Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information for “Solvent Processing for Improved Separation of Hydrothermal Liquefaction Products.”

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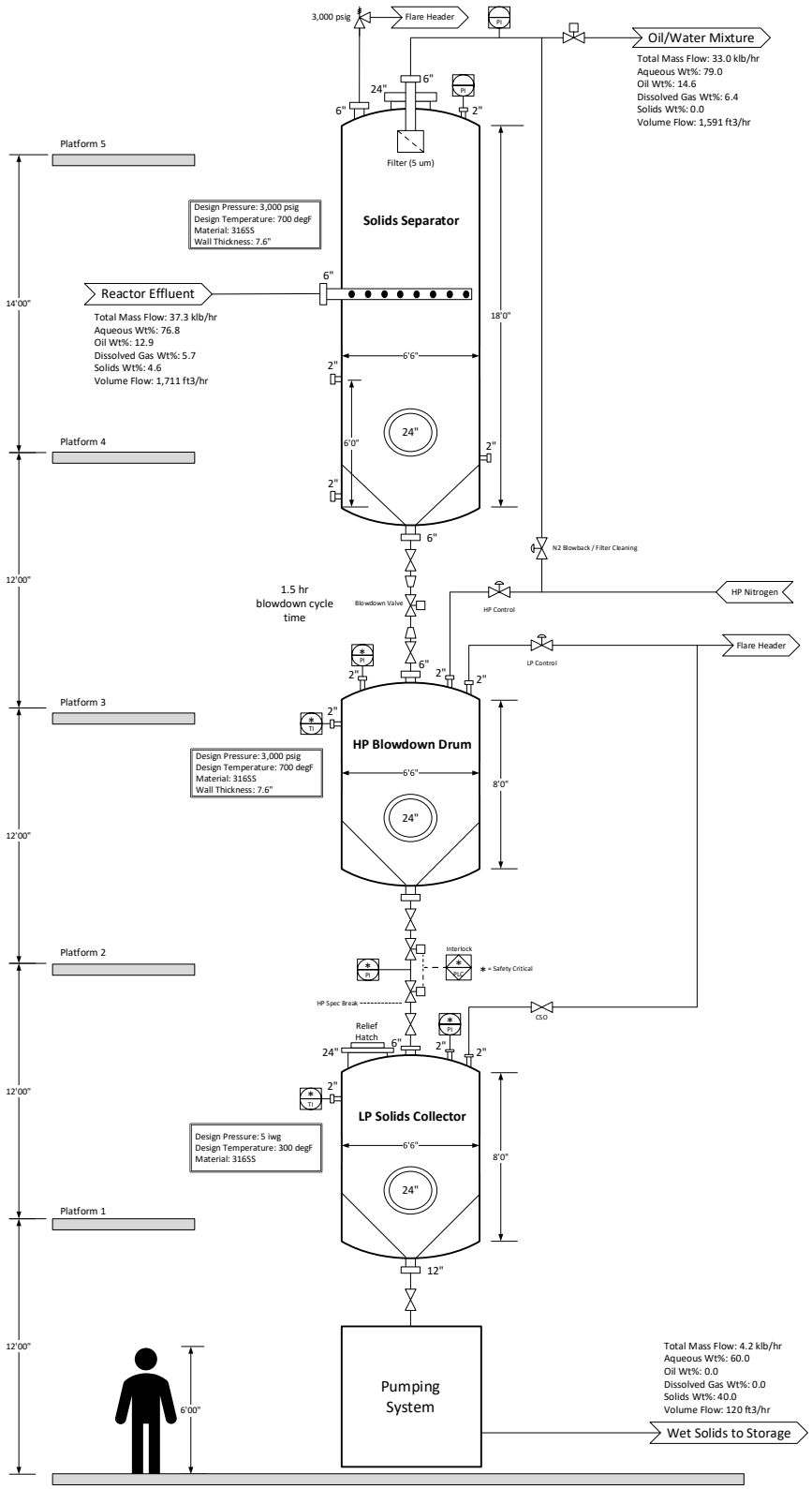

Figure S1. Conceptual Solids Blowdown at HTL temperature and pressure (110 DTPD PNNL SOT).

Figure S2. Image of the jacketed glass funnel used in this work.

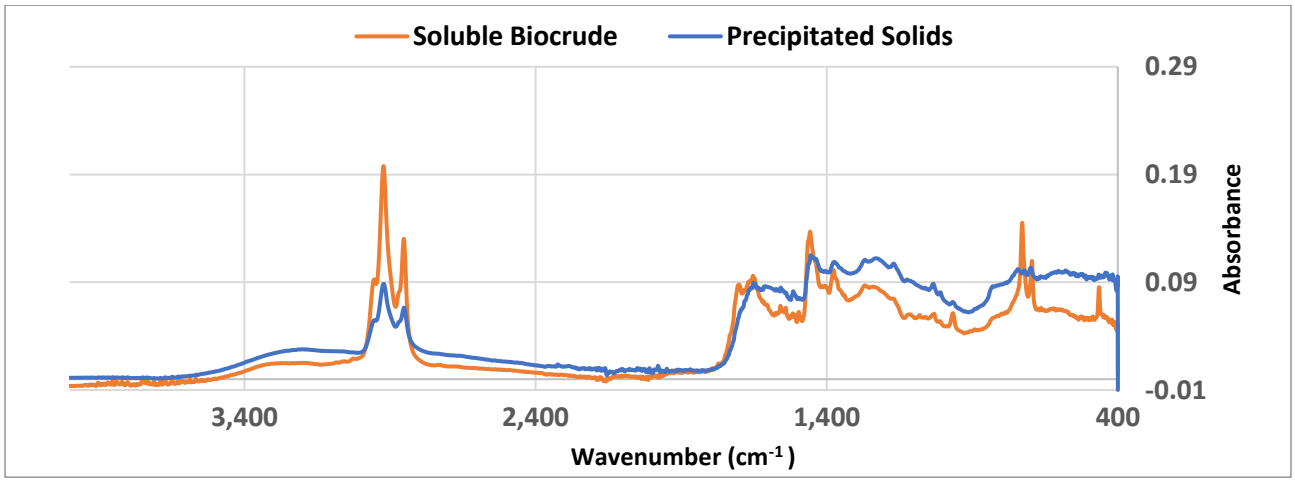

Figure S3. Infrared Spectra of biocrude soluble in Toluene/Heptane mixtures at room temperature and the precipitated solids.

Figure S4. (Left) Undissolved residual biocrude using n-decane. (Right) Undissolved residual biocrude using toluene.

