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

SUPPORTING INFORMATION

Probing Elemental Speciation in Hydrochar Produced from Hydrothermal Liquefaction of Anaerobic Digestates Using Quantitative X-Ray Diffraction

Hanifrahmawan Sudibyo,[a,b,*] Jefferson W. Tester[a]

[a]School of Chemical and Biomolecular Engineering and Energy Systems Institute, Cornell University, Ithaca, New York 14853, United States
[b]Chemical Engineering Department, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

*corresponding author: hs987@cornell.edu

Number of Figures : 15

Number of Tables : 25

Figure S1. HTL Experimental Steps using a 500-mL Parr 4575 SS316 reactor with a Parr 4878 controller to control reaction temperature and stirrer speed (150 rpm).

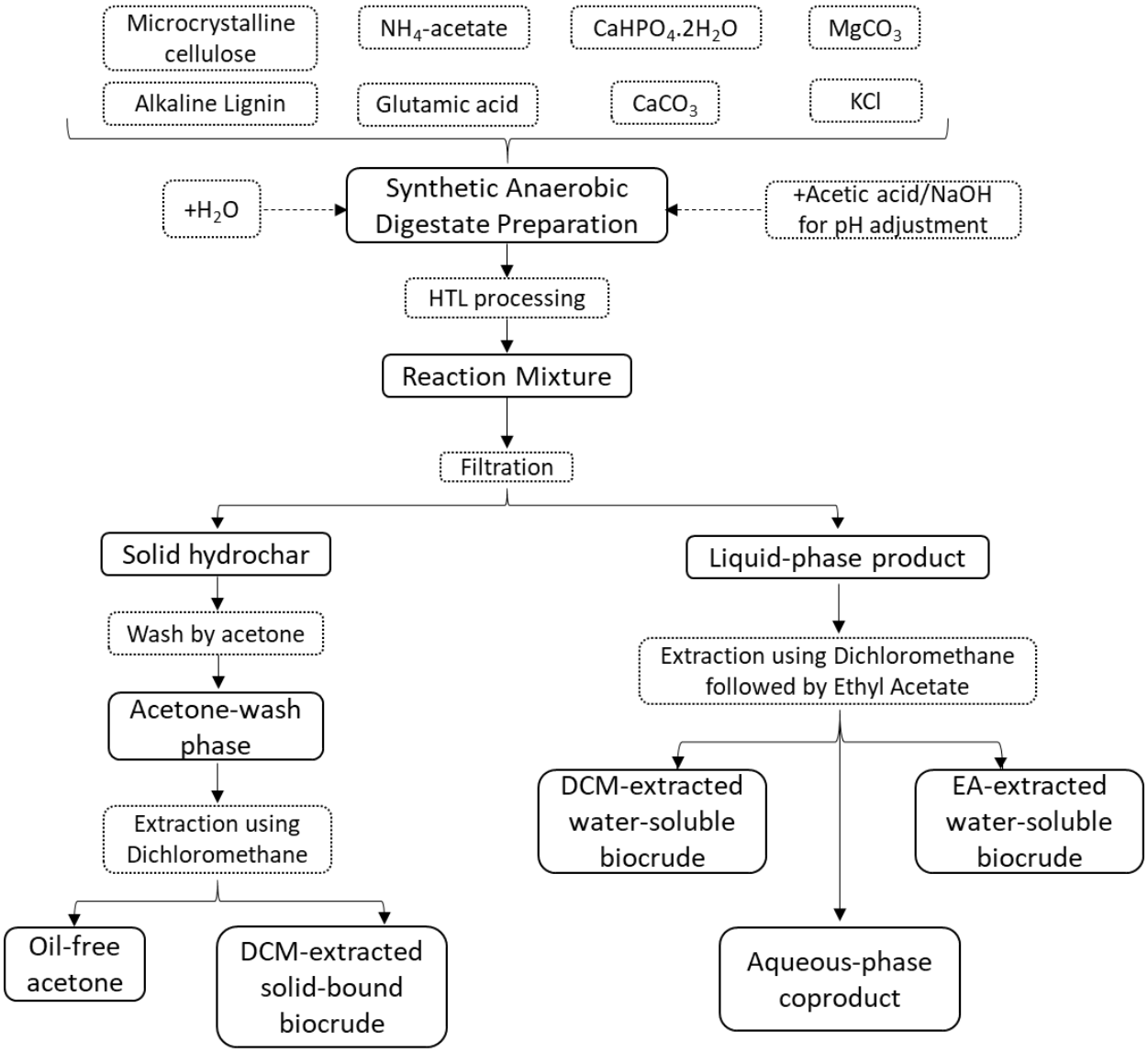
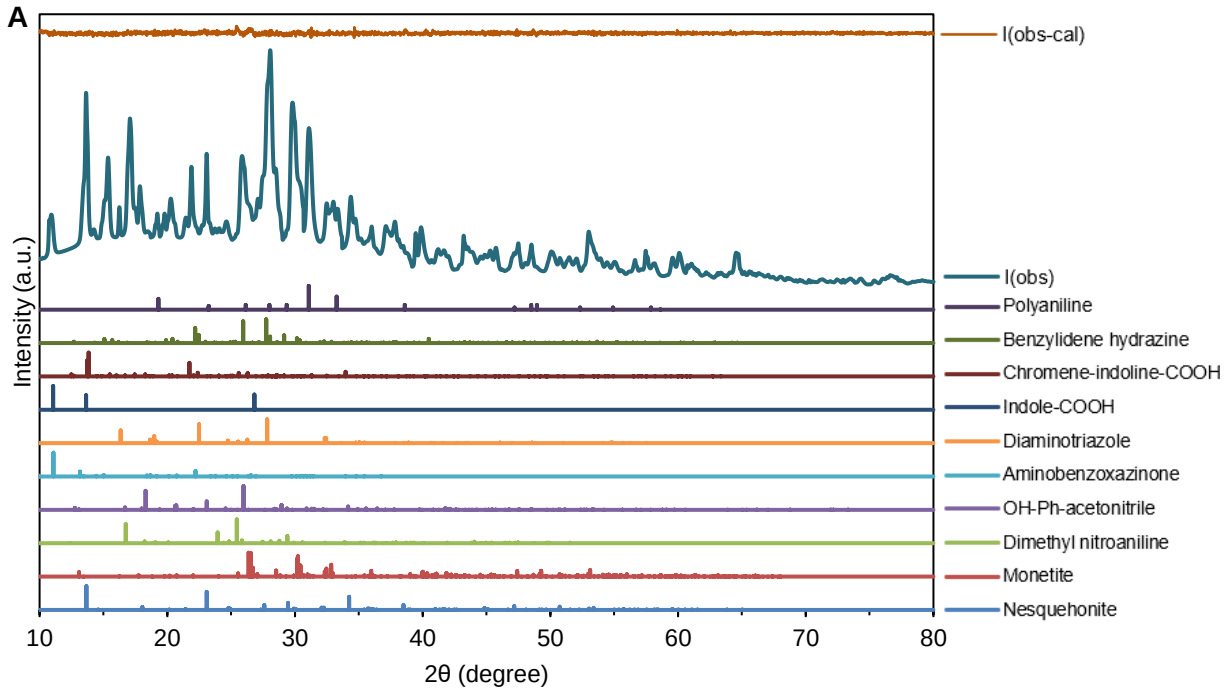
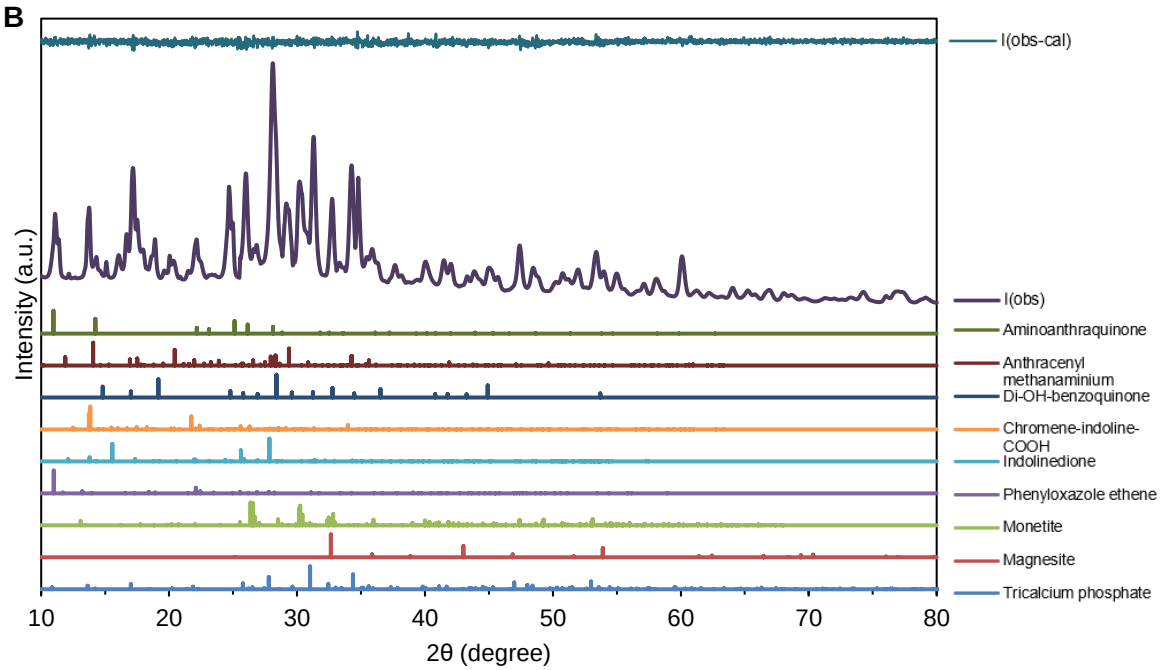
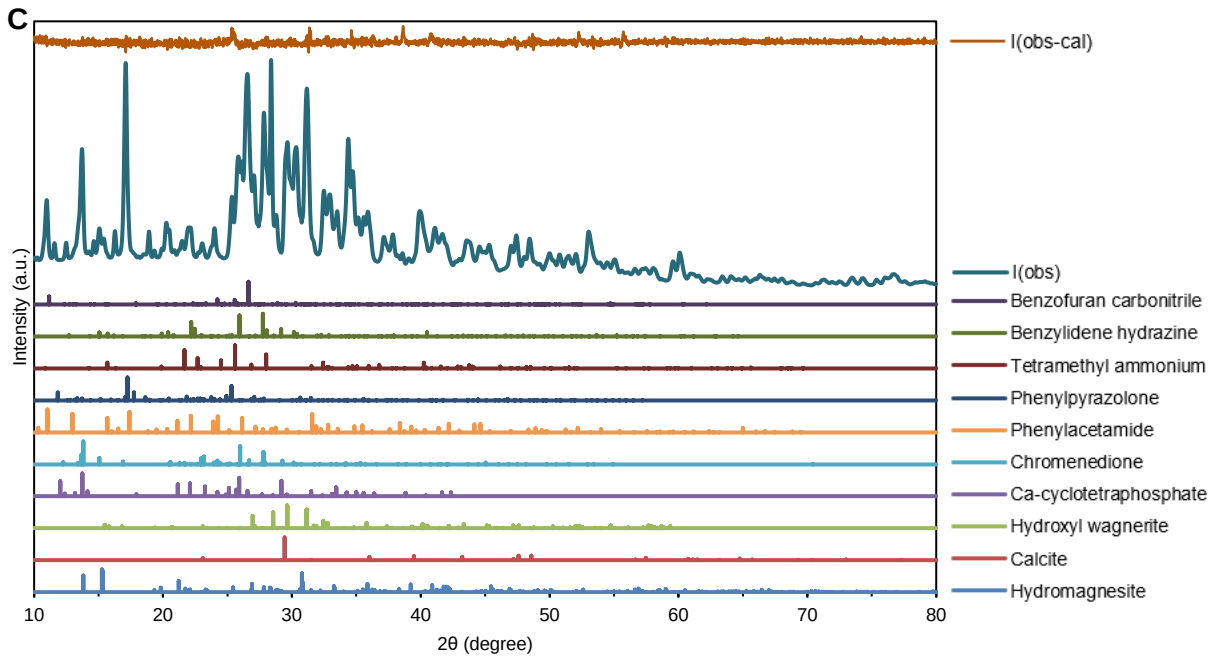


Figure S2. The XRD diffractograms for hydrochar produced from (A) Cel/Lig 0.2, pH 3.5, 320 ºC; (B) Cel/Lig 0.2, pH 3.5, 360 ºC; (C) Cel/Lig 0.2, pH 8, 320 ºC; and (D) Cel/Lig 0.2, pH 8, 360 ºC.






C
I(obs-cal)
I(obs)
Benzofuran carbonitrile
Benzylidene hydrazine
Tetramethyl ammonium
Phenylpyrazolone
Phenylacetamide
Chromenedione
Ca-cyclotetraphosphate
Hydroxyl wagnerite
Calcite
Hydromagnesite
Intensity (a.u.)
10
20
30
40
50
60
70
80
2θ (degree)

