006.92	1172.07	±	26.96		
Catechol	11149.22	±	1945.76	561.58	±	92.91		
Ethylbenzene	743.96	±	1052.12	410.81	±	110.78		
Fluorene				180.38	±	255.1		
% Total Conc.			*38.05%*			*54.88%*		
Oxygenated Aromatics								
Maltol	16367.72	±	1700.91	589.19	±	833.24		
% Total Conc.			*9.21%*			*1.50%*		
Other								
Indole				127.66	±	180.53		

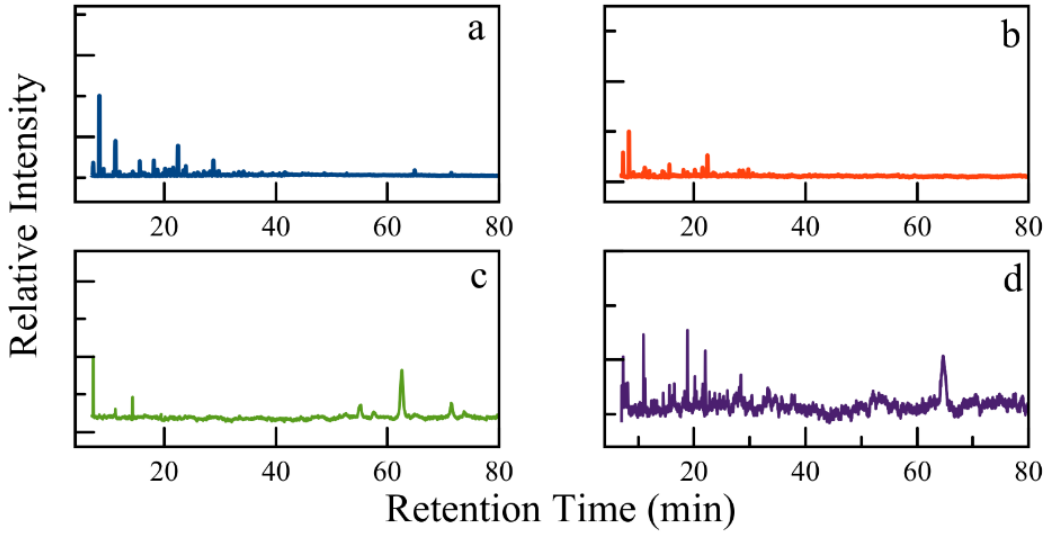

Figure S1: Gas chromatograms of biofuel analysis from pyrolysis of avocado pits (a) and avocado pits + Fuller's Earth (b) and hydrothermal carbonization at 250 °C of avocado pits (c) and avocado pits + Fuller's Earth (d). Chromatograms are normalized to relative intensity.

Table S2: HP-LC analysis of aqueous product from hydrothermal carbonization of avocado and avocado + bentonite clay. The detected compound concentrations are reported in ppm of the analyzed HTC water.

	Avocado	**Avocado + Bentonite Clay**
Compound	**Concentration (PPM)**	
Furan		
2 (5H) Furanone	1.32E+04	-
% Total Conc.	*100.00%*	
Carboxylic Acid		
Formic Acid	-	5.84E+03
Propionic Acid	-	1.55E+05
% Total Conc.		*100.00%*

Table S3: Water content of pyrolysis bio-oil determined in triplicate and reported as average %wt ± one standard deviation.

	Water Content (wt%)		
Pyrolysis Bio-Oil			
Avocado	2.42	±	0.39
Avocado + Clay	1.18	±	0.26
HTC Bio-oil			
Avocado	0.58	±	0.10
Avocado + Clay	2.24	±	0.04

Table S4: Pyrolysis and HTC yields and O/C ratios. Pyrolysis ran in triplicate and reported as an average ± one standard deviation, with the data ranges included below. HTC ran in duplicate and reported as an average of two values and data ranges below. O/C ratios determined for GC-MS detected compounds eluted between 6 – 200 minutes.

	Yield (Weight %)			**Bio-oil O/C Ratio**
	Solid	**Liquid**	**Gas**	
Pyrolysis @ 600°C for 0.5 hour				
Avocado	32.30 ± 4.49	36.86 ± 4.95	33.89 ± 3.30	0.62 ± 0.08
Data Range	*26.66 – 35.81*	*32.52 – 42.45*	*31.09 – 37.53*	*0.53 – 0.67*
Avocado + Clay	34.85 ± 1.66	40.45 ± 0.59	26.70 ± 2.25	0.45 ± 0.18
Data Range	*32.13 – 37.57*	*31.64 – 45.26*	*17.17 – 36.23*	*0.24 – 0.56*
HTC @ 250°C for 1 hour				
Avocado	26.33	54.29	19.38	0.73
Data Range	*15.89 – 36.78*	*49.70 – 58.88*	*13.52 – 25.23*	*0.69 – 0.77*
Avocado + Clay	35.98	41.40	22.62	0.35
Data Range	*33.40 – 38.56*	*37.33 – 45.48*	*15.96 – 29.27*	*0.23 – 0.66*