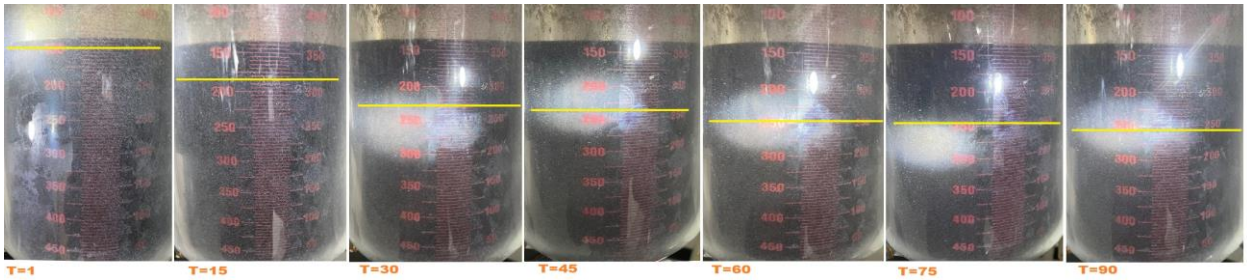

Figure S5. Settling images for stage 1 at 40°C, 0.7 toluene: emulsion mass ratio (13F St1).

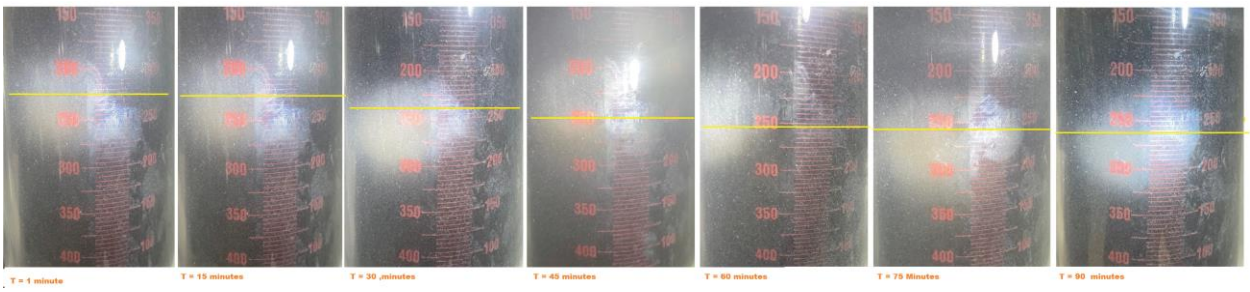

Figure S6. Settling images for stage 2 at 40°C, 0.7 toluene: emulsion mass ratio (13F St2).

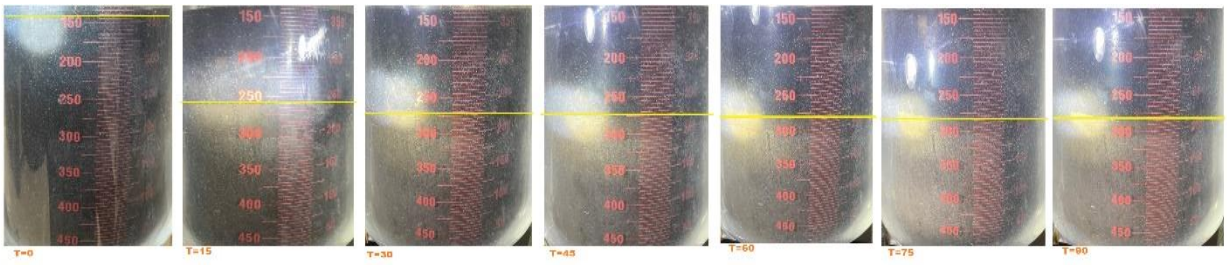

Figure S7. Settling images for stage 1 at 80°C, 0.7 toluene: emulsion mass ratio (13G St1).

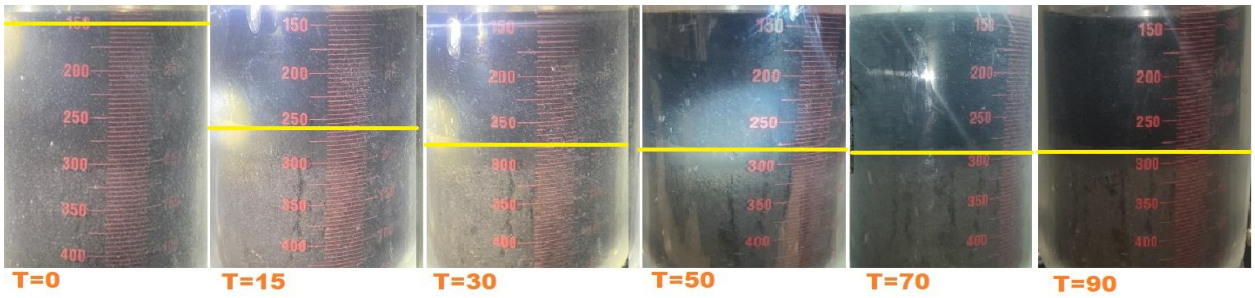

Figure S8. Settling images for stage 2 at 80°C, 0.7 toluene: emulsion mass ratio (13G St2).

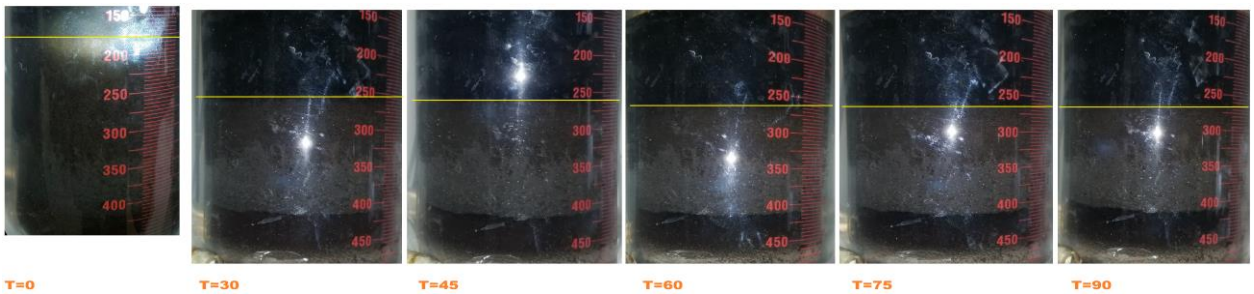

Figure S9. Settling images for stage 1 at 60°C, 0.7 toluene: emulsion mass ratio (13H St1).