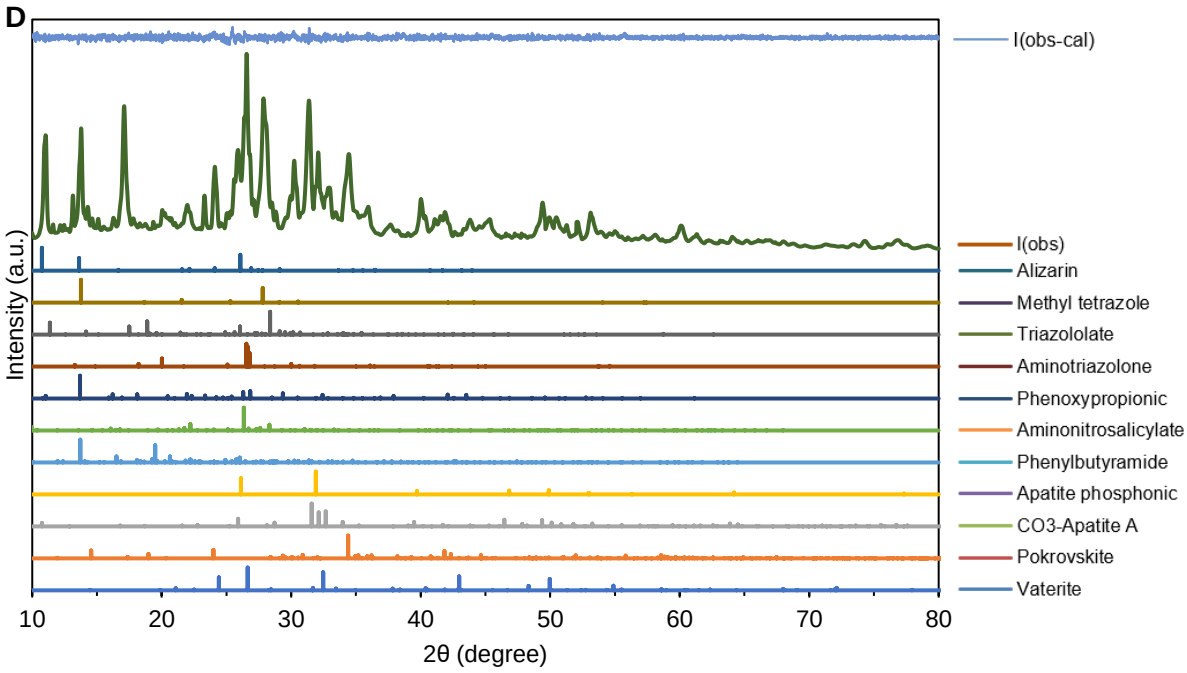
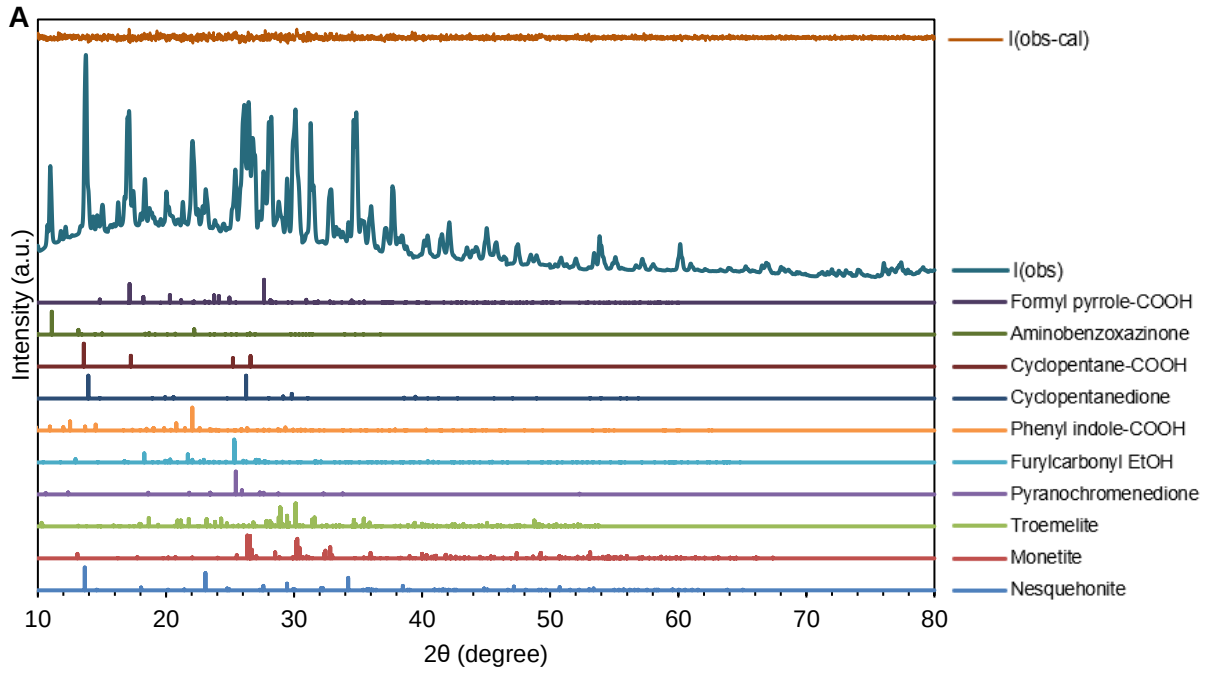
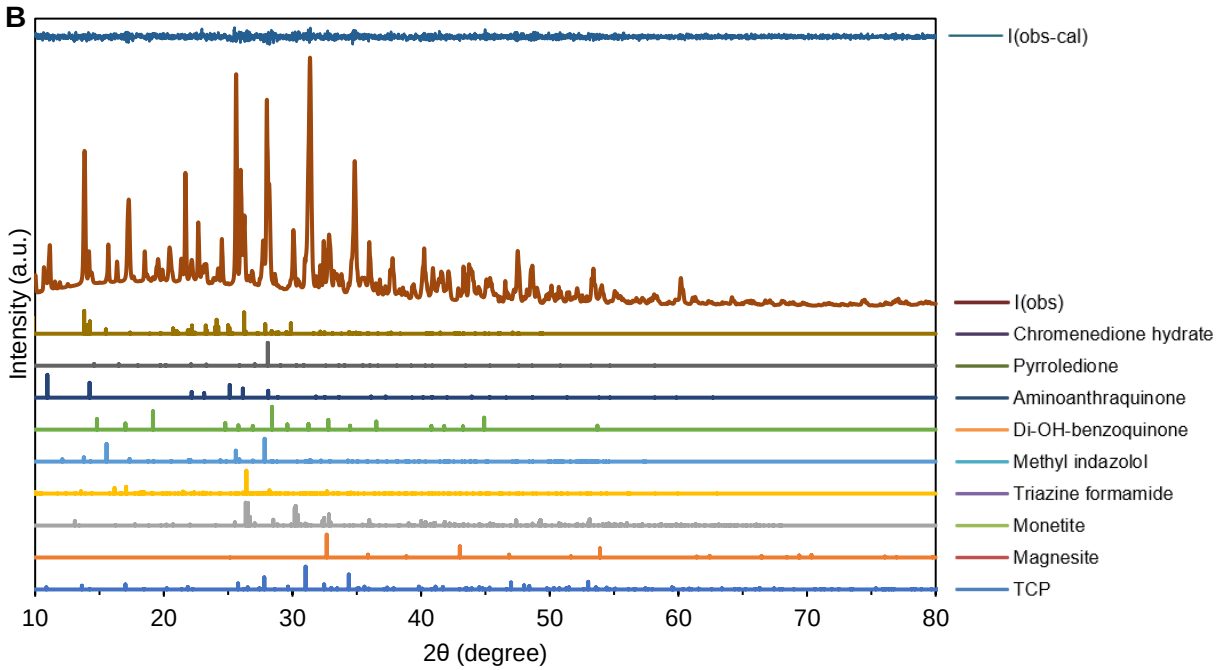
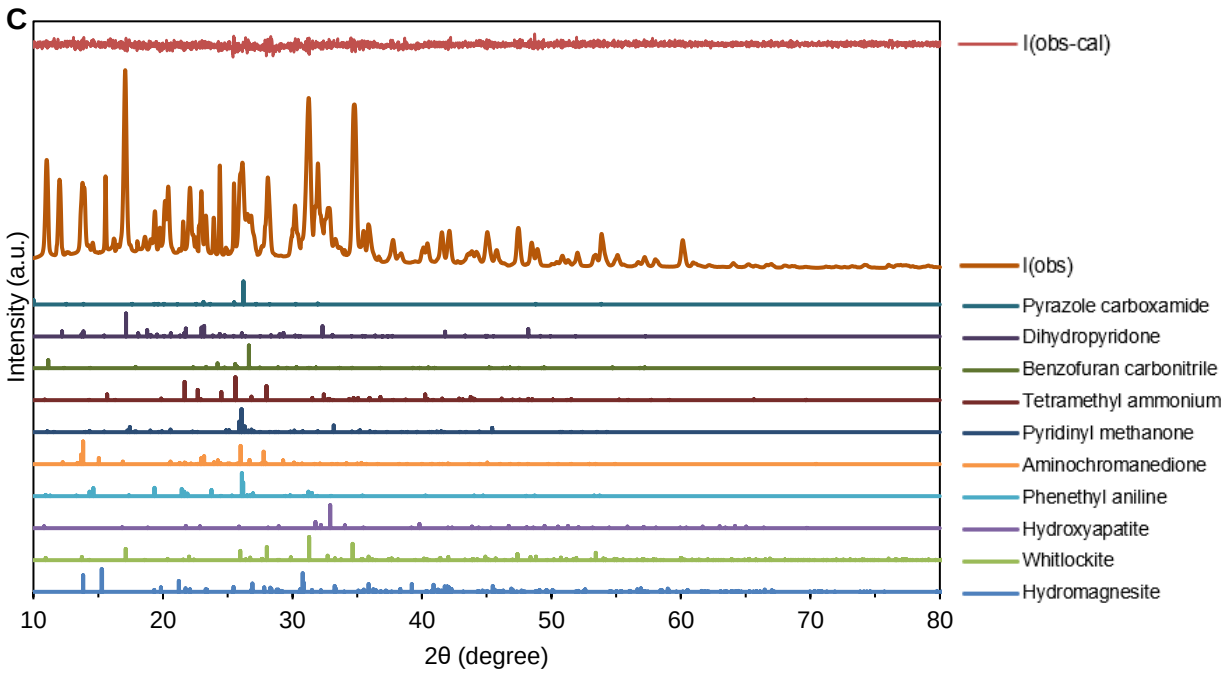

D
I(obs-cal)
I(obs)
Alizarin
Methyl tetrazole
Triazololate
Aminotriazolone
Phenoxypropionic
Aminonitrosalicylate
Phenylbutyramide
Apatite phosphonic
CO3-Apatite A
Pokrovskite
Vaterite
Intensity (a.u.)
10
20
30
40
50
60
70
80
2θ (degree)

Figure S3. The XRD diffractograms for hydrochar produced from (A) Cel/Lig 1.8, pH 3.5, 320 ºC; (B) Cel/Lig 1.8, pH 3.5, 360 ºC; (C) Cel/Lig 1.8, pH 3.5, 360 ºC; and (D) Cel/Lig 1.8, pH 8, 360 ºC






C
Intensity (a.u.)
2θ (degree)
10
20
30
40
50
60
70
80
I(obs-cal)
I(obs)
Pyrazole carboxamide
Dihydropyridone
Benzofuran carbonitrile
Tetramethyl ammonium
Pyridinyl methanone
Aminochromanedione
Phenethyl aniline
Hydroxyapatite
Whitlockite
Hydromagnesite

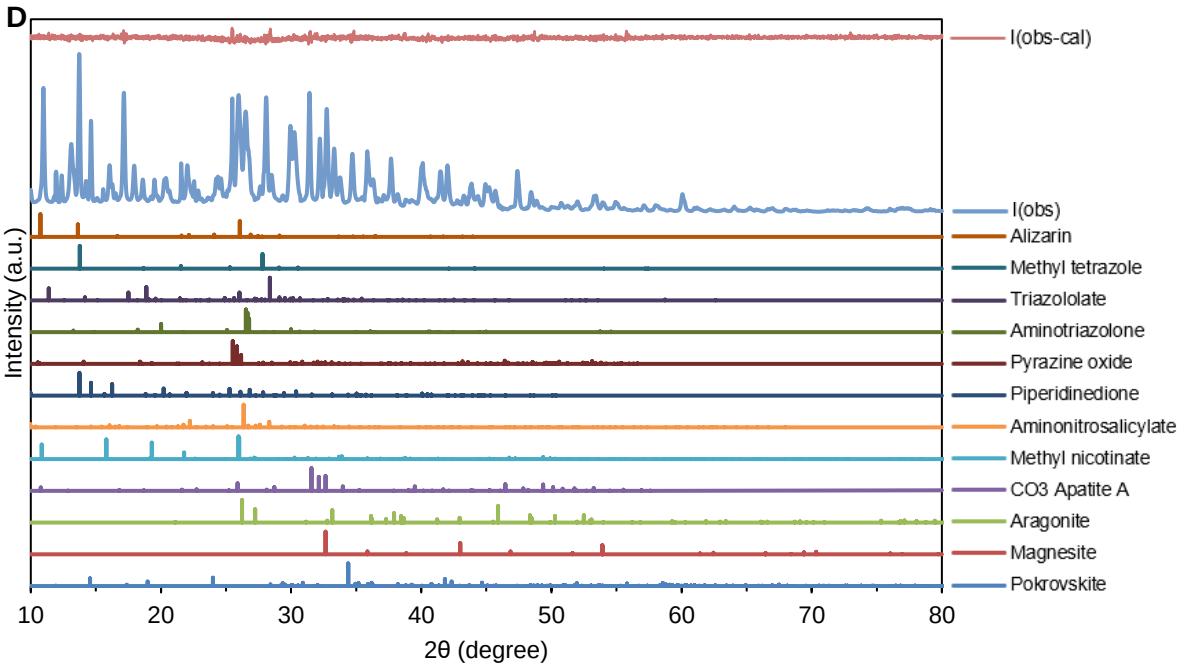

D
Intensity (a.u.)
2θ (degree)
10
20
30
40
50
60
70
80
I(obs-cal)
I(obs)
Alizarin
Methyl tetrazole
Triazololate
Aminotriazolone
Pyrazine oxide
Piperidinedione
Aminonitrosalicylate
Methyl nicotinate
CO3 Apatite A
Aragonite
Magnesite
Pokrovskite

Figure S4. The DP-MAS ^{13}C SS-NMR spectra of hydrochar: (a) Cel/Lig 0.2-pH 3.5-320 ºC; (b) Cel/Lig 0.2-pH 3.5-360 ºC; (c) Cel/Lig 0.2-pH 8-320 ºC; (d) Cel/Lig 0.2-pH 8-360 ºC, (e) Cel/Lig 1.8-pH 3.5-320 ºC, (f) Cel/Lig 1.8-pH 3.5-360 ºC; (g) Cel/Lig 1.8-pH 3.5-360 ºC and (h) Cel/Lig 1.8-pH 8-360 ºC.

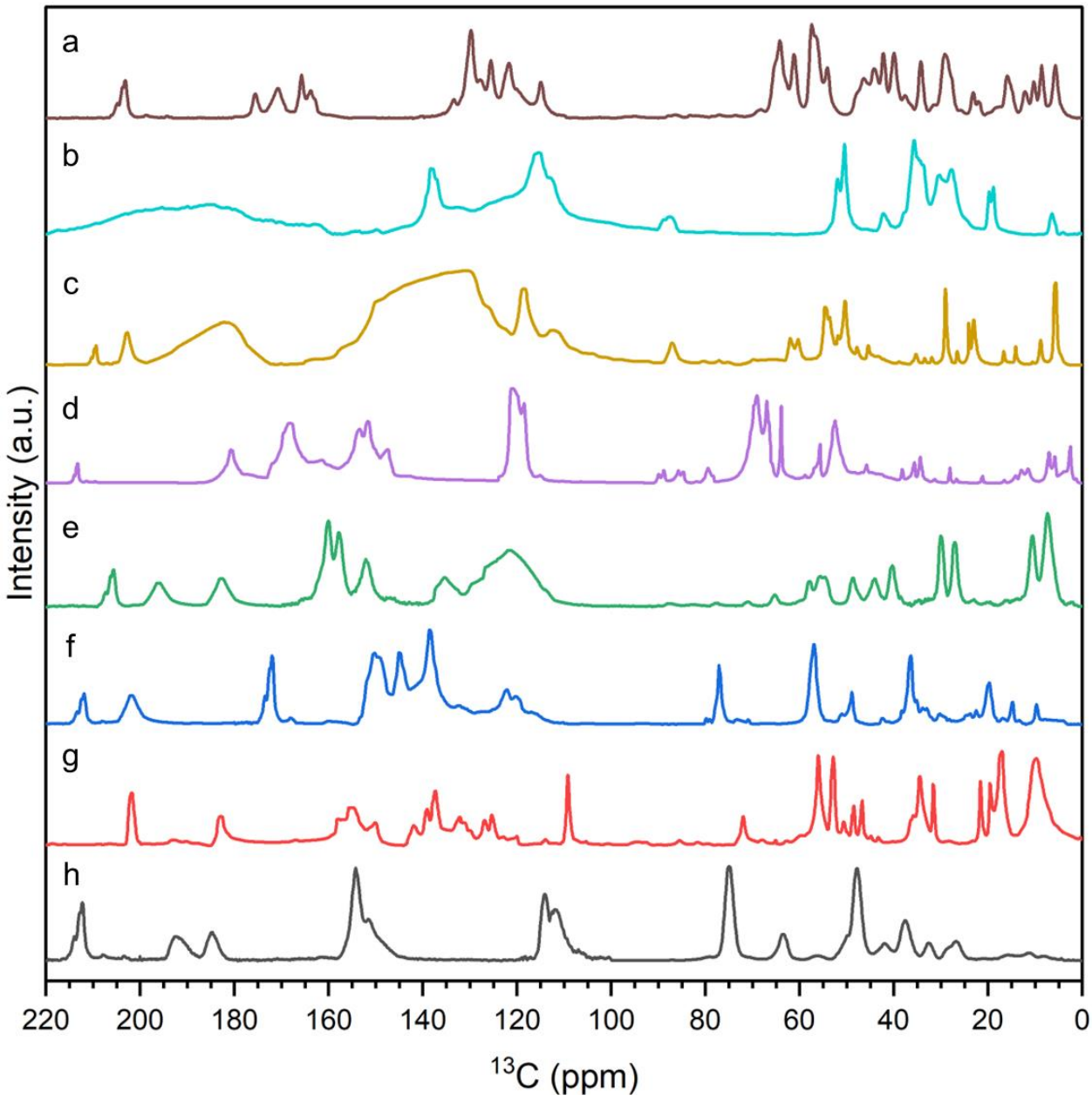


Figure S5. The ^{13}C NMR spectra of biocrude oil: (a) Cel/Lig 0.2-pH 3.5-320 ºC; (b) Cel/Lig 0.2-pH 3.5-360 ºC; (c) Cel/Lig 0.2-pH 8-320 ºC; (d) Cel/Lig 0.2-pH 8-360 ºC, (e) Cel/Lig 1.8-pH 3.5-320 ºC, (f) Cel/Lig 1.8-pH 3.5-360 ºC; (g) Cel/Lig 1.8-pH 3.5-360 ºC and (h) Cel/Lig 1.8-pH 8-360 ºC.

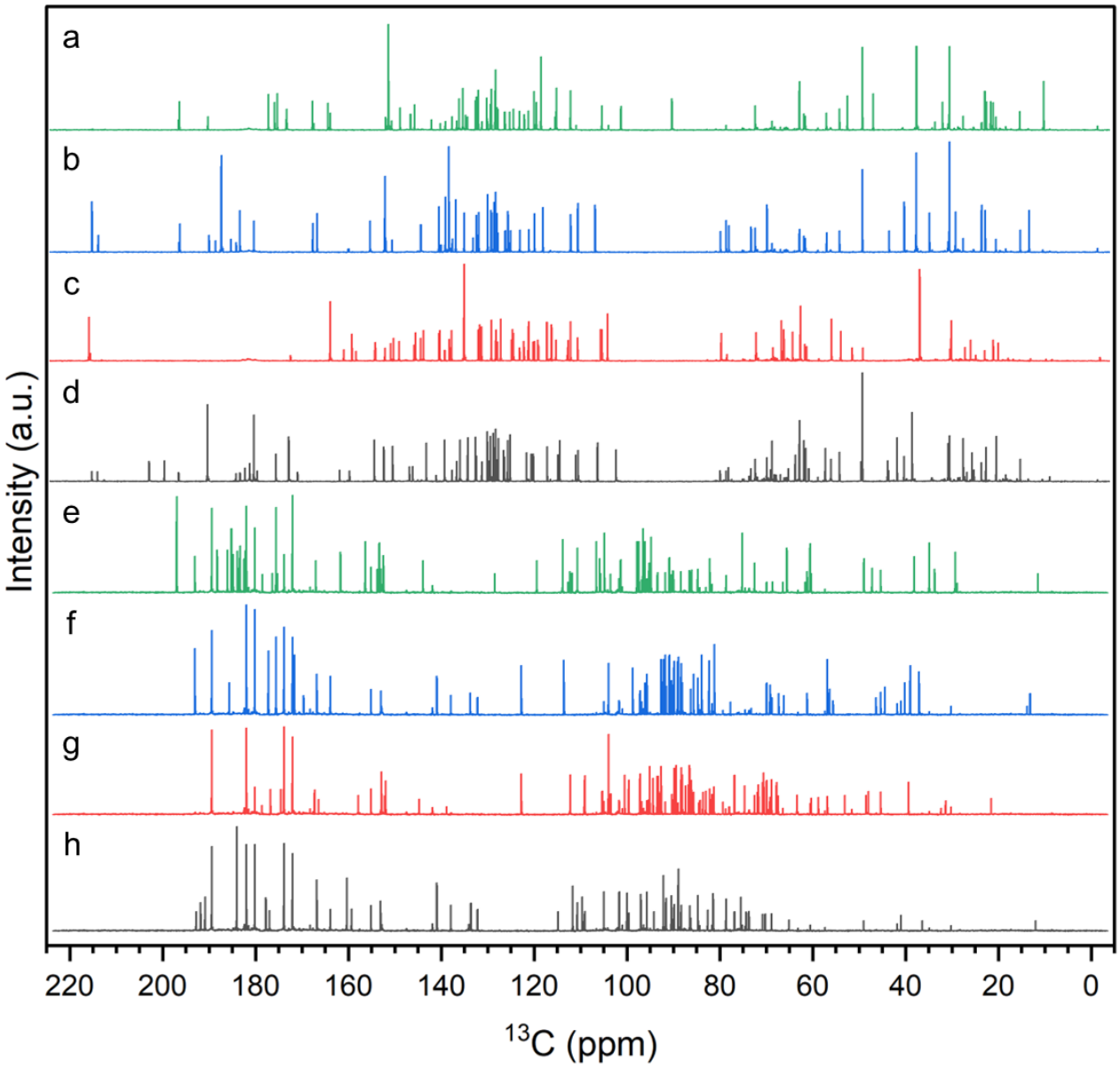


Figure S6. The ^{13}C NMR spectra of aqueous-phase coproduct: (a) Cel/Lig 0.2-pH 3.5-320 ºC; (b) Cel/Lig 0.2-pH 3.5-360 ºC; (c) Cel/Lig 0.2-pH 8-320 ºC; (d) Cel/Lig 0.2-pH 8-360 ºC, (e) Cel/Lig 1.8-pH 3.5-320 ºC, (f) Cel/Lig 1.8-pH 3.5-360 ºC; (g) Cel/Lig 1.8-pH 3.5-360 ºC and (h) Cel/Lig 1.8-pH 8-360 ºC.