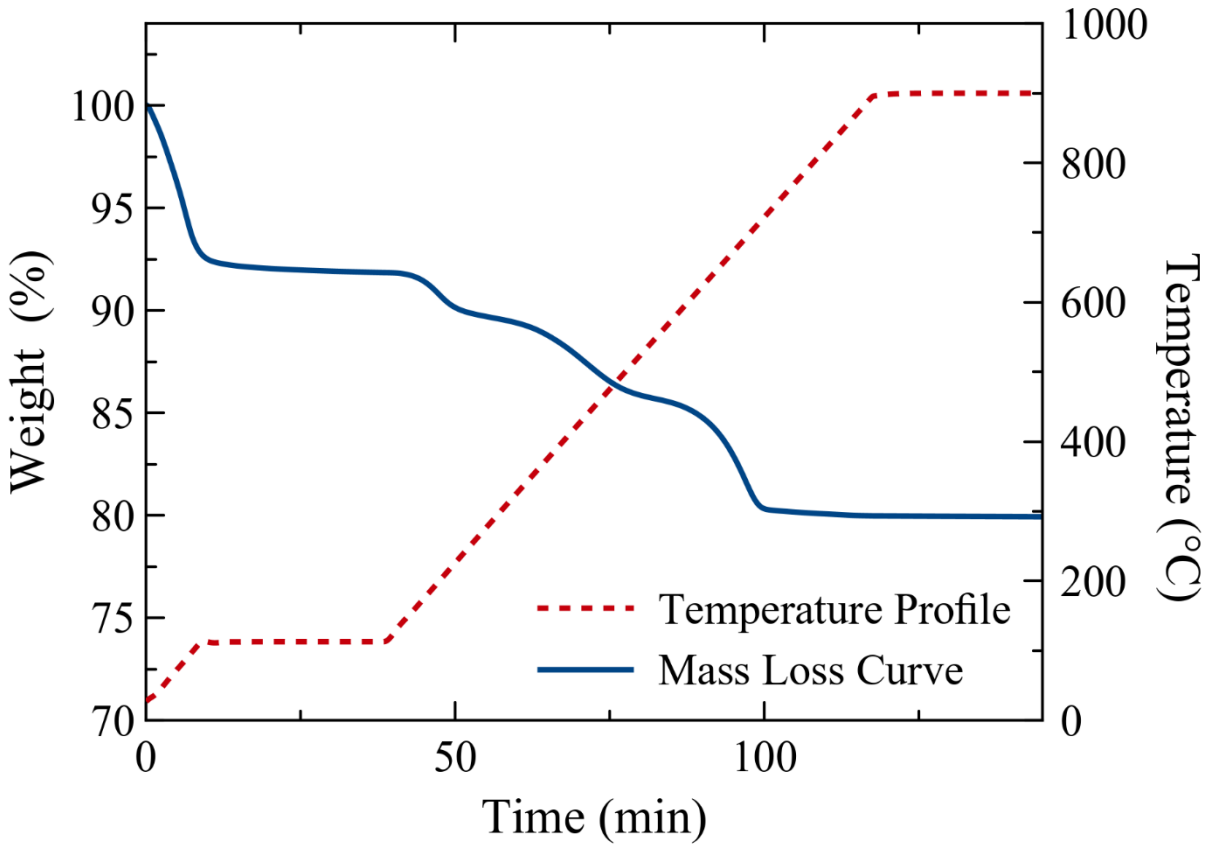

Figure S2: Thermal stability of bentonite clay in an inert atmosphere mimicking pyrolysis experiments.

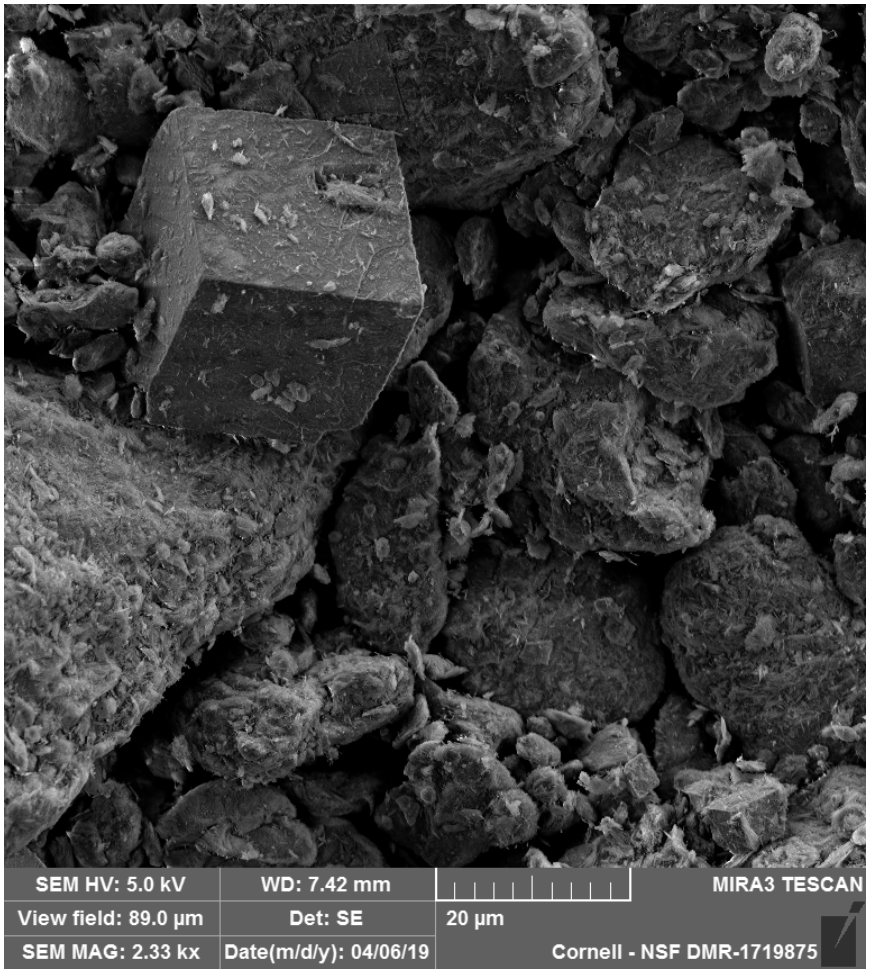

Figure S3: SEM image of bentonite clay. Scale bar indicates 20 µm.