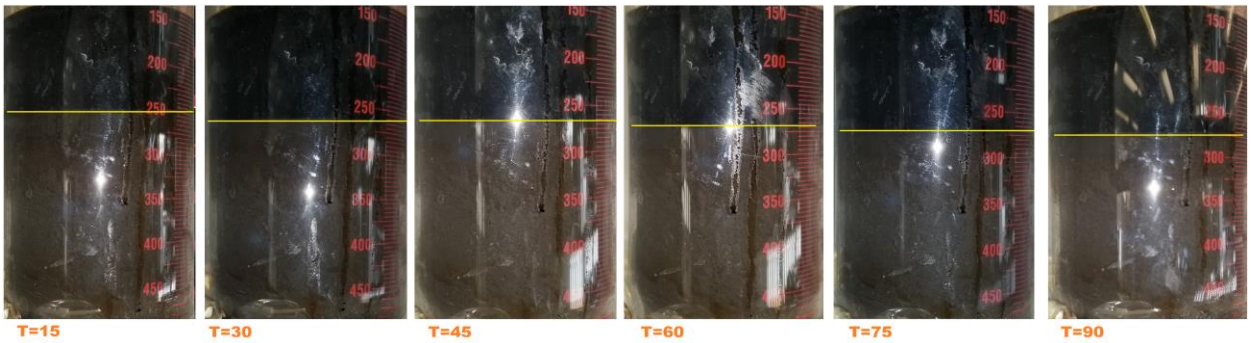

Figure S10. Settling images for stage 2 at 60°C, 0.7 toluene: emulsion mass ratio (13H St2).

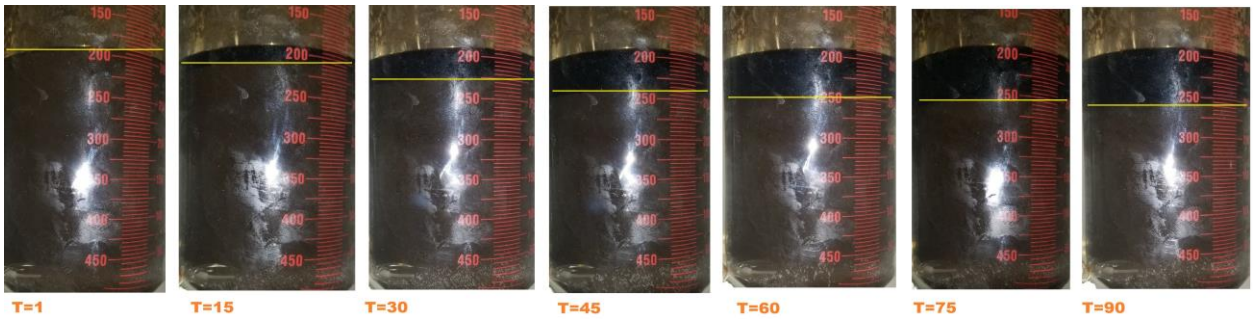

Figure S11. Settling images for stage 1 at 40°C, 0.5 toluene: emulsion mass ratio (13I St1).

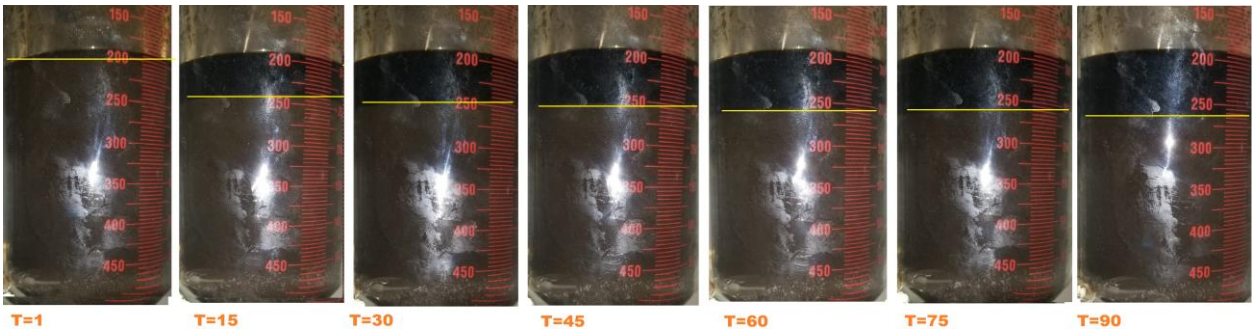

Figure S12. Settling images for stage 1 at 40C, 0.5 toluene: emulsion mass ratio (13I St2).

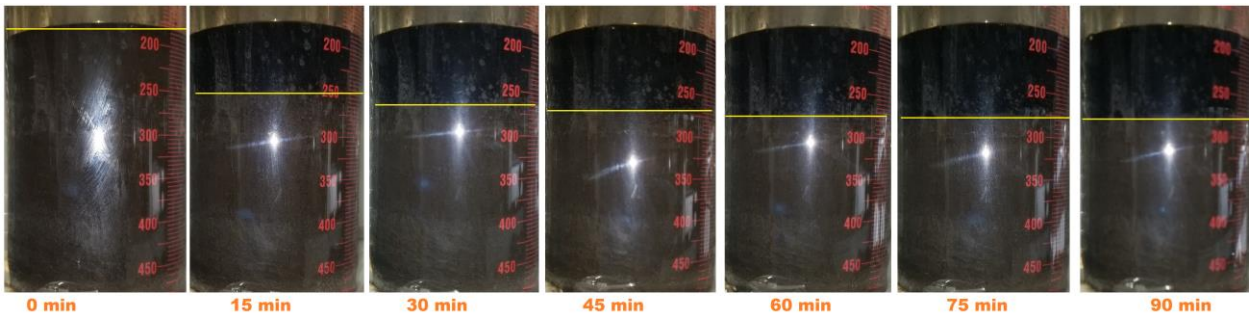

Figure S13. Settling images for stage 1 at 80°C, 0.5 toluene: emulsion mass ratio (13J St1)

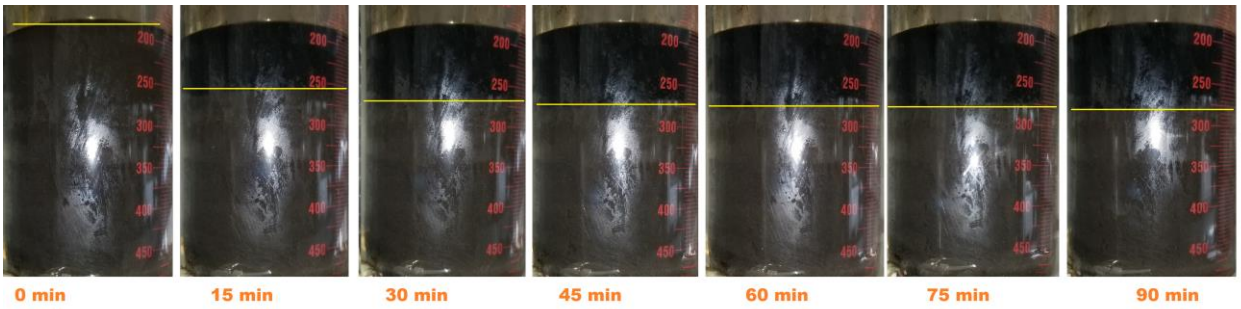

Figure S14. Settling images for stage 2 at 80°C, 0.5 toluene: emulsion mass ratio (13J st2).