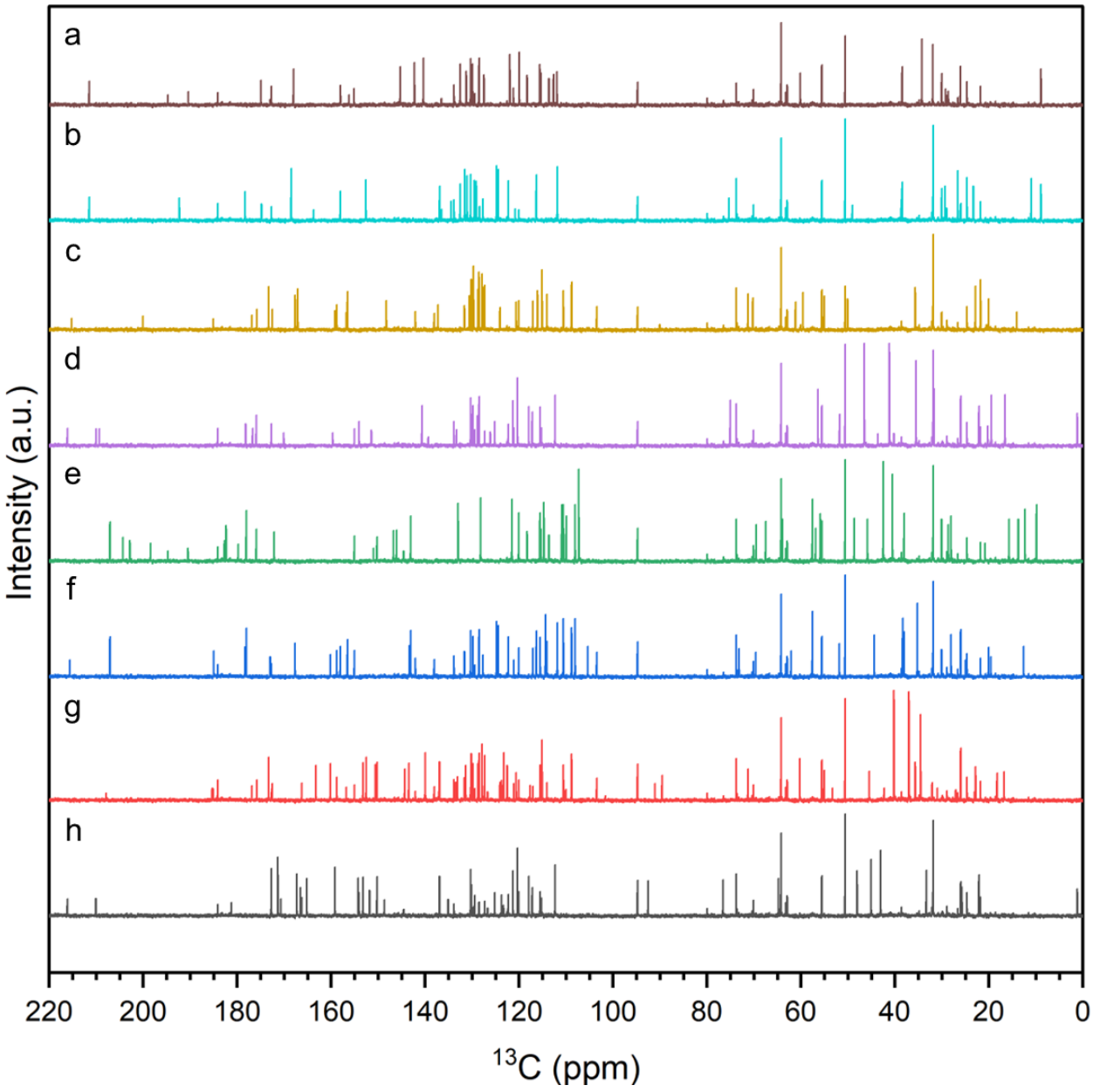


Figure S7. The ^{31}P NMR spectra of aqueous-phase coproduct: (a) Cel/Lig 0.2-pH 3.5-320 ºC; (b) Cel/Lig 0.2-pH 3.5-360 ºC; (c) Cel/Lig 0.2-pH 8-320 ºC; (d) Cel/Lig 0.2-pH 8-360 ºC, (e) Cel/Lig 1.8-pH 3.5-320 ºC, (f) Cel/Lig 1.8-pH 3.5-360 ºC; (g) Cel/Lig 1.8-pH 3.5-360 ºC and (h) Cel/Lig 1.8-pH 8-360 ºC.

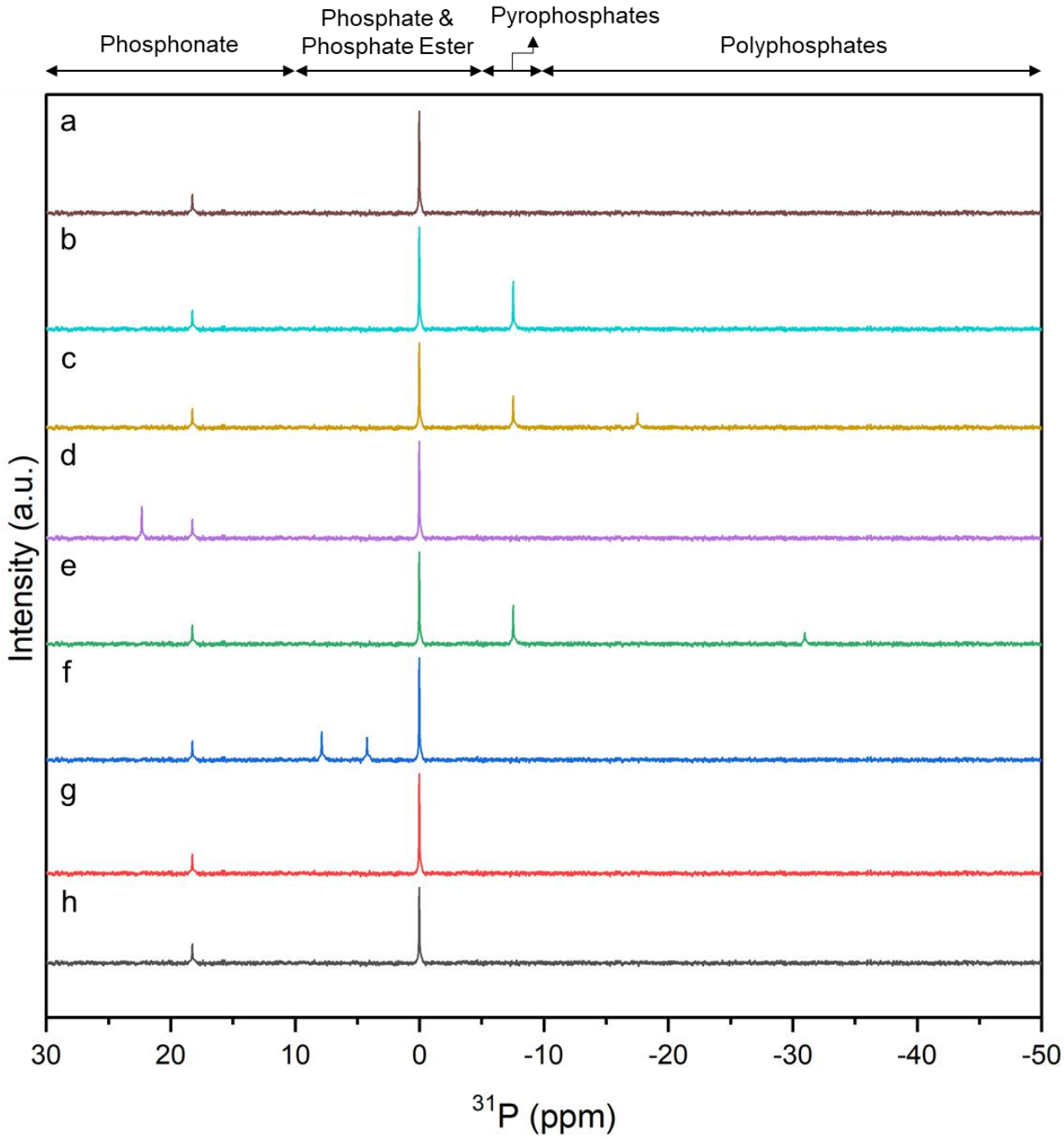


Figure S8. Solid-state NMR spectra of (a) ^{31}P, (b) ^{25}Mg, and (c) ^{43}Ca of hydrochar produced from (1) Cel/Lig 0.2–pH 3.5–320ºC; (2) Cel/Lig 0.2–pH 3.5–360ºC; (3) Cel/Lig 0.2–pH 8–320ºC; (4) Cel/Lig 0.2–pH 8–360ºC, (5) Cel/Lig 1.8–pH 3.5–320ºC, (6) Cel/Lig 1.8–pH 3.5–360ºC; (7) Cel/Lig 1.8–pH 3.5–360ºC and (8) Cel/Lig 1.8–pH 8–360ºC.