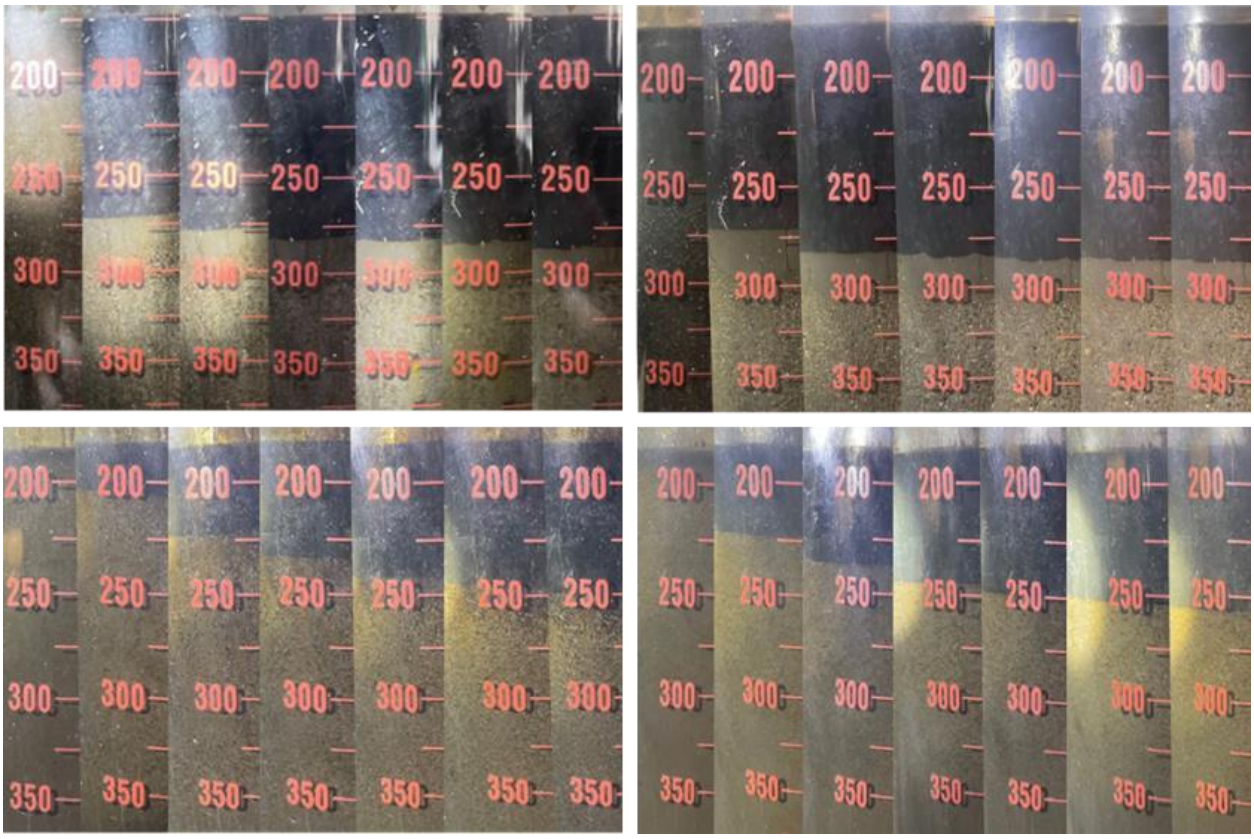

Figure S15. Settling images at 15-minute intervals for stages 1 and 2 at various temperatures and a toluene/heptane (80/20 by mass ratio). Clockwise from top left: 80 ℃, 0.5 solvent/emulsion mass ratio stage 1; 80 ℃, 0.5 solvent/emulsion mass ratio stage 2; 40 ℃, 0.5 solvent/emulsion mass ratio stage 1; 40 ℃, 0.5 toluene/emulsion mass ratio stage 2.