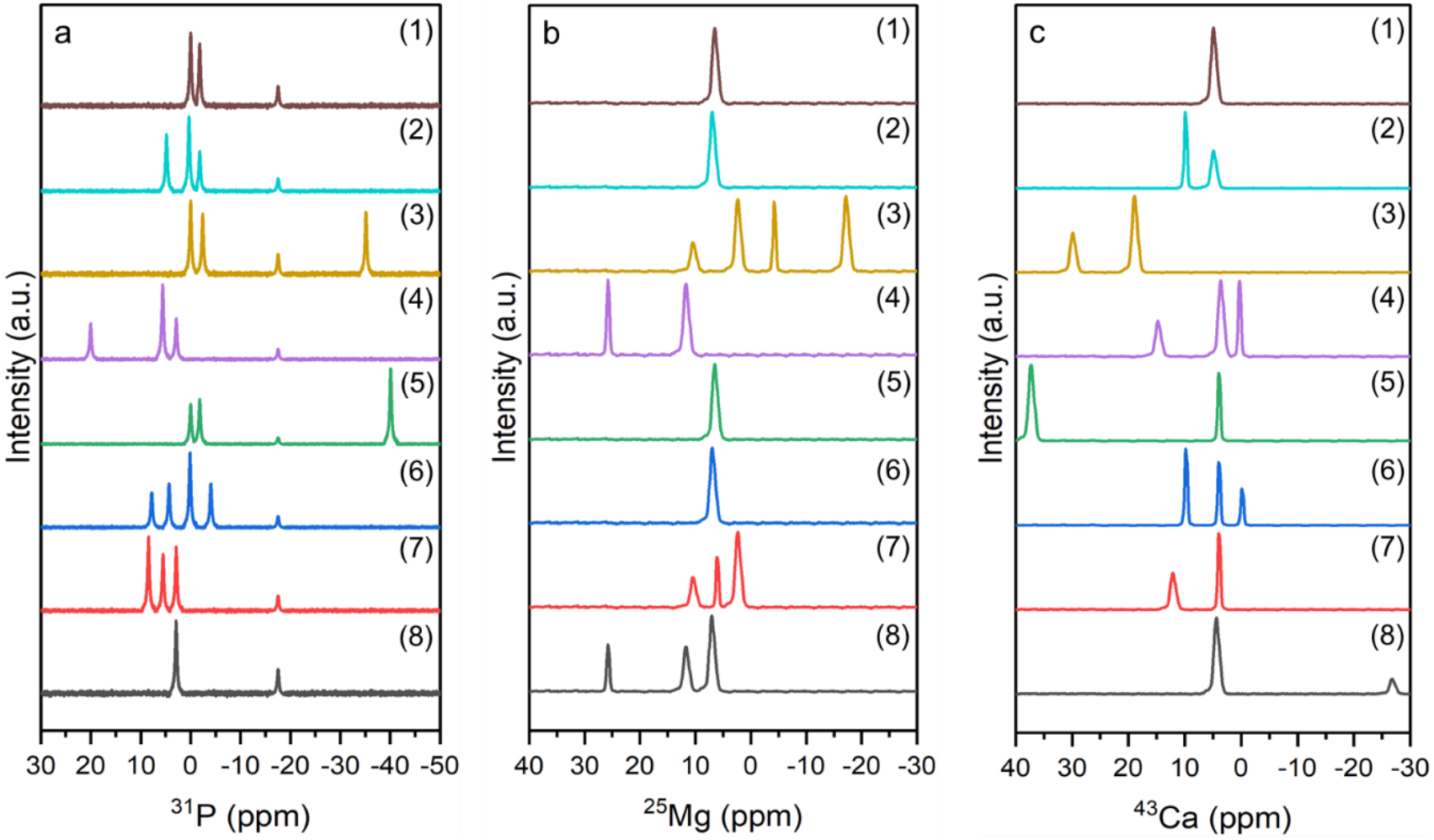


Figure S9. Product yield distribution

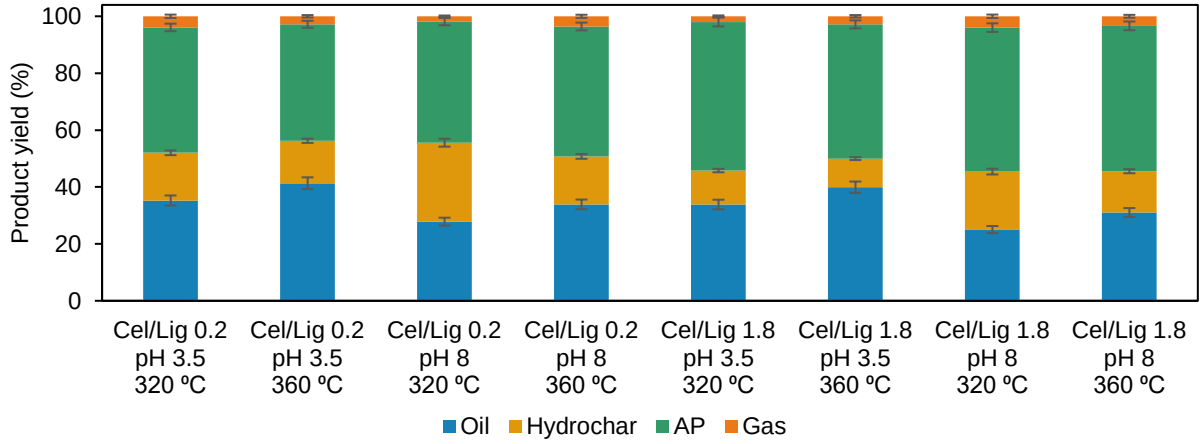


Figure S10. Carbon yield distribution

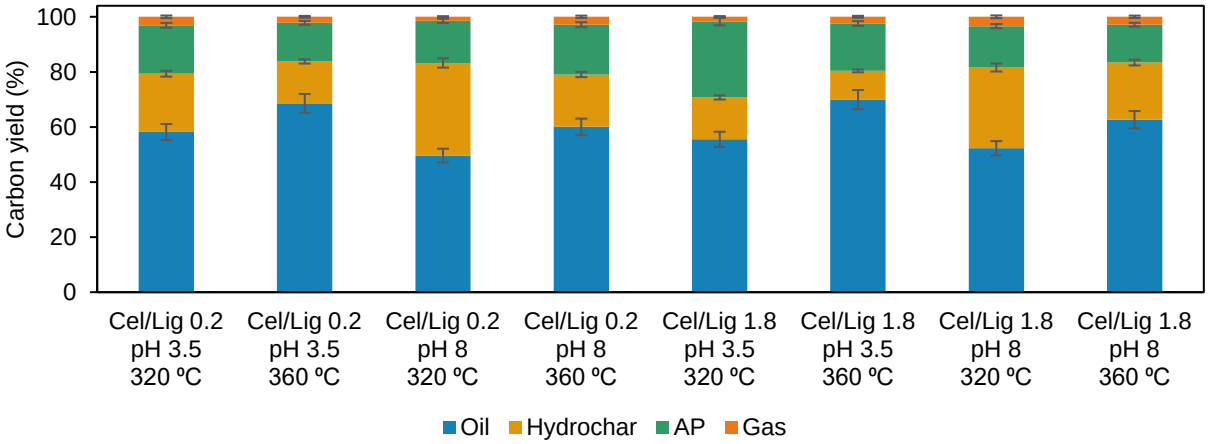


Figure S11. Nitrogen yield distribution

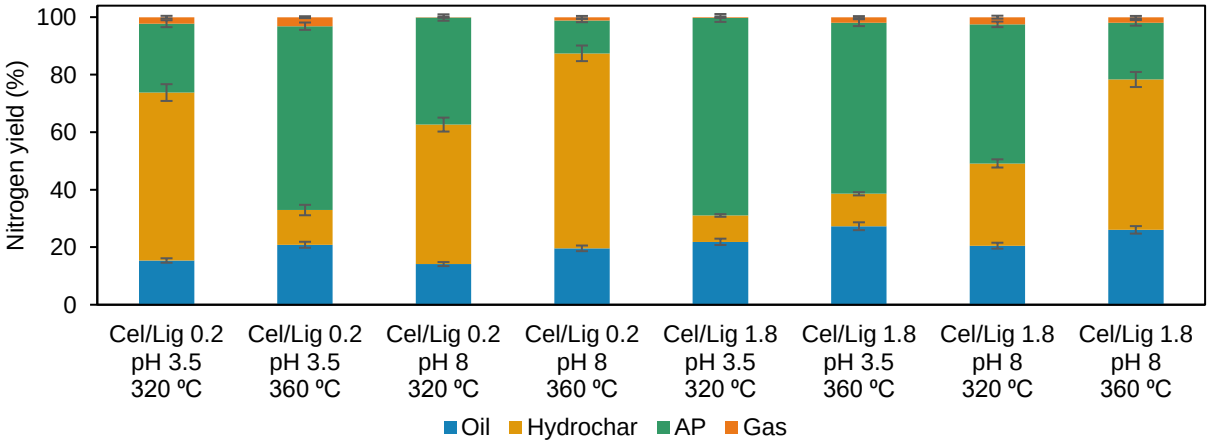


Figure S12. Phosphorus yield distribution

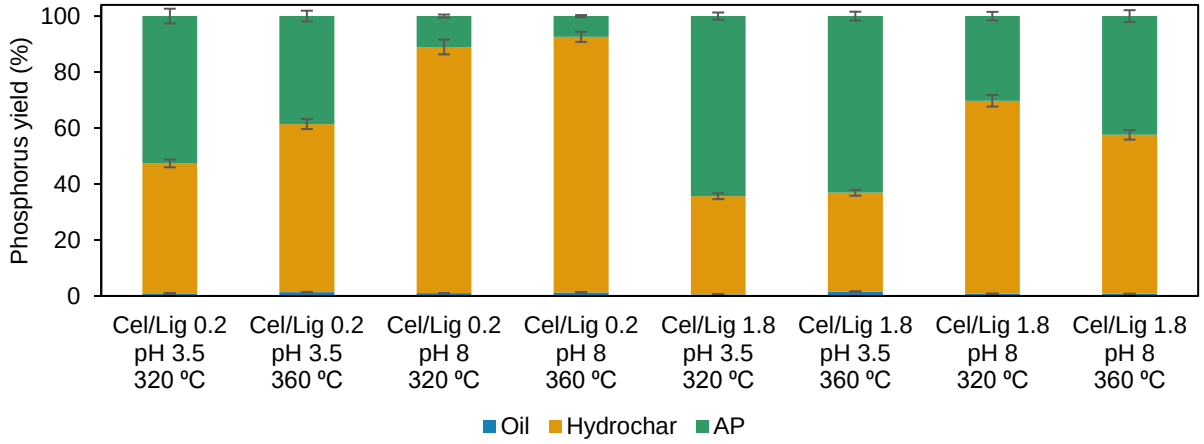


Figure S13. Calcium yield distribution

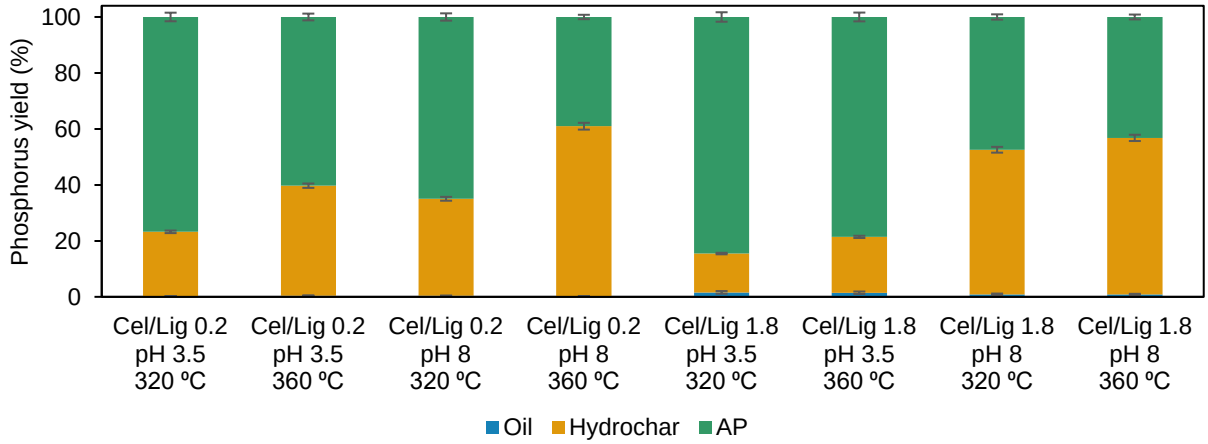


Figure S14. Magnesium yield distribution

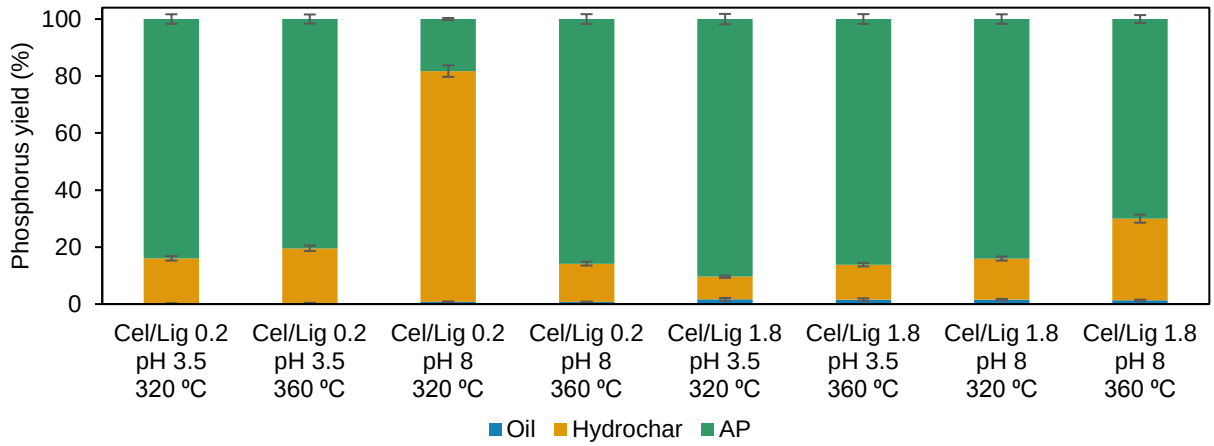


Figure S15. Percent distribution of (a) ^{31}P, (b) ^{25}Mg, and (c) ^{43}Ca functionalities based on quantitative DP-MAS SS-NMR. Figure S8 shows the corresponding SS-NMR spectra.

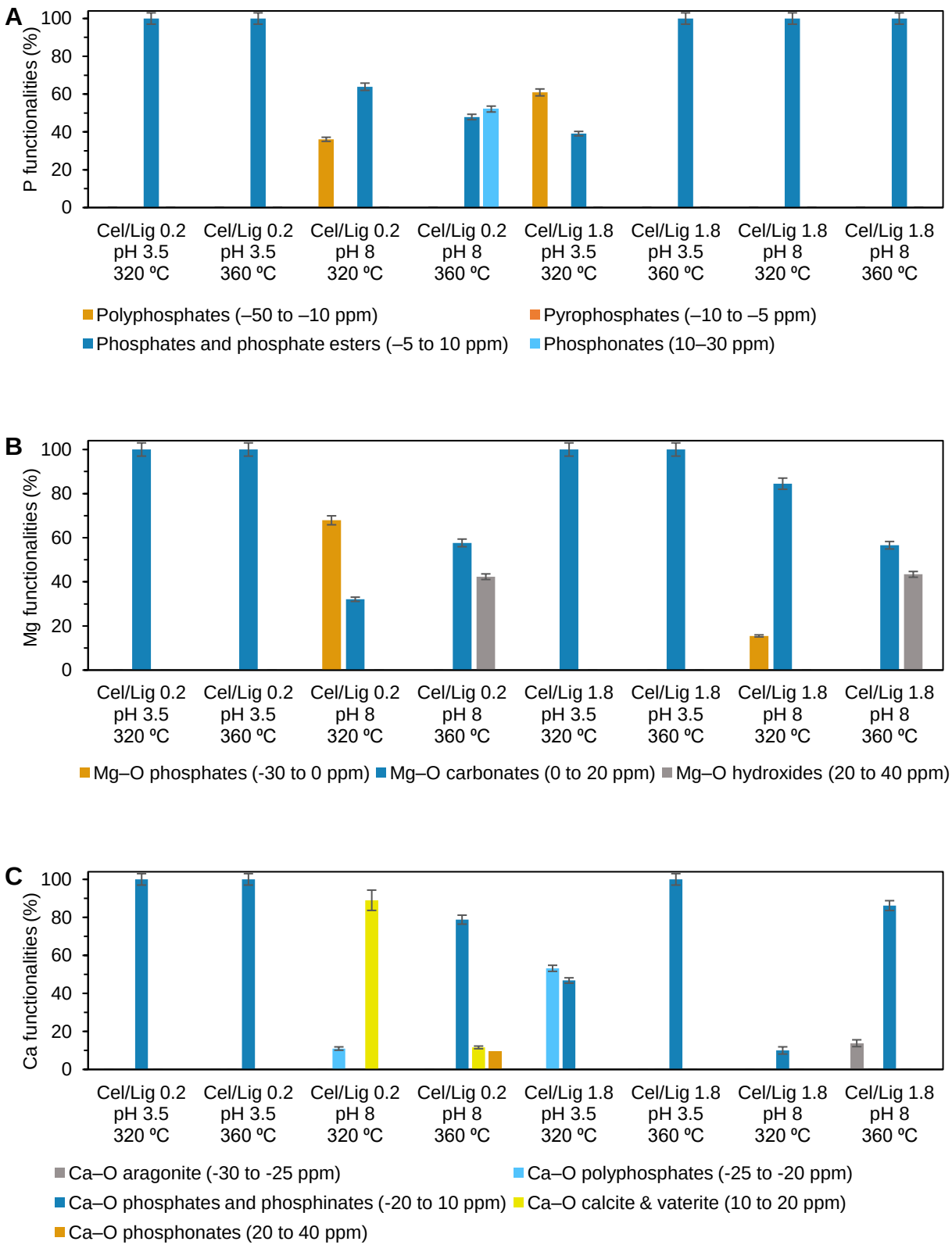


Table S1. Equation lists for product and element yields calculation.

Parameters	Equations
Product yield	$$Y_i = \frac{m_i}{m_{feedstock}} \times 100\%$$ *Y* is the mass yield, *i* indicates biocrude or hydro-char, *m* is mass (g), and $m_{\text{feedstock}}$ is the dry mass of feedstock (g).
The yield of carbon or nitrogen in the biocrude or hydrochar	$$X_{yield-i} = \frac{(\%X_i) \times m_i}{X_{feedstock}} \times 100\%$$ X_{yield} and $X_{feedstock}$ represent the product yield and mass in the feedstock (g), respectively of carbon or nitrogen, *i* indicates biocrude or hydrochar, and *%X* is the carbon or nitrogen content measured using Exeter Analytical CE-440.
The yield of carbon and nitrogen in the HTL-AP	$$C_{yield-AP} = \frac{[TOC]_{AP} \times (V_{AP})}{X_{feedstock}} \times 100\%$$ $$N_{yield-AP} = \frac{[TN]_{AP} \times (V_{AP})}{X_{feedstock}} \times 100\%$$ $C_{yield\text{-}AP}$ and $N_{yield\text{-}AP}$ are the carbon and nitrogen yield, respectively, in the HTL-AP and $[TOC]_{AP}$ and $[TN]_{AP}$ are the total concentration of organic carbon and nitrogen (mg/L), respectively.
The yield of carbon and nitrogen expelled to the gas phase during reaction ($C_{yield\text{-}Gas}$ and $N_{yield\text{-}Gas}$)	$$C_{yield-Gas} = 100\% - C_{yield-Biocrude} - C_{yield-HC} - C_{yield-AP}$$ $$N_{yield-Gas} = 100\% - N_{yield-Biocrude} - N_{yield-HC} - N_{yield-AP}$$
The yield of gas and aqueous-phase coproduct	$$Y_{Gas} = \frac{44}{12} \times \frac{C_{yield-Gas} \times C_{feedstock}}{m_{feedstock}} \times 100\%$$ $$Y_{AP} = 100\% - Y_{Biocrude} - Y_{HC} - Y_{Gas}$$
The yield of nutrient (*Z* – P, Ca, Mg, K, and Cl) in hydrochar (Z_{HC}) and HTL-AP (Z_{AP})	$$Z_{HC} = \frac{\%Z_{HC} \times m_{HC}}{Z_{feedstock}} \times 100\%$$ $$Z_{AP} = \frac{[Z]_{AP} \times V_{AP}}{Z_{feedstock}} \times 100\%$$ $Z_{feedstock}$ is the mass of *Z* in the feedstock (g), V_{AP} is the HTL-AP volume, and m_{HC} is the hydrochar mass (g), $\%Z_{HC}$ is the elemental content in hydrochar, and $[Z]_{AP}$ is the colorimetrically-measured nutrient concentration (mg/L).

Table S2. Operating conditions for DP-MAS solid-state NMR

Nuclei	Operating conditions					
	90º Pulse Length	Recycle Delay	MAS Rate	Number of transients	Proton-decoupling	Reference Compounds
^{13}C	2 μs	20 s	13 kHz	1024	Two-pulse phase-modulated proton-decoupling	Adamantane-d_{16} (≥ 98%, Sigma-Aldrich) with respect to tetramethylsilane (TMS)
^{31}P	4 μs	10 s	13 kHz	4096	Continuous heteronuclear decoupling ($^{31}P - {}^{1}H$) at 80 kHz	Triphenyl phosphate (*Trace*CERT, Supelco)
^{25}Mg	5 μs	10 s	13 kHz	3600	Continuous-wave (CW) proton decoupling at 42 kHz	1N $MgCl_2$ in D_2O (≥ 99%, Sigma Aldrich)
^{43}Ca	4 μs	4 s	12.5 kHz	3000	Spinal-64 ^{1}H decoupling at 100 kHz	1N $CaCl_2$ in D_2O (≥ 99%, Sigma Aldrich)

Table S3. The colorimetric concentration of different nitrogen species in the aqueous-phase coproducts.

HTL Operating Conditions					Nitrogen Species					
T, ºC	t, min	pH	Salt, wt%	Cel/Lig	$N_{organic}$, mg/l	NH_3-N, mg/l	NO_2^--N, mg/l	NO_3^--N, mg/l	N_2H_4-N, mg/l	Total Nitrogen, mg/l
320	50	3.5	5	0.2	383.6	751.1	1.16	10.4	9.2	1155.6
360	50	3.5	5	0.2	1024.6	2006.0	3.09	27.8	24.7	3086.2
320	50	8	5	0.2	596.6	1168.0	1.80	16.2	14.4	1796.9
360	50	8	5	0.2	182.8	357.9	0.55	5.0	4.4	550.7
320	50	3.5	5	1.8	1100.6	2154.9	3.32	29.8	26.5	3315.2
360	50	3.5	5	1.8	953.6	1867.0	2.87	25.9	23.0	2872.3
320	50	8	5	1.8	775.1	1517.6	2.33	21.0	18.7	2334.8
360	50	8	5	1.8	316.0	618.6	0.95	8.6	7.6	951.7

Table S4. The WPF and Rietveld refinement results for diffractograms of hydrochar produced from the HTL of digestates.

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Composition (wt%)	R_{Bragg} (%)	R_{WP} (%)	Crystallinity
Cel/Lig 0.2 pH 3.5 320 ºC	00-053-1717	Polyaniline	15.4 ± 1.1	6.34	10.14	75.93
	00-059-1090	1,2-Bis(2,6-dichlorobenzylidene)hydrazine	3.6 ± 0.6	7.28		
	00-055-1744	Ethyl-1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate	7.1 ± 0.3	8.55		
	00-055-1827	Indole-2-carboxylic acid 3,5-dinitrobenzoic acid	8.5 ± 1.8	5.72		
	00-054-2291	3,5-Diamino-1H-1,2,4-triazole	2.7 ± 0.6	6.06		
	00-051-2369	3-Amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2*H*-benzo[*e*][1,2]oxazin-6(5*H*)-one	4.5 ± 0.4	9.11		
	00-054-1622	2-(4-Hydroxyphenyl)acetonitrile	8.9 ± 0.9	8.35		
	00-015-0973	*N*,*N*-dimethyl-4-nitroaniline	19.8 ± 0.4	8.06		
	00-009-0080	Monetite	17.2 ± 1.4	5.69		
	00-020-0669	Nesquehonite	12.2 ± 0.3	6.99		
Cel/Lig 0.2 pH 3.5 360 ºC	00-048-2341	2-Aminoanthraquinone	7.2 ± 0.6	10.02	11.64	80.16
	00-062-1376	1-(Anthracen-9-yl)-*N*-(phenylmethyl)methanaminium chloride	10 ± 0.2	9.57		
	00-046-1758	2,5-Dihydroxy-p-benzoquinone	21.4 ± 0.7	8.75		
	00-055-1744	Ethyl-1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate	4.9 ± 0.5	8.04		
	00-037-1955	1*H*-Indoline-2,3-dione	12.9 ± 1.0	7.11		
	00-043-1767	(*E*)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene	3 ± 0.8	5.67		
	00-009-0080	Monetite	9.7 ± 0.3	6.16		
	01-086-0175	Magnesite	11 ± 0.4	6.36		
	00-055-0898	β-Tricalcium phosphate	19.9 ± 0.8	7.25		
Cel/Lig 0.2 pH 8 320 ºC	00-062-1368	5,6-Dimethoxy-2-(2-methoxyphenyl)benzofuran-3-carbonitrile	13.8 ± 0.6	9.46	12.07	82.86
	00-059-1090	1,2-Bis(2,6-dichlorobenzylidene)hydrazine	4.6 ± 0.2	7.37		

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Composition (wt%)	R_{Bragg} (%)	R_{WP} (%)	Crystallinity
	00-038-1730	Tetramethylammonium hydroxide pentahydrate	3.8 ± 0.1	7.05		
	00-059-1064	4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one	18.2 ± 0.9	8.18		
	00-062-1046	2-(2,4-dichlorophenoxy)-*N*-(3,4-dichlorophenyl)acetamide	3.7 ± 0.5	7.28		
	00-068-1289	(*Z*)-3-(1-((4-hydroxyphenyl)amino)-ethylidene)chromane-2,4-dione	19.2 ± 0.3	6.82		
	00-046-1716	Calcium ethylenediammonium cyclotetraphosphate dihydrate	5.5 ± 0.6	8.58		
	01-072-1358	Hydroxyl wagnerite	14.1 ± 0.7	8.19		
	01-086-4272	Calcite	9.6 ± 0.3	5.96		
	00-025-0531	Hydromagnesite	7.5 ± 0.4	5.89		
Cel/Lig 0.2 pH 8 360 ºC	00-014-0887	1,2-Dihydroxyanthraquinone	23.4 ± 0.4	10.49	10.38	86.35
	00-054-2290	5-Methyl-1*H*-tetrazole	3.9 ± 0.5	7.56		
	00-055-1762	Ethene-1,1-diaminium 3-nitro-1*H*-1,2,4-triazol-5-olate	6.1 ± 0.3	8.44		
	00-055-1773	5-Amino-3*H*-1,2,4-triazol-3-one	6.2 ± 0.6	8.39		
	00-054-2339	3-(2,4,5-Trichlorophenoxy)propanoic acid	8.4 ± 0.4	6.46		
	00-056-1803	Bis(2-ammonioethyl)ammonium 5-nitrosalicylate	4.7 ± 0.3	7.05		
	00-058-1458	2-Hydroxy-3-methyl-*N*-phenethylbutanamide	7.8 ± 0.2	6.84		
	00-069-0021	Hydroxyapatite methyl phosphonic dichloride	15.6 ± 1.3	9.48		
	00-066-0885	A-type carbonated apatite	16 ± 0.5	10.15		
	01-075-8878	Pokrovskite	4.4 ± 0.3	7.11		
	01-081-2503	Vaterite	3.5 ± 0.3	6.78		
Cel/Lig 1.8 pH 3.5 320 ºC	00-067-1136	5-Formyl-1*H*-pyrrole-2-carboxylic acid	10.7 ± 0.5	7.80	12.95	74.05
	00-051-2369	3-Amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2*H*-benzo[*e*][1,2]oxazin-6(5*H*)-one	7.5 ± 0.3	8.15		
	00-048-2136	3-(4-Methoxy-3-nitrobenzoyl)-1,2,2-trimethyl-cyclopentane-1-carboxylic acid	9.1 ± 0.4	6.94		
	00-043-1642	2-Methyl-cyclopentane-1,3-dione	11.9 ± 0.9	7.23		

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Composition (wt%)	R_{Bragg} (%)	R_{WP} (%)	Crystallinity
Cel/Lig 1.8 pH 3.5 360 ºC	00-069-1416	6-Methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	10.9 ± 1.1	8.23	10.96	91.82
	00-056-1846	1-(2,4-Dichlorophenyl)-2-(2-furylcarbonyl)ethanol	6.7 ± 0.3	9.55		
	00-051-2327	5-Hydroxy-4,8-dimethyl-4a,10a-dihydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-2-one	16.1 ± 0.2	6.03		
	01-076-4509	Troemelite	10.1 ± 0.8	9.16		
	00-009-0080	Monetite	7.5 ± 0.5	6.16		
	00-020-0669	Nesquehonite	9.4 ± 0.1	5.79		
	00-068-1288	(*Z*)-3-(1-((4-hydroxyphenyl)amino)-ethylidene)chromene-2,4-dione hydrate	10 ± 0.2	5.70		
	00-050-2384	1*H*-Pyrrole-2,5-dione	5 ± 0.1	5.93		
	00-048-2341	2-Aminoanthraquinone	14.1 ± 0.7	8.09		
	00-046-1758	2,5-Dihydroxy-p-benzoquinone	18.8 ± 0.9	5.78		
	00-044-1802	3-Methyl-2,3-dihydro-1*H*-indazol-3-ol	10.2 ± 0.3	5.98		
	00-060-1457	6-(2,3-Dichlorophenyl)-1,2,4-triazine-3,5-diamine dimethylformamide solvate	3.5 ± 0.2	6.04		
	00-025-1569	Calcium phosphinate acetylenedicarboxylate decahydrate	5.7 ± 0.3	9.26		
	00-009-0080	Monetite	8.8 ± 0.4	8.76		
	01-086-0175	Magnesite	10.9 ± 0.6	7.15		
	00-055-0898	β-TCP	12.9 ± 0.5	7.01		
Cel/Lig 1.8 pH 3.5 360 ºC	00-057-1224	3-Methyl-5-phenoxy-1*H*-pyrazole-4-carboxamide	9.7 ± 0.5	10.09	10.86	85.47
	00-048-2414	1-Methyl-4,5-diphenyl-3,4-dihydropyridin-2(1*H*)-one	22.3 ± 1.5	7.69		
	00-062-1368	5,6-Dimethoxy-2-(2-methoxyphenyl)benzofuran-3-carbonitrile	8.3 ± 0.3	5.81		
	00-038-1730	Tetramethylammonium hydroxide pentahydrate	2.7 ± 0.1	6.01		
	00-053-1398	(5-chloro-2-nitrophenyl)(λ^1-oxidaneyl)methanone·(4-	11.3 ± 0.4	6.64		

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Composition (wt%)	R_{Bragg} (%)	R_{WP} (%)	Crystallinity
		methoxyphenyl)(pyridin-4-yl)methanone				
	00-068-1289	(*Z*)-3-(1-((4-hydroxyphenyl)amino)-ethylidene)chromane-2,4-dione	6.6 ± 0.3	5.74		
	00-047-2253	4-(4-methoxy-2-methylphenethyl)aniline	9.0 ± 0.1	7.94		
	00-055-0592	Hydroxyapatite	14.7 ± 0.4	10.83		
	01-070-2064	Whitlockite	10.2 ± 0.2	9.85		
	00-025-0531	Hydromagnesite	5.2 ± 0.2	5.95		
Cel/Lig 1.8 pH 8 360 ºC	00-014-0887	1,2-Dihydroxyanthraquinone	16.1 ± 0.4	6.04	11.46	93.24
	00-054-2290	5-Methyl-1H-tetrazole	1.9 ± 0.1	5.73		
	00-055-1762	Ethene-1,1-diaminium 3-nitro-1*H*-1,2,4-triazol-5-olate	1.8 ± 0.1	9.06		
	00-055-1773	5-Amino-3*H*-1,2,4-triazol-3-one	4.4 ± 0.2	8.79		
	00-051-2160	2,3-Di(pyridin-2-yl)pyrazine 1-oxide	8.1 ± 0.6	7.95		
	00-051-2418	3,3-Diethyl-5-methylpiperidine-2,4-dione	18.1 ± 1.4	6.76		
	00-056-1803	Bis(2-ammonioethyl)ammonium 5-nitrosalicylate	2.2 ± 0.1	9.34		
	00-069-1336	Methyl nicotinate	7.7 ± 0.2	7.44		
	00-066-0885	A-type carbonated apatite	24.3 ± 0.6	7.15		
	01-075-9983	Aragonite	3.9 ± 0.4	7.35		
	01-086-0175	Magnesite	6.9 ± 0.3	8.37		
	01-075-8878	Pokrovskite	4.5 ± 0.9	9.09		

Table S5. The global WPF and Rietveld refinement parameters: (a) $R_{WP,expected}$, (b) goodness-of-fit (GOF), (c) polynomial coefficients for background fitting, (d) correction factors for zero offset, (d) skew, and (e) Lorentzian components

Operating Conditions	$R_{WP,\ expected}$ (%)	GOF	Polynomial Coefficients for Background Fitting	Zero Offset	Skew = s0 + s1 x 2θ + s2 x 2θ²	Lorentzian Component = p0 + p1 x 2θ
Cel/Lig 0.2 pH 3.5 320 ºC	9.24	1.10	c0 = 59.1957 c1 = -50.488 c2 = 73.9232 c3 = -81.0487 c4 = -81.3011 c5 = 100.446	0.03188	s0 = 0.16035 s1 = 0.01717 s2 = -0.43136	p0 = 0.55977 p1 = 0.30437
Cel/Lig 0.2 pH 3.5 360 ºC	9.75	1.19	c0 = 52.865 c1 = -39.791 c2 = 29.5528 c3 = -14.3716 c4 = -27.4027 c5 = 34.5093	0.02025	s0 = 0.07657 s1 = -0.00179 s2 = 0.00548	p0 = 0.49458 p1 = 0.0596
Cel/Lig 0.2 pH 8 320 ºC	9.57	1.26	c0 = 75.5173 c1 = -56.1838 c2 = 70.8742 c3 = -68.4163 c4 = -67.9919 c5 = 97.3807	0.02597	s0 = 0.11871 s1 = 0.50262 s2 = -0.00552	p0 = 0.50524 p1 = 0.1058
Cel/Lig 0.2 pH 8 360 ºC	9.68	1.07	c0 = 54.0208 c1 = -46.5546 c2 = 37.7602 c3 = -23.0276 c4 = -32.529 c5 = 43.4809	0.06898	s0 = 0.08917 s1 = 0.02838 s2 = 0.04914	p0 = 0.35587 p1 = -0.04341
Cel/Lig 1 pH 3.5 320 ºC	11.76	1.10	c0 = 44.8418 c1 = -34.1318 c2 = 5.24776 c3 = 12.2837	0.03454	s0 = 0.0985 s1 = 0.01412 s2 = 0.15485	p0 = 0.49043 p1 = 0.05384
Cel/Lig 1 pH 3.5 360 ºC	9.25	1.18	c0 = 65.5069 c1 = -51.194 c2 = 53.1437 c3 = -35.4933 c4 = -57.2507 c5 = 64.141	0.03192	s0 = -0.19069 s1 = 0 s2 = 0	p0 = 0.48135 p1 = 0
Cel/Lig 1 pH 3.5 360 ºC	9.16	1.19	c0 = 65.5782 c1 = -59.2886 c2 = 4.2048 c3 = 28.3708	0.06407	s0 = 0.14121 s1 = 0.17242 s2 = 0.07242	p0 = 0.38215 p1 = 0.0558
Cel/Lig 1 pH 8 360 ºC	9.51	1.21	c0 = 46.9688 c1 = -54.5649 c2 = 6.15403 c3 = 27.653	0.02387	s0 = 0.02649 s1 = -0.06423 s2 = -0.05071	p0 = 0.48513 p1 = 0.0271

Table S6. The phase-specific scale factor and coefficients for the full width at half maximum (FWHM) function generated from the WPF and Rietveld refinement of hydrochars' diffractograms.

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Refined Scale Factor	FWHM = f0 + f1 x 2θ + f2 x 2θ²
Cel/Lig 0.2 pH 3.5 320 ºC	00-053-1717	Polyaniline	3.9	f0 = 0.09466; f1 = -0.01522; f2 = 0.01906;
	00-059-1090	1,2-Bis(2,6-dichlorobenzylidene)hydrazine	0.9	f0 = 0.33335; f1 = -0.04168; f2 = 0.01498;
	00-055-1744	Ethyl-1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate	1.8	f0 = 0.06842; f1 = -0.04312; f2 = 0.06933;
	00-055-1827	Indole-2-carboxylic acid 3,5-dinitrobenzoic acid	2.2	f0 = 0.20663; f1 = -0.01568; f2 = 0.06051;
	00-054-2291	3,5-Diamino-1H-1,2,4-triazole	0.7	f0 = 0.10215; f1 = 0.03913; f2 = -0.05916;
	00-051-2369	3-Amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2*H*-benzo[*e*][1,2]oxazin-6(5*H*)-one	1.1	f0 = 0.43042; f1 = 0.33314; f2 = 0.52489;
	00-054-1622	2-(4-Hydroxyphenyl)acetonitrile	2.3	f0 = 0.10514; f1 = -0.01847; f2 = 0.10114;
	00-015-0973	*N*,*N*-dimethyl-4-nitroaniline	5.0	f0 = 0.10713; f1 = -0.01645; f2 = -0.00184;
	00-009-0080	Monetite	4.4	f0 = 0.50366; f1 = -0.08939; f2 = -0.1734;
	00-020-0669	Nesquehonite	3.1	f0 = 0.19023; f1 = -0.03407; f2 = -0.03467;
Cel/Lig 0.2 pH 3.5 360 ºC	00-048-2341	2-Aminoanthraquinone	1.6	f0 = 0.27121; f1 = -0.06718; f2 = -0.0727;
	00-062-1376	1-(Anthracen-9-yl)-*N*-(phenylmethyl)methanaminium chloride	2.3	f0 = 0.16414; f1 = -0.07914; f2 = 0.0;
	00-046-1758	2,5-Dihydroxy-p-benzoquinone	4.9	f0 = 0.46318; f1 = -0.09504; f2 = -0.14915;
	00-055-1744	Ethyl-1',3',3'-trimethyl-8-nitrospiro[chromene-2,2'-indoline]-5'-carboxylate	1.1	f0 = 0.21639; f1 = -0.05692; f2 = -0.04989;
	00-037-1955	1*H*-Indoline-2,3-dione	2.9	f0 = 1.2553; f1 = -0.31318; f2 = -0.28413;
	00-043-1767	(*E*)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene	0.7	f0 = 0.05944; f1 = -0.00895; f2 = 0.04279;
	00-009-0080	Monetite	2.2	f0 = 1.59637; f1 = 0.29212; f2 = -0.96029;
	01-086-0175	Magnesite	2.5	f0 = 1.72297; f1 = -0.09027; f2 = -0.1001;
	00-055-0898	β-Tricalcium phosphate	4.5	f0 = 0.23063; f1 = -0.00772; f2 = 0.05291;
Cel/Lig 0.2 pH 8 320 ºC	00-062-1368	5,6-Dimethoxy-2-(2-methoxyphenyl)benzofuran-3-carbonitrile	3.2	f0 = 0.22641; f1 = -0.05283; f2 = -0.04124;
	00-059-1090	1,2-Bis(2,6-dichlorobenzylidene)hydrazine	1.1	f0 = 0.27397; f1 = -0.10024; f2 = -0.05732;
	00-038-1730	Tetramethylammonium hydroxide pentahydrate	0.9	f0 = 0.10264; f1 = -0.0355; f2 = 0.06358;

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Refined Scale Factor	FWHM = f0 + f1 x 2θ + f2 x 2θ²
	00-059-1064	4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1*H*-pyrazol-3(2*H*)-one	4.2	f0 = 0.14301; f1 = -0.02857; f2 = 0.25721;
	00-062-1046	2-(2,4-dichlorophenoxy)-*N*-(3,4-dichlorophenyl)acetamide	0.8	f0 = 0.25713; f1 = -0.02038; f2 = 0.10009;
	00-068-1289	(*Z*)-3-(1-((4-hydroxyphenyl)amino)-ethylidene)chromane-2,4-dione	4.4	f0 = 0.09496; f1 = -0.02075; f2 = 0.0125;
	00-046-1716	Calcium ethylenediammonium cyclotetraphosphate dihydrate	1.3	f0 = 0.19132; f1 = 0.02579; f2 = 0.01184;
	01-072-1358	Hydroxyl wagnerite	3.2	f0 = 0.54373; f1 = -0.06168; f2 = -0.19124;
	01-086-4272	Calcite	2.2	f0 = 1.65315; f1 = 0.47743; f2 = -0.96238;
	00-025-0531	Hydromagnesite	1.7	f0 = 0.88092; f1 = -0.34167; f2 = 0.0;
Cel/Lig 0.2 pH 8 360 ºC	00-014-0887	1,2-Dihydroxyanthraquinone	4.7	f0 = 0.44208; f1 = -0.07084; f2 = -0.09334;
	00-054-2290	5-Methyl-1*H*-tetrazole	0.8	f0 = 0.2429; f1 = 0.05248; f2 = 0.06432;
	00-055-1762	Ethene-1,1-diaminium 3-nitro-1*H*-1,2,4-triazol-5-olate	1.2	f0 = 2.40666; f1 = -3.56213; f2 = 1.82797;
	00-055-1773	5-Amino-3*H*-1,2,4-triazol-3-one	1.2	f0 = 0.89039; f1 = -1.89266; f2 = 1.49957;
	00-054-2339	3-(2,4,5-Trichlorophenoxy)propanoic acid	1.7	f0 = 0.06428; f1 = 0.11408; f2 = -0.1008;
	00-056-1803	Bis(2-ammonioethyl)ammonium 5-nitrosalicylate	0.9	f0 = 0.65247; f1 = -0.33681; f2 = 0.0;
	00-058-1458	2-Hydroxy-3-methyl-*N*-phenethylbutanamide	1.6	f0 = 0.29806; f1 = 0.00075; f2 = 0.02059;
	00-069-0021	Hydroxyapatite methyl phosphonic dichloride	3.1	f0 = 0.16612; f1 = 0.0; f2 = 0.0;
	00-066-0885	A-type carbonated apatite	3.2	f0 = 0.16236; f1 = 0.00132; f2 = -0.01369;
	01-075-8878	Pokrovskite	0.9	f0 = 0.30566; f1 = 0.04533; f2 = 0.07523;
	01-081-2503	Vaterite	0.7	f0 = 1.20075; f1 = 0.0; f2 = 0.0;
Cel/Lig 1.8 pH 3.5 320 ºC	00-067-1136	5-Formyl-1*H*-pyrrole-2-carboxylic acid	4.1	f0 = 0.09111; f1 = -0.01211; f2 = 0.02116;
	00-051-2369	3-Amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2*H*-benzo[*e*][1,2]oxazin-6(5*H*)-one	2.9	f0 = 0.16666; f1 = 0.0; f2 = 0.0;
	00-048-2136	3-(4-Methoxy-3-nitrobenzoyl)-1,2,2-trimethyl-cyclopentane-1-carboxylic acid	3.5	f0 = 0.22782; f1 = 0.0; f2 = 0.0;
	00-043-1642	2-Methyl-cyclopentane-1,3-dione	4.6	f0 = 1.41023; f1 = 0.01183; f2 = 0.06152;