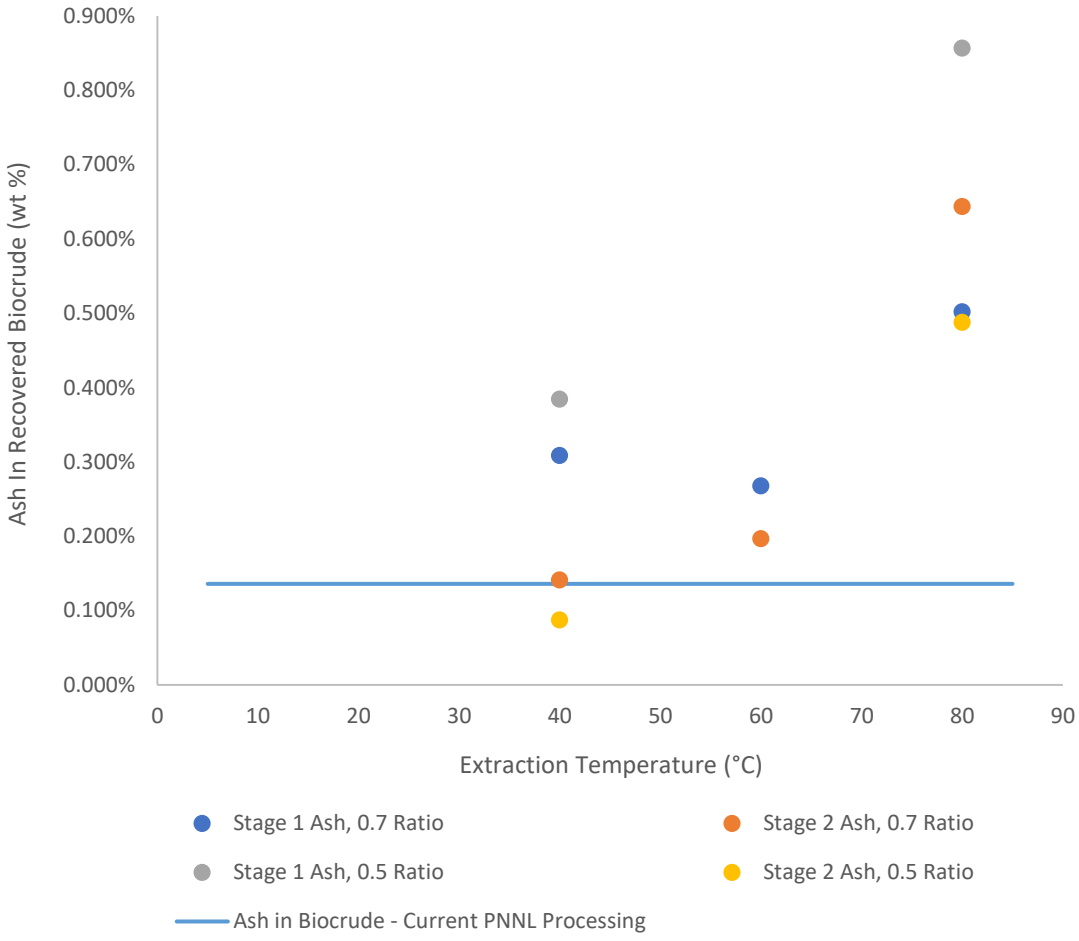

Figure S16. Ash in biocrude. Emulsion processed in toluene.

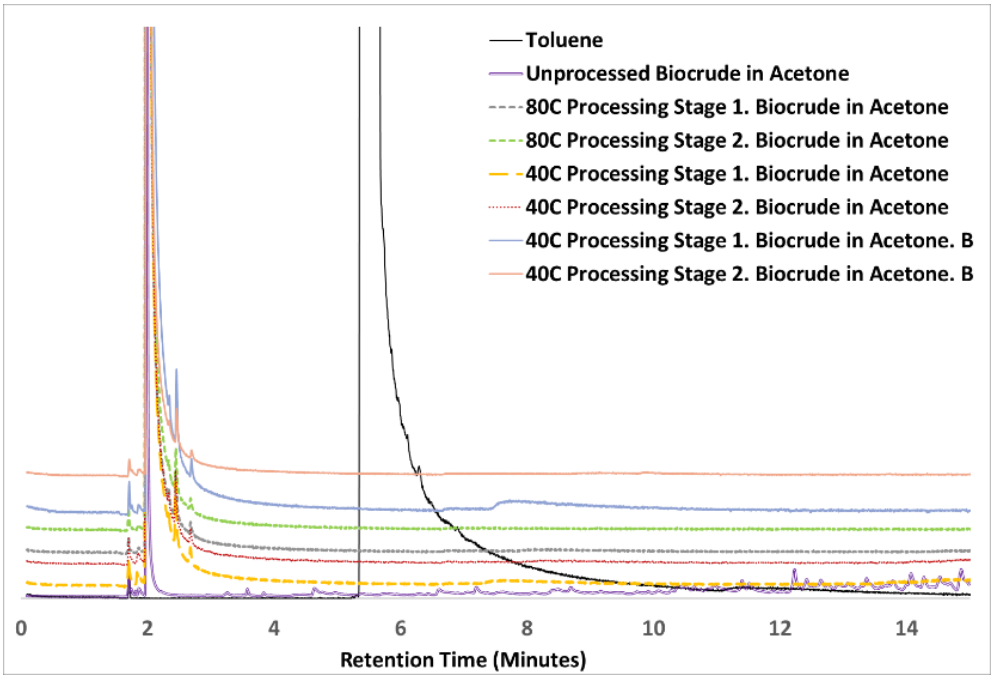

Figure S17. GC-MS spectra of solvent-processed biocrudes, unprocessed biocrude, and toluene.

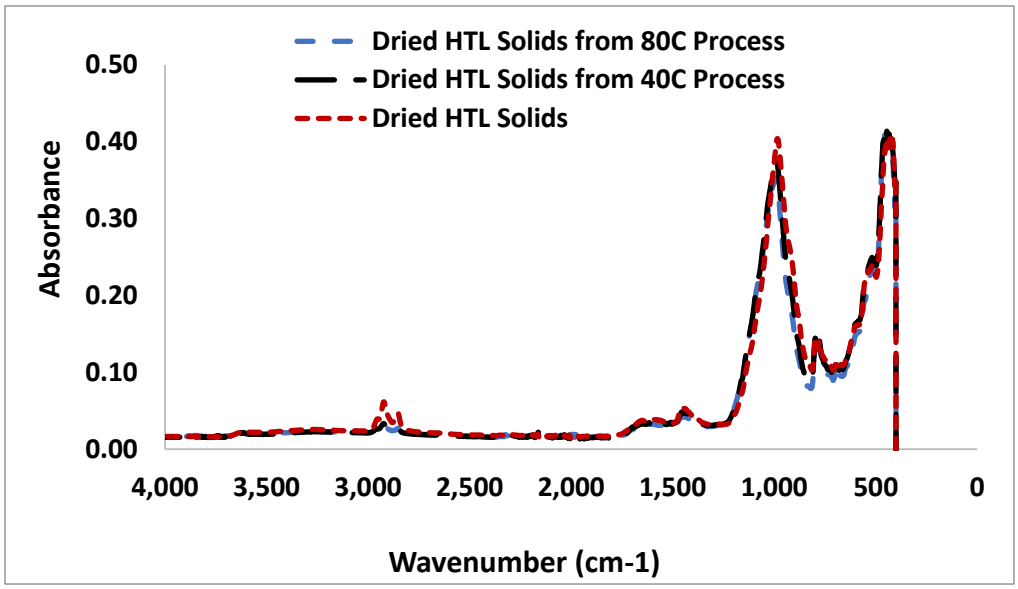

Figure S18. Infrared Spectrum of dried, processed HTL solids (15A, B, WW28).

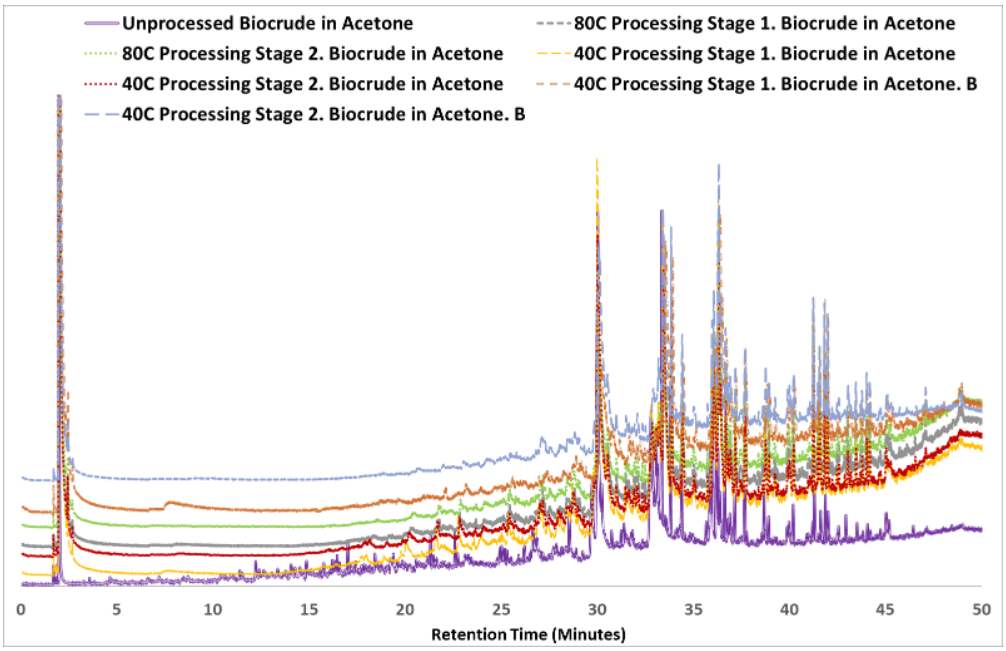

Figure S19. Gas chromatogram of HTL biocrude, and solvent processed HTL biocrude.

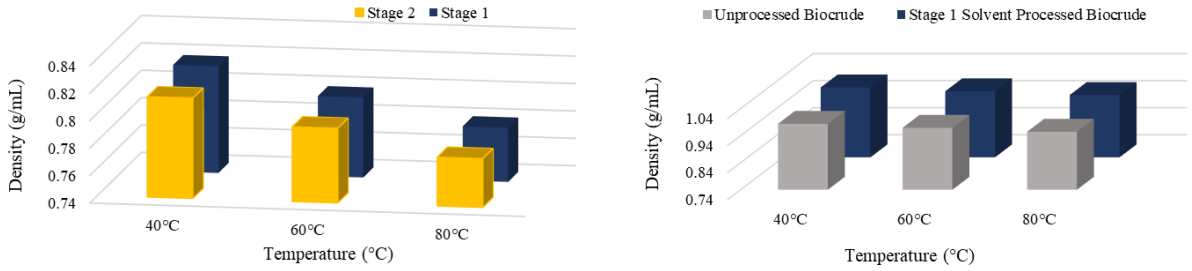

Figure S20. Density of extracted organics and biocrudes.

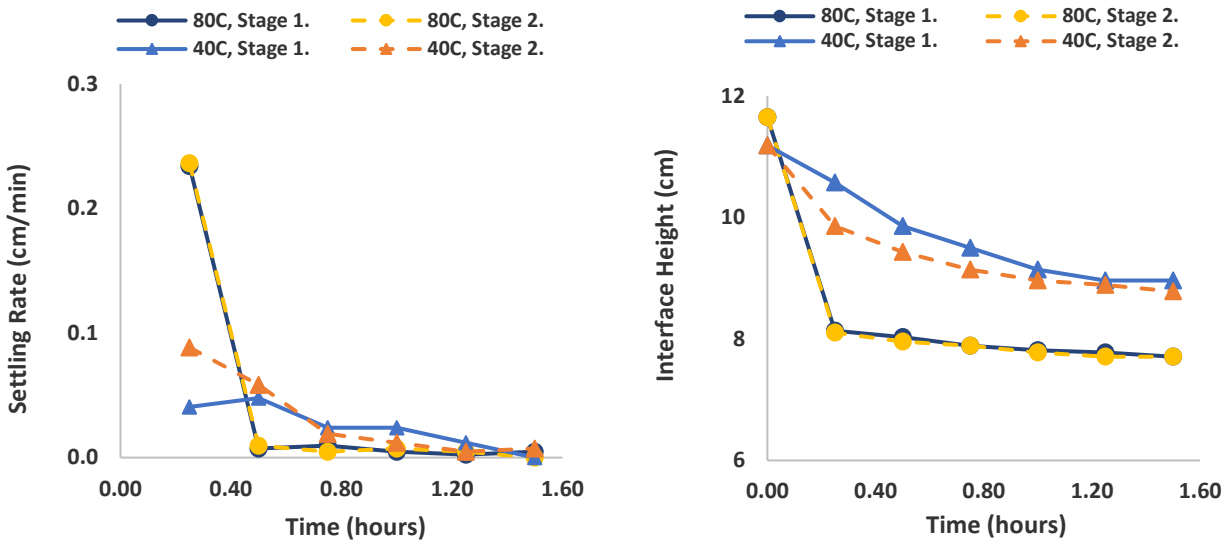

Figure S21. Settling data (settling rate, right; interface height, left) for HTL products processed in an 80/20 toluene/heptane mixture; 0.5 solvent/HTL product mass ratio.

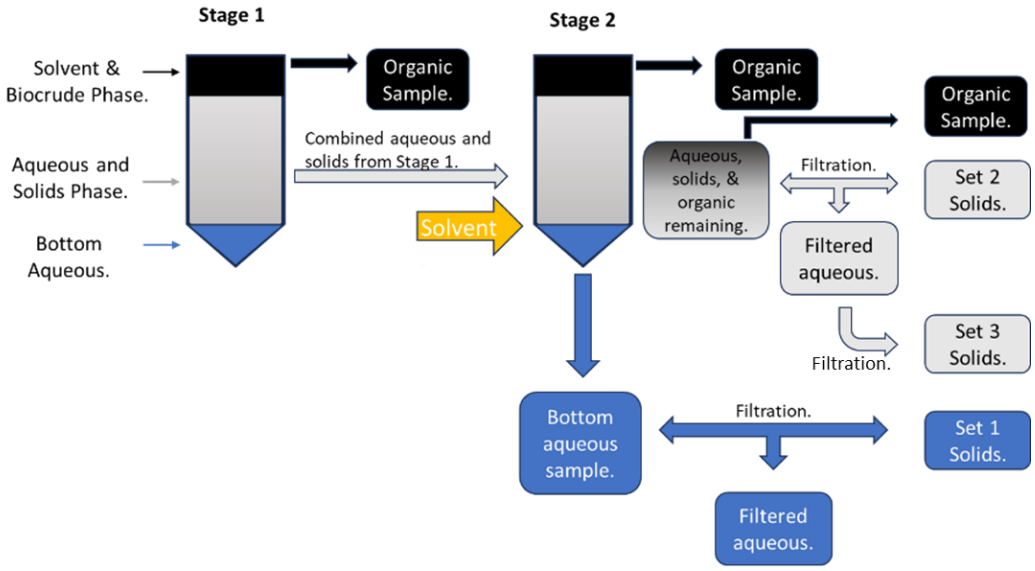

Figure S22. Stage 1 & 2 aqueous and organic sampling.