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Refined Scale Factor	FWHM = f0 + f1 x 2θ + f2 x 2θ²
	00-069-1416	6-Methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	4.2	f0 = 0.51023; f1 = 0.09831; f2 = 0.16043;
	00-056-1846	1-(2,4-Dichlorophenyl)-2-(2-furylcarbonyl)ethanol	2.6	f0 = 0.52098; f1 = 0.16247; f2 = 0.31725;
	00-051-2327	5-Hydroxy-4,8-dimethyl-4a,10a-dihydro-2*H*,6*H*-pyrano[3,2-*g*]chromen-2-one	6.2	f0 = 0.17498; f1 = -0.00612; f2 = 0.00912;
	01-076-4509	Troemelite	3.9	f0 = 0.0696; f1 = -0.02283; f2 = 0.13723;
	00-009-0080	Monetite	2.9	f0 = 0.46706; f1 = 0.11156; f2 = 0.00771;
	00-020-0669	Nesquehonite	3.6	f0 = 0.07882; f1 = -0.00837; f2 = 0.00225;
Cel/Lig 1.8 pH 3.5 360 ºC	00-068-1288	(*Z*)-3-(1-((4-hydroxyphenyl)amino)-ethylidene)chromene-2,4-dione hydrate	2.8	f0 = 0.15852; f1 = -0.02152; f2 = -0.02252;
	00-050-2384	1*H*-Pyrrole-2,5-dione	1.4	f0 = 0.23234; f1 = -0.03375; f2 = 0.0;
	00-048-2341	2-Aminoanthraquinone	4.0	f0 = 0.47114; f1 = -0.01464; f2 = -0.05639;
	00-046-1758	2,5-Dihydroxy-p-benzoquinone	5.3	f0 = 1.06376; f1 = -0.11534; f2 = 0.0;
	00-044-1802	3-Methyl-2,3-dihydro-1*H*-indazol-3-ol	2.9	f0 = 0.25035; f1 = -0.01125; f2 = 0.03098;
	00-060-1457	6-(2,3-Dichlorophenyl)-1,2,4-triazine-3,5-diamine dimethylformamide solvate	1.0	f0 = 0.69397; f1 = -0.06813; f2 = -0.28169;
	00-025-1569	Calcium phosphinate acetylenedicarboxylate decahydrate	1.6	f0 = 0.30074; f1 = 0.02469; f2 = 0.12931;
	00-009-0080	Monetite	2.5	f0 = 1.38821; f1 = -0.09497; f2 = -0.05629;
	01-086-0175	Magnesite	3.1	f0 = 0.26511; f1 = -0.01798; f2 = 0.10129;
	00-055-0898	β-TCP	3.7	f0 = 0.92606; f1 = -0.08864; f2 = 0.62359;
Cel/Lig 1.8 pH 3.5 360 ºC	00-057-1224	3-Methyl-5-phenoxy-1*H*-pyrazole-4-carboxamide	2.1	f0 = 0.66781; f1 = -0.05897; f2 = 0.59681;
	00-048-2414	1-Methyl-4,5-diphenyl-3,4-dihydropyridin-2(1*H*)-one	4.9	f0 = 1.48831; f1 = -0.12787; f2 = 1.12835;
	00-062-1368	5,6-Dimethoxy-2-(2-methoxyphenyl)benzofuran-3-carbonitrile	1.8	f0 = 0.16775; f1 = -0.01298; f2 = 0.19827;
	00-038-1730	Tetramethylammonium hydroxide pentahydrate	0.6	f0 = 0.5742; f1 = -0.04132; f2 = 0.72391;
	00-053-1398	(5-chloro-2-nitrophenyl)(λ^1-oxidaneyl)methanone·(4-methoxyphenyl)(pyridin-4-yl)methanone	2.5	f0 = 0.45046; f1 = 0.0; f2 = 0.0;

Operating Conditions	PDF ID	Detected Organic/Mineral Phases	Refined Scale Factor	FWHM = f0 + f1 x 2θ + f2 x 2θ²
	00-068-1289	(*Z*)-3-(1-((4-hydroxyphenyl)amino)-ethylidene)chromane-2,4-dione	1.5	f0 = 0.17944; f1 = 0.02728; f2 = 0.03379;
	00-047-2253	4-(4-methoxy-2-methylphenethyl)aniline	2.0	f0 = 0.05207; f1 = -0.03914; f2 = 0.15497;
	00-055-0592	Hydroxyapatite	3.2	f0 = 0.08458; f1 = -0.02891; f2 = 0.14367;
	01-070-2064	Whitlockite	2.2	f0 = 0.0991; f1 = -0.0435; f2 = 0.1092;
	00-025-0531	Hydromagnesite	1.1	f0 = 0.12433; f1 = -0.01123; f2 = -0.00418;
Cel/Lig 1.8 pH 8 360 ºC	00-014-0887	1,2-Dihydroxyanthraquinone	3.3	f0 = 0.22801; f1 = 0.02146; f2 = 0.14655;
	00-054-2290	5-Methyl-1H-tetrazole	0.4	f0 = 0.14384; f1 = -0.03373; f2 = 0.0;
	00-055-1762	Ethene-1,1-diaminium 3-nitro-1*H*-1,2,4-triazol-5-olate	0.4	f0 = 1.82326; f1 = -0.13282; f2 = -0.26647;
	00-055-1773	5-Amino-3*H*-1,2,4-triazol-3-one	0.9	f0 = 0.06321; f1 = 0.0075; f2 = 0.04839;
	00-051-2160	2,3-Di(pyridin-2-yl)pyrazine 1-oxide	1.7	f0 = 0.15589; f1 = -0.01237; f2 = 0.0;
	00-051-2418	3,3-Diethyl-5-methylpiperidine-2,4-dione	3.7	f0 = 1.98286; f1 = -0.23916; f2 = 2.28412;
	00-056-1803	Bis(2-ammonioethyl)ammonium 5-nitrosalicylate	0.5	f0 = 0.35597; f1 = -0.02374; f2 = 0.0;
	00-069-1336	Methyl nicotinate	1.6	f0 = 1.99489; f1 = =-0.23981; f2 = 1.81236;
	00-066-0885	A-type carbonated apatite	5.0	f0 = 0.15612; f1 = -0.0357; f2 = 0.26493;
	01-075-9983	Aragonite	0.8	f0 = 0.20504; f1 = -0.00431; f2 = 0.05502;
	01-086-0175	Magnesite	1.4	f0 = 0.08613; f1 = -0.01203; f2 = 0.02482;
	01-075-8878	Pokrovskite	0.9	f0 = 0.19628; f1 = -0.00184; f2 = -0.00391;

Table S7. Percent contribution of elements from detected minerals to the total content of corresponding elements in the hydrochar.

HTL Conditions	Detected Minerals by XRD	XRD			NMR		
		$\%P_{contributed}$	$\%Ca_{contributed}$	$\%Mg_{contributed}$	$\%P_{contributed}$	$\%Ca_{contributed}$	$\%Mg_{contributed}$
Cel/Lig 0.2 pH 3.5 320 ºC	Monetite	100%	100%	0%	100%	100%	0%
	Nesquehonite	0%	0%	100%	0%	0%	100%
Cel/Lig 0.2 pH 3.5 360 ºC	Monetite	35.7%	27.0%	0%	33.9%	28.2%	0%
	Magnesite	0%	0%	100%	0%	0%	100%
	β-Tricalcium phosphate	64.3%	73.0%	0%	66.1%	71.8%	0%
Cel/Lig 0.2 pH 8 320 ºC	Calcium ethylenediammonium cyclotetraphosphate dihydrate	35.5%	11.2%	0%	36.1%	11.0%	0%
	Hydroxyl wagnerite	64.5%	0%	68.7%	63.9%	0%	67.9%
	Calcite	0%	88.8%	0%	0%	89.0%	0%
	Hydromagnesite	0%	0%	31.3%	0%	0%	32.1%
Cel/Lig 0.2 pH 8 360 ºC	Hydroxyapatite methyl phosphonic dichloride	53.1%	28.4%	0%	52.1%	27.6%	0%
	A-type carbonated apatite	46.9%	58.4%	0%	47.9%	60.8%	0%
	Pokrovskite	0%	0%	100%	0%	0%	100%
	Vaterite	0%	13.2%	0%	0%	11.6%	0%
Cel/Lig 1.8 pH 3.5 320 ºC	Troemelite	62.8%	53.0%	0%	60.9%	53.2%	0%
	Monetite	37.2%	47.0%	0%	39.1%	46.8%	0%
	Nesquehonite	0%	0%	100%	0%	0%	100%
Cel/Lig 1.8 pH 3.5 360 ºC	Calcium phosphinate acetylenedicarboxylate decahydrate	19.6%	8.7%	0%	19%	7.9%	0%
	Monetite	35.2%	31.2%	0%	35%	31.6%	0%
	Magnesite	0%	0%	100%	0%	0%	100%
	β-TCP	45.2%	60.1%	0%	46%	60.5%	0%
Cel/Lig 1.8 pH 3.5 360 ºC	Hydroxyapatite	56.4%	62.6%	0%	56.7%	63.2%	0%
	Whitlockite	43.6%	37.4%	14.8%	43.3%	36.8%	15.5%
	Hydromagnesite	0%	0%	85.2%	0%	0%	84.5%
Cel/Lig 1.8 pH 8 360 ºC	A-type carbonated apatite	100%	85.8%	0%	100%	86.2%	0%
	Aragonite	0%	14.2%	0%	0%	13.8%	0%
	Magnesite	0%	0%	56.4%	0%	0%	56.6%
	Pokrovskite	0%	0%	43.6%	0%	0%	43.4%

Table S8. Comparison between the C, P, Ca, and Mg content of hydrochar estimated using SS-NMR and directly measured using the elemental analyzers.

HTL Process Conditions	Techniques	%C	%P	%Ca	%Mg
Cel/Lig 0.2 pH 3.5 320 ºC	Elemental Analyzer	45.22 ± 0.90	3.92 ± 0.20	5.06 ± 0.51	2.12 ± 0.11
	SS-NMR	45.04 ± 0.69	3.89 ± 0.93	5.15 ± 0.92	2.08 ± 0.20
Cel/Lig 0.2 pH 3.5 360 ºC	Elemental Analyzer	39.51 ± 0.79	6.19 ± 0.31	10.56 ± 1.06	3.14 ± 0.16
	SS-NMR	39.61 ± 0.36	6.39 ± 1.59	10.62 ± 0.77	3.25 ± 0.15
Cel/Lig 0.2 pH 8 320 ºC	Elemental Analyzer	40.86 ± 0.82	4.23 ± 0.21	4.32 ± 0.43	6.16 ± 0.31
	SS-NMR	40.67 ± 0.52	4.25 ± 0.75	4.45 ± 0.79	6.2 ± 0.13
Cel/Lig 0.2 pH 8 360 ºC	Elemental Analyzer	32.54 ± 0.98	6.16 ± 0.31	10.63 ± 1.08	1.49 ± 0.17
	SS-NMR	32.33 ± 0.41	6.26 ± 1.01	10.53 ± 0.68	1.53 ± 0.43
Cel/Lig 1 pH 3.5 320 ºC	Elemental Analyzer	46.89 ± 1.41	4.6 ± 0.23	4.69 ± 0.49	1.63 ± 0.09
	SS-NMR	46.72 ± 0.64	4.63 ± 0.25	4.76 ± 0.63	1.67 ± 0.19
Cel/Lig 1 pH 3.5 360 ºC	Elemental Analyzer	39.49 ± 0.79	5.7 ± 0.29	8.3 ± 0.82	3.11 ± 0.16
	SS-NMR	39.52 ± 0.39	5.76 ± 0.18	8.32 ± 0.29	3.3 ± 0.26
Cel/Lig 1 pH 3.5 360 ºC	Elemental Analyzer	47.81 ± 0.96	4.83 ± 0.24	9.35 ± 0.96	1.57 ± 0.08
	SS-NMR	47.75 ± 0.60	4.9 ± 0.29	9.4 ± 0.32	1.69 ± 0.24
Cel/Lig 1 pH 8 360 ºC	Elemental Analyzer	38.11 ± 1.14	4.39 ± 0.22	11 ± 0.83	3.49 ± 0.87
	SS-NMR	38.31 ± 0.51	4.44 ± 0.39	11.03 ± 0.21	3.58 ± 0.11

Table S9. Comparison between the elemental content or concentration of biocrude oil and HTL-AP estimated using liquid-state NMR and directly measured using the elemental analyzers.

HTL Process Conditions	Techniques	Biocrude				HTL-AP		
		%C	%H	%N	%O	[C], mg/L	[N], mg/L	[P], mg/L
Cel/Lig 0.2 pH 3.5 320 ºC	Elemental Analyzer	55.62 ± 0.15	5.34 ± 0.16	1.25 ± 0.09	37.79 ± 0.05	9981.85	1155.56	1183.03
	Liquid-state NMR	55.89 ± 0.09	5.37 ± 0.26	1.26 ± 0.04	37.98 ± 0.23	10012.33	1190.23	1193.32
Cel/Lig 0.2 pH 3.5 360 ºC	Elemental Analyzer	55.93 ± 0.20	5.38 ± 0.11	1.44 ± 0.19	37.24 ± 0.45	7972.88	3086.17	866.78
	Liquid-state NMR	55.57 ± 0.14	5.35 ± 0.09	1.44 ± 0.26	37 ± 0.41	8018.68	3147.89	884.12
Cel/Lig 0.2 pH 8 320 ºC	Elemental Analyzer	60.11 ± 0.12	5.62 ± 0.22	1.45 ± 0.30	32.83 ± 0.35	8678.44	1796.91	247.98
	Liquid-state NMR	60.41 ± 0.36	5.64 ± 0.12	1.46 ± 0.17	32.99 ± 0.36	8791.47	1868.79	242.03
Cel/Lig 0.2 pH 8 360 ºC	Elemental Analyzer	59.71 ± 0.19	5.59 ± 0.24	1.66 ± 0.10	33.05 ± 0.26	10273.74	550.66	166.15
	Liquid-state NMR	60 ± 0.27	5.62 ± 0.20	1.66 ± 0.34	33.21 ± 0.22	10229.05	539.65	174.46
Cel/Lig 1 pH 3.5 320 ºC	Elemental Analyzer	51.31 ± 0.13	5.12 ± 0.16	1.85 ± 0.41	41.72 ± 0.26	14515.33	3315.19	1446.08
	Liquid-state NMR	50.98 ± 0.29	5.08 ± 0.14	1.84 ± 0.24	41.46 ± 0.38	14449.39	3348.34	1489.47
Cel/Lig 1 pH 3.5 360 ºC	Elemental Analyzer	54.79 ± 0.21	5.48 ± 0.32	1.96 ± 0.14	37.78 ± 0.28	9081.02	2872.3	1418.22
	Liquid-state NMR	55.06 ± 0.28	5.5 ± 0.11	1.97 ± 0.16	37.97 ± 0.18	9205.23	2840.7	1375.67
Cel/Lig 1 pH 3.5 360 ºC	Elemental Analyzer	65.27 ± 0.31	6.34 ± 0.24	2.35 ± 0.27	26.04 ± 0.19	7915.84	2334.77	679.95
	Liquid-state NMR	64.85 ± 0.30	6.3 ± 0.26	2.33 ± 0.22	25.87 ± 0.20	7777.59	2381.47	720.75
Cel/Lig 1 pH 8 360 ºC	Elemental Analyzer	63.14 ± 0.29	6.15 ± 0.15	2.4 ± 0.39	28.31 ± 0.29	7249.48	951.68	953.53
	Liquid-state NMR	63.46 ± 0.41	6.18 ± 0.05	2.41 ± 0.45	28.45 ± 0.06	7312.5	946.92	991.67