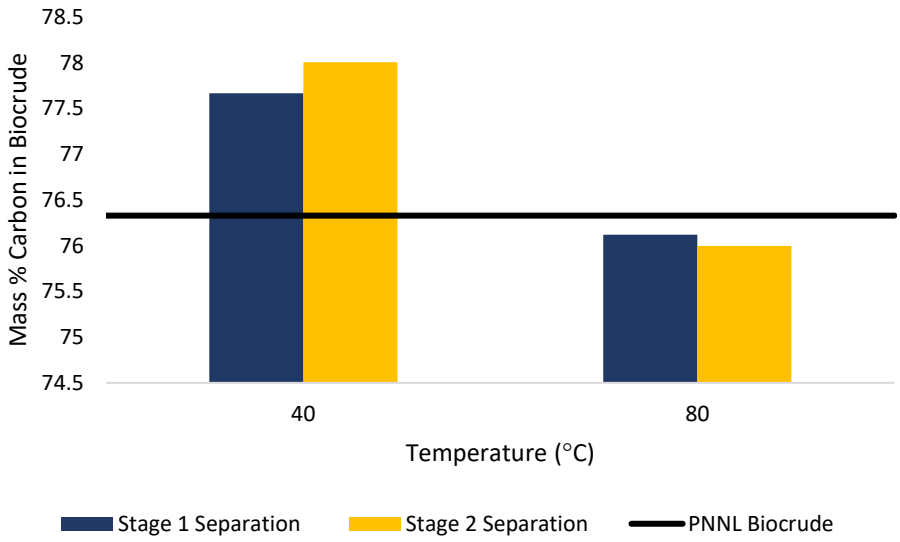

Figure S23. Carbon in solvent-processed/extracted BC. 0.5 solvent (toluene/heptane) to HTL product emulsion ratio. 80 ℃, 2 stages, 90 minutes each. PNNL HTL BC from high pressure/temperature process, Dried at 105 ℃ for 18 hours.

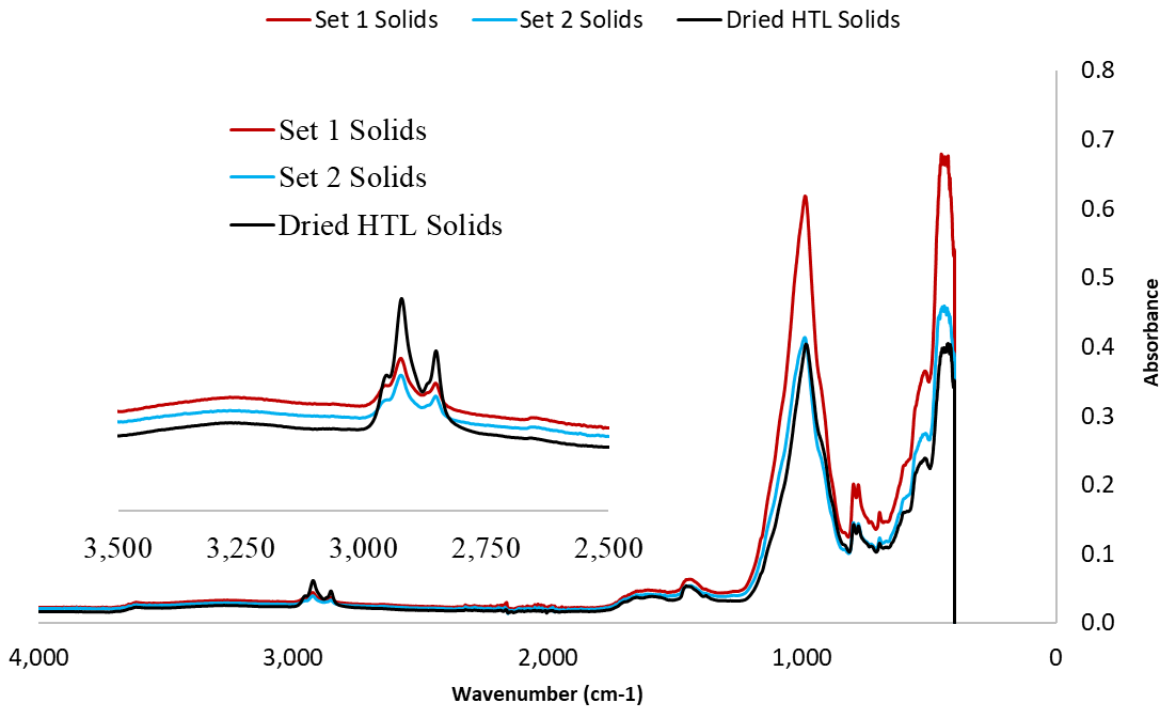

Figure S24. Infrared spectrum of dried solvent-processed hydro-char. Inset: C-H stretch region. C-H Stretching bands at 2950, 2920, and 2850 cm-1.

Table S1. ICP analysis on HTL starting products (used for HTL product emulsions) and solvent extraction samples. All values are given in (ug/mL).

Analyte Name	***Wet Solids[a]***	***Dry Solids[b]***	***Btm. Aq. Filt. Solids[c]***	***Rem. Filt. Solids[d]***	***Int. Filt. Solids[e]***	***Stg 1 BC[f]***	***Stg 2 BC[g]***	***Starting BC[h]***	***Filt. Btm. Aq.[i]***	***Starting Aq.[j]***
Al	16220	38605	43690	43740	38725	685	364	143	-	1
Ba	271	712	751	767	726	-	-	-	-	-
Ca	20450	47870	58980	61070	55155	975	536	130	-	-
Co	-	-	48	50	-	-	-	-	-	-
Cr	1121	2570	3273	3428	2942	60	26	-	-	-
Cu	272	635	711	731	670	27	-	-	-	-
Fe	38320	90065	101035	103900	96785	3731	2347	118	16	-
K	4944	11615	12140	11730	11155	162	103	89	352	260
Mg	6665	15965	18160	18190	16590	309	173	42	9	-
Mn	211	528	559	574	539	-	-	-	-	-
Na	1345	4600	3110	2868	2580	-	-	524	179	130
Ni	500	1323	1300	1356	1231	89	74	-	-	-
P	21715	52260	57830	60380	54805	917	521	-	91	18
Pb	-	-	-	85	-	-	-	-	-	-
Sr	138	326	345	354	334	-	-	-	-	-
Zn	603	1504	1609	1665	1639	102	76	-	-	-
Mo	114	300	297	309	283	-	-	-	1	-
Si	49900	67415	133650	124000	116050	1336	784	3443	142	285
Ti	1359	3597	3725	3829	3428	80	38	-	-	-
S	2986	7601	7522	7923	7802	8684	8293	7708	281	214
Zr	72	186	184	190	181	-	-	-	-	-

a. HTL hydro-char slurry used for reconstituted HTL product emulsion. Wet solids analysis.

b. Hydro-char slurry used for reconstituted HTL product emulsion. The solids were fully dried at 105°C.

c. Approximately 30% of the volume of aqueous and solids product mixture was taken as a bottom aqueous and solids sample from an 80°C, 0.5 solvent/emulsion ratio, and 90-minute residence time solvent extraction batch experiment. The sample was vacuum filtered with a Buchner funnel and the solids were oven dried at 105°C for ~12 hours.

d. The remaining aqueous and solids after a stage 2 separation (remnant aqueous) was drained (see note c. for experiment parameters). The aqueous and solids were vacuum filtered with a Buchner funnel and the solids were dried for ~12 hours at 105°C.

e. The remnant filtered aqueous underwent a second vacuum filtration. The solids were dried for ~12 hours at 105°C.

f. The stage 1 organic sample was processed through rotary evaporation and the resulting biocrude was dried for ~12 hours at °C (see note c. for experiment parameters).

g. The stage 2 organic sample was processed through rotary evaporation and the resulting biocrude was dried for ~12 hours at °C (see note c. for experiment parameters).

h. HTL biocrude used for reconstituted HTL product emulsions in the solvent extraction experiments, dried at 105°C for ~12 hours.

i. Filtered aqueous from the bottom aqueous and solids stage 2 sample filtration.

j. HTL-AP used for the reconstituted HTL product emulsions.

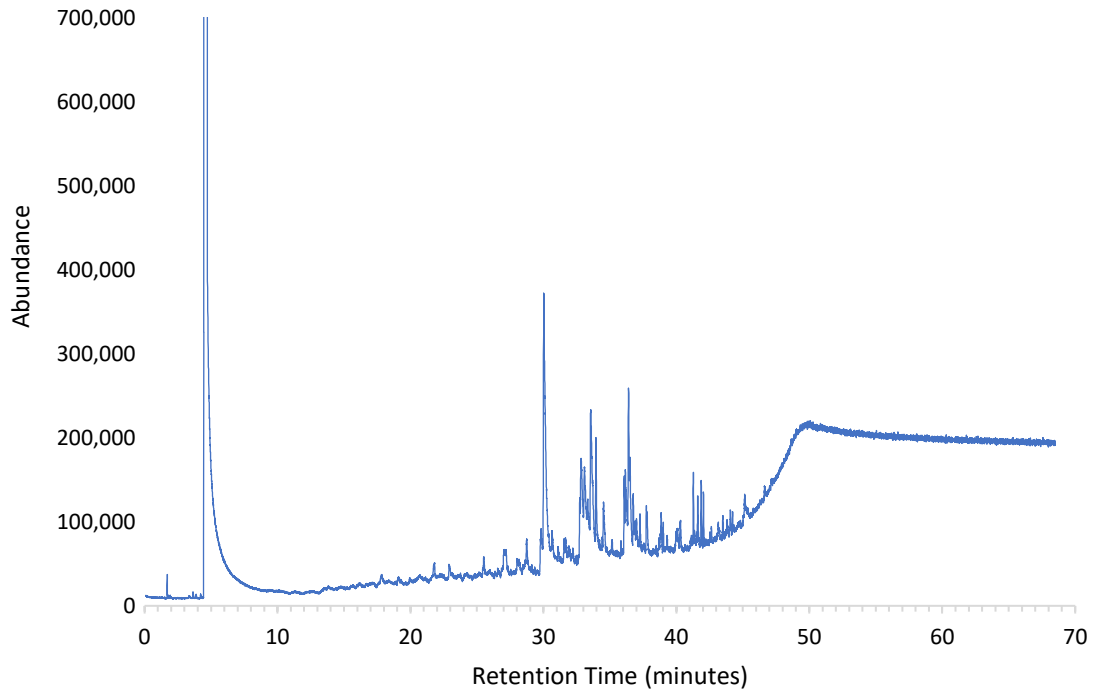

Figure S25. GC-MS of organic extract from hydro-char slurry. Toluene was mixed with the slurry at a ratio of 1:14 (slurry to solvent).

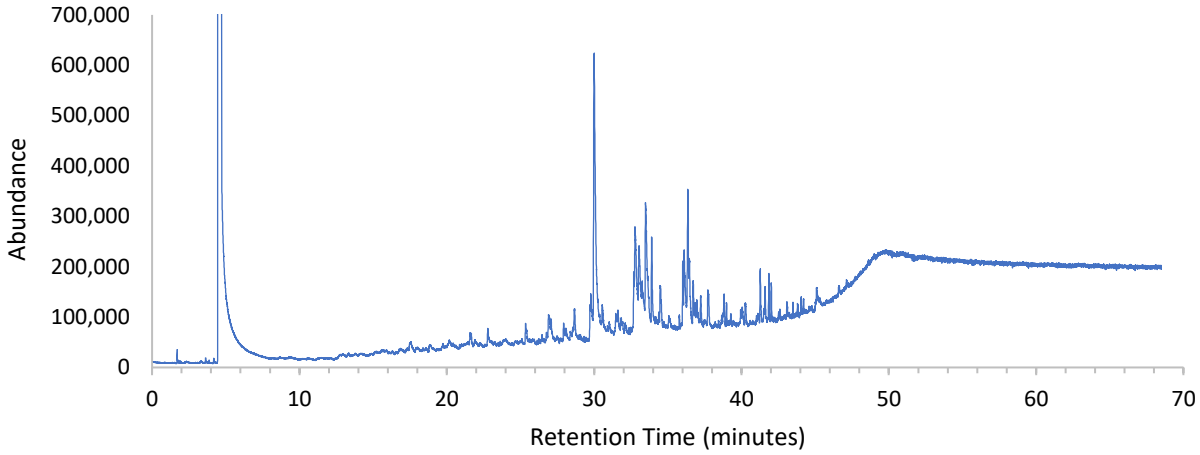

Figure S26. GC-MS of organic extract from hydro-char slurry. Toluene was mixed with the slurry at a ratio of 1:10 (slurry to solvent).