BIOCRUDE OIL COMPOSITION

Table S10. Chemical composition of biocrude oil from HTL of lignin-rich digestates at pH 3.5 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
aniline	115.07, 118.39, 129.30, 146.50	2.0%
4-methyl-N,N-diphenylaniline	20.57, 122.13, 123.25, 124.5, 128, 129.6, 132.5, 145.5, 147.5	1.5%
2,4-dimethylaniline	17.05, 20.25, 115, 122.5, 127.5, 131, 143.15	1.7%
N,N-dimethylbenzylamine	45, 64.55, 126.5, 128, 139.5	1.0%
n-nonylamine	14.86, 23.5, 27.5, 29.85, 32, 34.5, 42	1.0%
N-phenylacetamide	33.43, 131.13, 132.50, 136.58, 173.34	2.3%
Subtotal amine & amide		*9.5%*
nitrosalicylaldehyde	119.86, 130.04, 131.88, 140.01, 167.68, 196.34	4.7%
4-hydroxy-benzenemethanol	63.5, 115, 128.5, 132, 156.5	3.7%
2-methoxy-4-vinylphenol	55.4, 107, 11, 114.6, 120.5, 130.3, 136.8, 145.7, 146.5	3.0%
4-ethyl-2-methoxyphenol	16, 19, 56, 110.15, 119.35, 120.2, 136, 144, 146	3.7%
2-methoxy-4-methoxymethyl-phenol	55.55, 57.5, 74.56, 110.67, 114.55, 120.5, 130, 145.5, 146.9	3.9%
4-hydroxy-3-methoxy-benzyl alcohol	58.2, 66.8, 115, 124, 135.5, 147, 150	3.0%
Subtotal phenols		*22.0%*
3,5-dinitrobenzoic acid	121.96, 129.06, 134.61, 148.76, 163.82	5.3%
1,2,2-trimethyl-cyclopentane-1,3-dioic acid	20.92, 21.43, 22.32, 46.76, 52.33, 56.80, 175.24,177.16	3.2%
Subtotal carboxylic acid & ester		*8.5%*
benzophenone	128.21, 129.96, 132.33, 137.58, 196.50	4.3%
2,5-furandione	10.04, 142.11, 167.45	3.8%
5-methyl-2-(1-methylethyl)-cyclohexanone	19.5, 22.3, 25, 29.4, 30.05, 30.65, 34.3, 36.2, 44, 48.5, 52, 60.65, 77.5, 78, 210.3	2.6%
3-methyl-2-cyclopenten-1-one	19.5, 34, 35.3, 130.5, 179, 209	2.5%
2,3-dimethyl-2-cyclopenten-1-one	7.5, 16.8, 31, 34, 136, 169.5, 209.2	1.7%
Subtotal ketone		*14.9%*
trimethyl indole	15.11, 22.66, 56.87, 121, 123, 125, 126, 139.01, 150.57, 190.02	2.4%
2-acetyl-pyrrole	25.6, 76,78, 79.5, 110.5, 117.5, 125.5	2.2%
3-methyl pyrrole	11.87, 109.6, 115.3, 117.5	1.1%
1-methyl-2-pyrrolidone	18.1, 29.6, 30.4, 49.6, 175	1.5%
1H-indole-2-carboxylic acid	101.14, 105.26, 129.31, 132.04, 145.66, 151.19, 164.32	1.5%
Subtotal N-heterocyclic		*8.7%*
phenylhydrazine	112.04, 119.82, 129.06, 151.87	4.6%
Subtotal azine & nitrile		*4.6%*
phenanthrene	66.9, 76.75, 122.5, 126.5, 128.5, 130, 131.7	4.5%
pyrene	124.6, 125.3, 127.5, 131	2.9%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
α-phellandrene	20, 20.75, 26, 31.5, 40, 120.5, 128, 131, 131.46	3.5%
n-tetradecane	14.8, 23.5, 29.4, 32.5	2.6%
Subtotal alkane		*13.5%*
1,3-benzodioxole	100.2, 108.2, 121.7, 153.6	5.3%
(Z)-5-(propen-1-yl)-1,3-benzodioxole	14, 102, 108.2, 109.6, 125.5, 133.5, 146, 148, 149.6	2.3%
2-ethyl-furan	12.5, 21, 104, 110, 140.5, 158	2.5%
2H-chromen-2-one	79.7, 119.3, 127.5, 130, 134, 146.4, 156.8, 163.8	5.2%
3,5,7-trihydroxy-2H-1-benzopyran-2-one	102.5, 111, 112.5, 129.6, 144.65, 155.5, 160.5, 161.2	3.0%
Subtotal furans, ether, & O-heterocyclic		*18.3%*
Total		100%

Table S11. Chemical composition of biocrude oil from HTL of lignin-rich digestates at pH 3.5 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
1-pentanamine	13.8, 23, 29.5, 34, 42.5	3.5%
1-butanamine	14, 20.3, 36, 41.7	3.0%
1-hexanamine	14. 22.5, 26.5, 32, 34, 42	2.1%
Subtotal amine & amide		*8.6%*
nitrosalicylaldehyde	119.86, 130.04, 131.88, 140.01, 167.68, 196.34	4.7%
3-ethyl-5-methyl-phenol	13.6, 20.3, 17.5, 113.8, 115.5, 125.5, 137.8, 143.3, 153.5	4.0%
4-hydroxybenzyl alcohol	63.75, 115, 127.9, 132, 166.5	3.3%
4-ethyl-2-methoxyphenol	16, 29.2, 55.5, 110.3, 114, 120.2, 136, 143.7, 146	3.7%
2,6-dimethoxy-phenol	56, 105.6, 119, 135.4, 147.5	4.3%
2-methoxy-4-methoxymethyl-phenol	55.55, 57.5, 74.56, 110.67, 114.55, 120.5, 130, 145.5, 146.9	1.6%
Subtotal phenols		*21.6%*
quinic acid	40.11, 43.42, 69.71, 73.15, 77.94, 79.74, 184.16	3.4%
3,4-dimethoxymandelic acid methyl ester	52.5, 72.5, 76, 77.5, 126.5, 128.8, 138, 173.9	2.5%
3-methyl-4-propyl-2,4-hexadienedioic acid dimethyl ester	17.5, 19.7, 28.2, 37.5, 41, 41.8, 51, 173, 177	4.1%
3-phenylcoumarin	75.5, 77, 78.5, 116, 120, 124.5, 128.6, 131, 134.7, 140, 153.7, 160	4.2%
Subtotal carboxylic acid & ester		*14.2%*
benzoquinone	136.84, 188.65	2.3%
benzophenone	128.21, 129.96, 132.33, 137.58, 196.50	2.5%
cyclopentenone	29.08, 34.68, 135.04, 166.73, 213.94	4.4%
2-methyl-2-cyclopenten-1-one	10, 26, 34.3, 142, 158, 210	2.2%
Subtotal ketone		*11.4%*
trimethyl indole	15.11, 22.66, 56.87, 121, 123, 125, 126, 139.01, 150.57, 190.02	3.1%
1-methyl-pyrrolidine	24, 41.6, 56	1.1%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
3,6-bis(2-methylpropyl)-2,5-piperazinedione	40.3, 45, 57, 128, 129.5, 131.5, 137.5, 166.8, 169	1.2%
1-ethyl-2,6-dimethylpiperidine	23.2, 25, 34, 52.4	1.0%
Subtotal N-heterocyclic		*6.4%*
1,2-bis(diphenylmethylene)-hydrazine	127.95, 128.55, 129.25	1.0%
phenylhydrazine	112.04, 119.82, 129.06, 151.87	3.2%
Subtotal azine & nitrile		*4.2%*
1,3-butadiene	117.25, 138.3	3.1%
1-phenyl-1-butene	14, 21.4, 131, 134, 134.7, 138.2	1.0%
α-phellandrene	20, 20.75, 26, 31.5, 40, 120.5, 128, 131, 131.46	1.6%
anthracene	125.57, 126.23, 129.26, 132.35	5.5%
1,5,8-p-menthatriene	49.8, 62, 77, 113.5, 122.2, 123.21, 126.89, 129.94, 131.41, 147.53, 157.35	1.6%
chrysene	121.3, 122.78, 126.2, 127.5, 128.66, 130.5, 132	2.3%
perylene	120.3, 126.5, 128, 129, 131, 135	1.0%
Subtotal alkane		*16.1%*
2-methyl-furan	13.20, 106.78, 110.52, 140.46, 152.04	5.4%
3,5,7-trihydroxy-2H-1-benzopyran-2-one	102.5, 111, 112.5, 129.6, 144.65, 155.5, 160.5, 161.2	4.2%
2,3-dihydrobenzofuran	29.65, 70.5, 109.3, 120.3, 125, 127, 127.5, 160	3.9%
1,3-benzodioxane-5-ol	100.2, 108.3,120.2, 147.8	4.0%
Subtotal furans, ether, & O-heterocyclic		*17.5%*
Total		100%

Table S12. Chemical composition of biocrude oil from HTL of lignin-rich digestates at pH 8 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
13-docosenamide	14, 22.25, 25.5, 27, 29.2, 31.57, 35.5, 129.6, 175.6	8.1%
9-octadecenamide	14.5, 22.5, 26, 27, 29.5, 32, 36.5, 130, 176.8	6.0%
Subtotal amine & amide		*14.1%*
2-ethoxy-5-(1-propenyl)phenol	14.56, 18, 65, 76, 77.5, 79, 112, 118.5, 124, 131, 132, 145, 145.5	4.7%
4-ethyl-2-methoxyphenol	16, 29, 55.5, 110.3, 114, 120.3, 136, 143.5, 145.5	6.4%
4-chlorodiphenyl ether	119, 120, 124, 128.5, 129.6, 155.5, 156.1	3.3%
2,4-dinitro-phenetole	66.72, 121,04, 158.89, 140, 131.5, 131.04	9.1%
2,4-dihydroxy-phenetole	104.04, 105.5, 116.04, 137.5, 145.5, 150.5	4.9%
2,6-dimethoxyphenol	56, 105.5, 119.3, 135.5, 147.5	1.2%
4-hydroxy-3-methoxy-benzyl alcohol	58.2, 66.8, 115, 124, 135.5, 147, 150	1.4%
Subtotal phenols		*31.0%*
2-formyl-6-hydroxy-3,4-dimethoxybenzoic acid	56.07, 110.5, 112.59, 121.89, 124.67, 148.84, 153.90, 172.09	4.5%
isoamyl acetate	20.5, 22.5, 25.5, 38.1, 63	2.8%
Subtotal carboxylic acid & ester		*7.3%*
benzophenone	128.21, 129.96, 132.33, 137.58, 196.50	5.3%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
3-ethyl-2-cyclopenten-1-one	19.5, 32.5, 35.5, 130.5, 179, 209	4.3%
carvone	15.5, 20.5, 3, 42.5, 109, 136, 144.5, 147, 199.8	2.7%
Subtotal ketone		*12.3%*
2-phenyl-1H-pyrazol-3(2H)-one	120, 122, 127, 129, 138, 139, 150, 158, 215	4.3%
2-ethyl-pyrazine	13.2, 29, 142, 144.4, 159	1.6%
pyrazinamide	67.5, 136, 139.8, 150, 165.6	1.5%
5-methylpyrazine-2-carboxylic acid	21, 141, 144.5, 157, 165	2.1%
3-ethyl-2,5-dimethyl-pyrazine	12.5, 20.7, 28.5, 140.5, 143.5, 150.5, 160.25	1.4%
4-(anilinomethylene)-3-methyl-2-pyrazolin-5-one	12.5, 102, 117, 124.8, 129.65, 139, 144, 147.5, 169	1.3%
5-methyl-1H-indole-2,3-dione	20.2, 112, 117.5, 124.7, 132.5, 139, 148.6, 159.8, 184.65	1.9%
1-phenyl-1H-indole-2,3-dione	40, 110.3, 117.5, 123.5, 124, 126, 128, 129.5, 132.5, 137.5, 151.5, 157, 182.5	1.2%
carbazole	110.5, 118, 119.5, 122.5, 125.5, 140	1.0%
Subtotal N-heterocyclic		*16.3%*
phenylhydrazine	112.04, 119.82, 129.06, 151.87	2.8%
Subtotal azine & nitrile		*2.8%*
benzodioxane	64.33, 117.06, 120.93, 144.13	4.2%
3-acetyl-4-hydroxy-2H-chromen-2-one	116.51, 118.89, 124.43, 127.95, 131.79, 143.48, 153.99, 160.63	2.3%
dihydro-2,5-furandione	111.5, 113.5, 119.6, 121.5, 122.5, 124, 127, 128, 129.5, 137.5, 138.4	2.5%
2-phenoxymethyl-oxirane	44, 50, 68.5, 114.5, 121, 129.5, 158.7	1.0%
7-carboxycoumarin	118, 122.5, 126, 129, 134.8, 144.5, 153.75, 161, 167.5	1.5%
7-diethylamino-4-methylcoumarin	12.3, 18.4, 44.6, 97.5, 108.5, 125.5, 151, 152.5, 156, 162	1.3%
4-hydroxy-2H-chromen-2-one	91.5, 116, 124, 132.3, 154, 163, 166	3.4%
Subtotal furans, ether, & O-heterocyclic		*16.2%*
Total		100%

Table S13. Chemical composition of biocrude oil from HTL of lignin-rich digestates at pH 8 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
N,N-dimethylbenzamide	35.5, 39, 127, 128.2, 129.5, 136.5, 171	3.4%
1-pentanamine	13.8, 23, 29.5, 34, 42.5	3.6%
nonylamine	14.5, 23.1, 27.5, 30, 32.5, 34.6, 42	2.5%
phthalimide	39, 39.5, 40.5, 123, 132.5, 134, 169.6	2.5%
Subtotal amine & amide		*12.0%*
2,6-dimethoxy-phenol	56, 105.2, 119, 135.6, 147.5	8.5%
guaiacol	55.84, 110.89, 114.69, 120.04, 121.49, 146.02, 146.71	6.4%
4-ethyl-2-methoxyphenol	16, 29, 55.5, 110.3, 114, 120.3, 136, 143.5, 145.5	11.1%
Subtotal phenols		*26.0%*

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
quinic acid	40.11, 43.42, 69.71, 73.15, 77.94, 79.74, 184.16	5.4%
Subtotal carboxylic acid & ester		*5.4%*
anthraquinone	127.53, 134.11, 183.27	2.4%
benzophenone	128.21, 129.96, 132.33, 137.58, 196.50	2.6%
3-ethyl-2-cyclopenten-1-one	19.5, 32.5, 35.5, 130.5, 179, 209	1.5%
pyrone	106.19, 117.03, 143.11, 152.26, 161.78	2.8%
cyclohexanone	25.42, 27.32, 41.57, 214.02	1.0%
2-methylcyclohexanone	14.5, 25.5, 28, 37, 41.5, 46	1.1%
Subtotal ketone		*11.4%*
caprolactam	25, 30.5, 31.8, 37.7, 45	1.6%
7-methyl-2,3-dihydro-1H-indole	22.5, 38, 55, 109, 118, 124.5, 127.5, 128.78, 151	1.9%
1-methylimidazolidine-2,4,5-trione	24, 154.5, 158, 159.3	1.8%
hydantoin	38.5, 39, 40, 40.5, 47.5, 77.5, 79, 80, 158.5, 174	2.0%
4-piperidinone	42, 46, 214.5	2.2%
2,8-dimethyl-indolizine	99.6, 110.3, 112.63, 114, 117.5, 119.5, 125.5, 133.5	1.5%
1-(p-methoxyphenyl)piperazine, succinate	34.6, 44.5, 48.9, 57, 67.5, 116, 121, 145, 155, 183	1.5%
Subtotal N-heterocyclic		*12.5%*
methylcyclohexane	25, 32, 33.5, 36	3.3%
2,2,4-trimethyl-pentane	25, 25.5, 30.3, 30.9, 53.25	2.8%
2-methyl-naphthalene	21.65, 77, 125, 125.5, 126, 127.5, 131, 134, 135.5	2.9%
anthracene	125.57, 126.23, 129.26, 132.35	5.8%
α-phellandrene	20, 20.75, 26, 31.5, 40, 120.5, 128, 131, 131.46	2.1%
n-hexadecane	14, 23, 29.6, 30, 32.4	2.4%
Subtotal alkane		*19.3%*
2-methyl-2-phenyloxirane	22.44, 63.56, 114.35, 120.05, 129.86, 159.64	3.3%
isocoumarin	107, 121.75, 125.5, 128, 129.5, 134.5, 136, 145, 162	3.7%
ethoxybenzene	15.04, 63.56, 114.35, 120.05, 129.86, 159.64	4.0%
Subtotal furans, ether, & O-heterocyclic		*11.0%*
2-phenylacetaldehyde	49.35, 131.13, 132.50, 136.58, 199.6	2.4%
Subtotal aldehyde		*2.4%*
Total		100%

Table S14. Chemical composition of biocrude oil from HTL of cellulose-rich digestates at pH 3.5 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
2-methoxyaniline	55.04, 110.04, 115.04, 119, 121, 137, 148	5.2%
n-nonylamine	14.86, 23.5, 27.5, 29.85, 32, 34.5, 42	3.2%
Subtotal amine & amide		*8.4%*
4-ethyl-2-methoxyphenol	16, 29.2, 55.5, 110.3, 114, 120.2, 136, 143.7, 146	4.1%
4-hydroxy-benzenemethanol	63.5, 115, 128.5, 132, 156.5	4.8%
2-methoxy-4-methoxymethyl-phenol	55.55, 57.5, 74.56, 110.67, 114.55, 120.5, 130, 145.5, 146.9	5.6%
2-ethoxy-5-(1-propenyl)phenol	14.56, 18, 65, 76, 77.5, 79, 112, 118.5, 124, 131, 132, 145, 145.5	2.4%
4-hydroxy-3-methoxy-benzyl alcohol	58.2, 66.8, 115, 124, 135.5, 147, 150	3.3%
Subtotal phenols		*20.2%*
1,2,2-trimethyl-cyclopentane-1,3-dioic acid	21.15, 22.5, 32.04, 39.85, 45.95, 52.04, 55.1, 175, 177	3.0%
2-methylbutyrate	11.2, 16.34, 27.5, 41.25, 51.5	5.0%
Subtotal carboxylic acid & ester		*8.0%*
2-methylcyclopentane-1,3-dione	5.5, 30.04, 198.04	7.2%
3-ethyl-2-cyclopenten-1-one	19.5, 32.5, 35.5, 130.5, 179, 209	3.4%
butyrolactone	22.35, 28.57, 69	1.8%
3-methyl-2-cyclopenten-1-one	19.5, 34, 35.3, 130.5, 179, 209	4.4%
Subtotal ketone		*16.8%*
1-methyl-2-pyrrolidone	18.1, 29.6, 30.4, 49.6, 175	1.2%
5-formyl-1H-pyrrole-2-carboxylic acid	109.85, 115, 122, 162	2.0%
6-methoxy-1H-indole-2-carboxylic acid	10, 55.51, 94.35, 109, 111, 119, 120.5, 122.5, 137, 156	1.0%
2,8-dimethyl-indolizine	99.6, 110.3, 112.63, 114, 117.5, 119.5, 125.5, 133.5	1.4%
2-acetyl-pyrrole	25.6, 76,78, 79.5, 110.5, 117.5, 125.5	1.3%
3-methyl pyrrole	11.87, 109.6, 115.3, 117.5	1.0%
pyrazinamide	67.5, 136, 139.8, 150, 165.6	1.1%
Subtotal N-heterocyclic		*9.0%*
(2-methoxyphenyl)hydrazine	56.5, 112.5, 119, 122, 127, 132.5, 151	3.3%
Subtotal azine & nitrile		*3.3%*
1,1-dimethyl-cyclohexane	22.19, 26.65, 29.12, 30.04, 39.85	3.5%
n-tetradecane	14.8, 23.5, 29.4, 32.5	2.5%
n-octadecane	14, 23.15, 29.95, 32.05	1.5%
phenanthrene	66.9, 76.75, 122.5, 126.5, 128.5, 130, 131.7	2.7%
Subtotal alkane		*10.2%*
3,5,7-trihydroxy-2H-1-benzopyran-2-one	102.5, 111, 112.5, 129.6, 144.65, 155.5, 160.5, 161.2	2.0%
1,3-benzodioxane-5-ol	100.2, 108.3,120.2, 147.8	3.9%
2,5-dimethylfuran	13.25, 106.5, 150.05	1.5%
(Z)-5-(propen-1-yl)-1,3-benzodioxole	14, 102, 108.2, 109.6, 125.5, 133.5, 146, 148, 149.6	1.6%
pentyl furan	14, 22.5, 28, 31, 104.35, 110, 140.5, 166.08	2.6%
2-ethyl-furan	12.5, 21, 104, 110, 140.5, 158	1.3%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
5-hydroxy-3,6-dimethyl-2H-chromen-2-one	18, 102, 102.5, 103, 110, 126, 152.5, 155, 160.5, 161	1.7%
Subtotal furans, ether, & O-heterocyclic		*14.6%*
2,5-dihydroxy-3,6-dimethyl-benzaldehyde	19, 20.5, 132, 132.5, 134, 136, 137.5, 192.5	2.8%
2-methoxy-4,5-dimethyl-benzaldehyde	15.54, 19.46, 55.51, 112.55, 124.13, 127.5, 134, 141, 162, 191.15	6.7%
Subtotal aldehyde		*9.5%*
Total		100%

Table S15. Chemical composition of biocrude oil from HTL of cellulose-rich digestates at pH 3.5 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
1-butanamine	14, 20.3, 36, 41.7	3.3%
1-pentanamine	13.8, 23, 29.5, 34, 42.5	3.0%
Subtotal amine & amide		*6.3%*
2-methoxy-4-methoxymethyl-phenol	55.55, 57.5, 74.56, 110.67, 114.55, 120.5, 130, 145.5, 146.9	8.5%
2,6-dimethoxy-phenol	56, 105.6, 119, 135.4, 147.5	3.2%
1,3,5-benzenetriol	103.21, 105.57, 116.58, 137.86, 146.04, 150.69	3.0%
4-ethyl-2-methoxyphenol	16, 29.2, 55.5, 110.3, 114, 120.2, 136, 143.7, 146	3.8%
Subtotal phenols		*18.5%*
quinic acid	40.11, 43.42, 69.71, 73.15, 77.94, 79.74, 184.16	4.5%
3-methyl-4-propyl-2,4-hexadienedioic acid dimethyl ester	17.5, 19.7, 28.2, 37.5, 41, 41.8, 51, 173, 177	4.2%
Subtotal carboxylic acid & ester		*8.7%*
anthraquinone	127.53, 134.11, 183.27	4.2%
benzoquinone	136.84, 188.65	3.5%
benzophenone	128.21, 129.96, 132.33, 137.58, 196.5	3.1%
cyclopentenone	28.15, 34.56, 135, 166, 216	3.5%
2,3-dimethyl-2-cyclopenten-1-one	7.5, 17.04, 136, 169.73, 209.48	1.0%
2-methyl-2-cyclopenten-1-one	10, 26, 34.3, 142, 158, 210	1.0%
3-methyl-2-cyclopenten-1-one	19.5, 34, 35.3, 130.5, 179, 209	1.0%
tetrahydro-2H-pyran-2-one	21, 27.80, 33.64, 63, 172.35	1.0%
Subtotal ketone		*18.3%*
3,6-bis(2-methylpropyl)-2,5-piperazinedione	40.3, 45, 57, 128, 129.5, 131.5, 137.5, 166.8, 169	2.5%
3-amino-2,6-dimethoxy-pyridine	53.5, 100.9, 107.35, 136, 156, 162.35	2.0%
1-methyl-pyrrolidine	24, 42.35, 56.55	1.5%
1-ethyl-2,6-dimethylpiperidine	23.2, 25, 34, 52.4	2.0%
Subtotal N-heterocyclic		*8.0%*
phenylhydrazine	112.04, 119.82, 129.06, 151.87	3.3%
Subtotal azine & nitrile		*3.3%*
anthracene	125.57, 126.23, 129.26, 132.35	3.8%
1,3-butadiene	117.25, 138.3	4.2%
1-phenyl-1-butene	14, 22, 126.5, 128, 134.5, 138	5.0%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
phenanthrene	66.9, 76.75, 122.5, 126.5, 128.5, 130, 131.7	3.0%
Subtotal alkane		*16.0%*
furan-2,5-dione	10.04, 142.11, 167.45	4.5%
2-methyl-furan	13.20, 106.78, 110.52, 140.46, 152.04	2.3%
2,5-dimethyltetrahydrofuran	23.05, 35, 76.5	1.8%
2(5H)-furanone	72.5, 120.19, 155, 174	2.3%
3-acetyl-4-hydroxy-2H-chromen-2-one	30, 101, 121, 125, 126,127, 128, 151, 154, 178	2.5%
4-hydroxy-2H-chromen-2-one	90.5, 118, 121.5, 133, 152, 161, 166.5	2.0%
1,3-benzodioxane-5-ol	100.2, 108.3,120.2, 147.8	1.6%
Subtotal furans, ether, & O-heterocyclic		*17.0%*
octanal	14.1, 22.5, 29.6, 31.85, 44	3.9%
Subtotal aldehyde		*3.9%*
Total		100%

Table S16. Chemical composition of biocrude oil from HTL of cellulose-rich digestates at pH 8 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
13-docosenamide	14, 22.25, 25.5, 27, 29.2, 31.57, 35.5, 129.6, 175.6	3.1%
Subtotal amine & amide		*3.1%*
2-ethoxy-5-(1-propenyl)phenol	14.56, 18, 65, 76, 77.5, 79, 112, 118.5, 124, 131, 132, 145, 145.5	5.4%
4-ethyl-2-methoxyphenol	16, 29, 55.5, 110.3, 114, 120.3, 136, 143.5, 145.5	4.6%
2,4-dihydroxy-phenetole	104.04, 105.5, 116.04, 137.5, 145.5, 150.5	3.1%
2,6-dimethoxyphenol	56, 105.5, 119.3, 135.5, 147.5	2.3%
Subtotal phenols		*15.4%*
isoamyl acetate	20.5, 22.5, 25.5, 38.1, 63	2.2%
2-formyl-6-hydroxy-3,4-dimethoxybenzoic acid	56.07, 110.5, 112.59, 121.89, 124.67, 148.84, 153.9, 172.09	4.5%
3,5-dinitrobenzoic acid	121.96, 129.06, 134.61, 148.76, 163.82	3.6%
Subtotal carboxylic acid & ester		*10.3%*
3-methyl-2-cyclopenten-1-one	19.5, 34, 35.3, 130.5, 179, 209	1.5%
3-ethyl-2-cyclopenten-1-one	19.5, 32.5, 35.5, 130.5, 179, 209	1.0%
carvone	15.5, 20.5, 3, 42.5, 109, 136, 144.5, 147, 199.8	1.7%
benzophenone	128.21, 129.96, 132.33, 137.58, 196.5	3.0%
pyrone	106.19, 117.03, 143.11, 152.26, 161.78	4.2%
Subtotal ketone		*11.4%*
2-ethyl-pyrazine	13.2, 29, 142, 144.4, 159	1.5%
pyrazinamide	67.5, 136, 139.8, 150, 165.6	1.7%
quinoxaline		1.3%
3-ethyl-2,5-dimethyl-pyrazine	12.5, 20.7, 28.5, 140.5, 143.5, 150.5, 160.25	2.0%
1,3-dimethyl-1H-pyrazole-4-carbaldehyde	39.55, 106, 131, 151.5, 186	10.3%
benzoyl pyridine	125, 126, 128, 131, 133, 137.5, 148, 155, 194	7.1%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
pyridinone	122, 123, 124, 136, 137, 138, 149, 150, 151	4.6%
2,3-dimethyl indole	8, 10.65, 106.75, 110, 118, 119, 120.5, 129.5, 130.5, 135.5	1.1%
2-methyl-imidazole	13.5, 120.65, 144.5	1.1%
Subtotal N-heterocyclic		*30.7%*
phenylhydrazine	112.04, 119.82, 129.06, 151.87	4.1%
Subtotal azine & nitrile		*4.1%*
1,5,8-p-menthatriene	49.8, 62, 77, 113.5, 122.2, 123.21, 126.89, 129.94, 131.41, 147.53, 157.35	3.1%
octylamine	14, 23, 27.5, 29.5, 32, 34.5, 42	4.5%
m-terphenyl	126.67, 128.2, 129.8, 141, 141.6	3.4%
Subtotal alkane		*11.0%*
4-hydroxy-2H-chromen-2-one	90.5, 116, 124.3, 132.5, 152, 162, 166	2.3%
2(5H)-furanone	72.5, 120.5, 155, 174.56	2.1%
5-methyl-2-furancarboxaldehyde	14.3, 109.86, 124.72, 152, 159.89, 176.86	1.5%
2-methyl-2-phenyloxirane	22.44, 26.57, 57.09, 72.11, 125.04, 128.69, 140.96	2.2%
4-methoxy-phenylethene	40.53, 65.33, 129.19, 131.79, 141.83	2.5%
4-chlorodiphenyl ether	119, 120, 123.66, 128.56, 129.57, 155.5, 156.25	0.4%
Subtotal furans, ether, & O-heterocyclic		*11.0%*
octanal	14.1, 22.5, 29.6, 31.85, 44	3.0%
Subtotal aldehyde		*3.0%*
Total		100%

Table S17. Chemical composition of biocrude oil from HTL of cellulose-rich digestates at pH 8 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
nonylamine	14.5, 23.1, 27.5, 30, 32.5, 34.6, 42	3.2%
1-pentanamine	13.8, 23, 29.5, 34, 42.5	4.0%
9-octadecenamide	14.5, 22.5, 26, 27, 29.5, 32, 36.5, 130, 176.8	3.8%
Subtotal amine & amide		*11.0%*
4-ethyl-2-methoxyphenol	16, 29, 55.5, 110.3, 114, 120.3, 136, 143.5, 145.5	5.7%
guaiacol	55.84, 110.89, 114.69, 120.04, 121.49, 146.02, 146.71	3.4%
2-methoxy-4-methoxymethyl-phenol	55.55, 57.5, 74.56, 110.67, 114.55, 120.5, 130, 145.5, 146.9	4.5%
2,6-dimethoxy-phenol	56, 105.6, 119, 135.4, 147.5	3.0%
1,3,5-benzenetriol	103.21, 105.57, 116.58, 137.86, 146.04, 150.69	1.9%
Subtotal phenols		*18.5%*
1,5-dimethyl-2-methylpentanedioate	17.1, 20.4, 32.5, 36.2, 51, 62, 169, 175	4.0%
quinic acid	40.11, 43.42, 69.71, 73.15, 77.94, 79.74, 184.16	5.5%
Subtotal carboxylic acid & ester		*9.5%*
anthraquinone	127.53, 134.11, 183.27	3.2%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
benzophenone	128.21, 129.96, 132.33, 137.58, 196.5	3.6%
pyrone	106.19, 117.03, 143.11, 152.26, 161.78	3.0%
3-methyl-2-cyclopenten-1-one	19.5, 34, 35.3, 130.5, 179, 209	2.0%
3-ethyl-2-cyclopenten-1-one	19.5, 32.5, 35.5, 130.5, 179, 209	1.4%
Subtotal ketone		*13.2%*
2,3-diethylpyrazine	12.5, 27.5, 77.5, 141, 156.5	3.7%
3,5-dimethyl-pyrazole	11.45, 104.33, 145	3.1%
pyrazolidine	28.43, 48.66	3.5%
1,4-dimethylpiperazine	46.35, 55, 77.46	3.0%
7-methyl-2,3-dihydro-1H-indole	22.5, 38, 55, 109, 118, 124.5, 127.5, 128.78, 151	3.1%
1-methylimidazolidine-2,4,5-trione	24, 154.5, 158, 159.3	2.3%
1,3-diallyl-imidazolidine	52, 58.23, 75.56, 116.77, 135.5	1.9%
3,6-bis(2-methylpropyl)-2,5-piperazinedione	40.3, 45, 57, 128, 129.5, 131.5, 137.5, 166.8, 169	1.1%
4-piperidinone	42, 46, 214.5	1.0%
2,8-dimethyl-indolizine	99.6, 110.3, 112.63, 114, 117.5, 119.5, 125.5, 133.5	1.0%
1-methyl-pyrrolidine	24, 42.35, 56.55	1.0%
Subtotal N-heterocyclic		*24.7%*
n-hexadecane	14, 23, 29.6, 30, 32.4	5.0%
anthracene	125.57, 126.23, 129.26, 132.35	6.0%
Subtotal alkane		*11.0%*
2-pentyl-furan	14, 22.5, 28, 31, 104.35, 110, 140.5, 166.08	6.9%
Subtotal furans, ether, & O-heterocyclic		*6.9%*
octanal	14.1, 22.5, 29.6, 31.85, 44	5.2%
Subtotal aldehyde		*5.2%*
Total		100%

HTL-AP COMPOSITION

Table S18. Chemical composition of HTL-AP from HTL of lignin-rich digestates at pH 3.5 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
4-nitroaniline	112.56, 127.36, 136.43, 156.11	3.1%
acetamide	22.11, 170.66	6.4%
Subtotal amine & amide		*9.5%*
3-isopropylpyrocatechol	22.5, 27, 113.5, 117.5, 119.8, 135.5, 142.5, 144.6	5.8%
4-(hydroxymethyl)phenol	60.04, 111.82, 131.13, 132.42, 133.60, 167.90	4.3%
phenol	115.48, 121.09, 129.79, 155.02	5.8%
o-cresol	17.5, 118. 123.5, 127.5, 129.7, 134, 153.4	4.9%
Subtotal phenols		*20.8%*
pyruvic acid	29.22, 172.98	3.2%
benzoic acid	128.49, 129.40, 130.28, 133.83, 172.70	3.1%
acetic acid	25.98, 184.11	7.4%
3,5-dihydroxybenzoic acid	107, 108.41, 132.5, 158.7, 164	3.6%
2-oxovaleric acid	13.4, 17, 35.5, 40, 162, 186.5	3.2%
trans-cinnamic acid	126.5, 130, 132, 137.8, 143.8, 178.6	2.8%
4-acetyl benzoic acid	27, 39.02, 40.02, 40.54, 77, 78.5, 128.2, 130, 135, 140, 167.5	3.2%
Subtotal carboxylic acid & ester		*26.5%*
butanone	8.89, 30.03, 38.44, 211.47	8.0%
methyl vinyl ketone	26, 129, 138, 199.5	8.3%
Subtotal ketone		*16.3%*
pyrrole	107.5, 118	6.7%
Subtotal N-heterocyclic		*6.7%*
4-acetyl-anisole	26, 55.2, 114, 130.5, 163.5, 195.6	6.8%
Subtotal furans, ether, & O-heterocyclic		*6.8%*
glyoxal	28.62, 190.40, 194.74	2.4%
acetaldehyde	30.55, 199.68	6.5%
benzaldehyde	129.08, 129.48, 134.43, 136.47, 192.28	4.5%
Subtotal aldehyde		*13.4%*
Total		100%

Table S19. Chemical composition of HTL-AP from HTL of lignin-rich digestates at pH 3.5 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
acetamide	22.11, 170.66	2.8%
benzylamine	49.05, 128.40, 131.13, 132.50	2.6%
Subtotal amine & amide		*5.4%*
phenol	115.48, 121.09, 129.79, 155.02	4.5%
o-cresol	17.5, 118. 123.5, 127.5, 129.7, 134, 153.4	3.4%
catechol	119.5, 124, 146.2	6.6%
Subtotal phenols		*14.5%*
3,5-dihydroxycinnamic acid	114.5, 115, 115.4, 121.4, 126, 145, 145.5, 148.3, 167.8	5.0%
2-oxovaleric acid	13.4, 17, 35.5, 40, 162, 186.5	4.0%
acetic acid	25.98, 184.11	9.3%
benzoic acid	128.49, 129.40, 130.28, 133.83, 172.70	7.2%
Subtotal carboxylic acid & ester		*25.5%*

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
hydroquinone	111.82, 124.74, 158.02, 178.29	5.9%
butanone	8.89, 30.03, 38.44, 211.47	2.6%
acetophenone	28.98, 131.04, 131.53, 136.87	4.4%
2-pentanone	13.5, 17.8, 29.7, 45.5, 208	3.0%
Subtotal ketone		*15.9%*
pyrrole	107.5, 118	4.1%
Subtotal N-heterocyclic		*4.1%*
2-hydroxy-2-methyl-propanenitrile	10.95, 120.79	2.0%
mandelic acid nitrile	120, 75.30, 174.77, 131.13, 132.5, 163.73	2.9%
Subtotal azine & nitrile		*4.9%*
4-acetyl-anisole	26, 55.2, 114, 130.5, 163.5, 195.6	12.4%
Subtotal furans, ether, & O-heterocyclic		*12.4%*
benzaldehyde	129.08, 129.48, 134.43, 136.47, 192.28	8.3%
acetaldehyde	30.55, 199.68	9.0%
Subtotal aldehyde		*17.3%*
Total		

Table S20. Chemical composition of HTL-AP from HTL of lignin-rich digestates at pH 8 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
benzidine	116, 127.5, 130.54, 148.23	6.3%
succinimide	30.2, 184	2.0%
Subtotal amine & amide		*8.3%*
catechol	119.5, 124, 146.2	3.7%
phenol	115.48, 121.09, 129.79, 155.02	2.0%
2-aminophenol	114, 117, 120, 138, 142	5.8%
resorcinol	103.45, 108.79, 131.59, 158.77	6.4%
p-cresol	21.7, 117.7, 133, 156	6.6%
3-isopropylpyrocatechol	22.5, 27, 113.5, 117.5, 119.8, 135.5, 142.5, 144.6	4.0%
Subtotal phenols		*28.5%*
2-(2-methoxyphenyl)-acetic acid	35.65, 55.04, 110.54, 120.04, 124.04, 128.69, 130.14, 156.74, 172.5	6.6%
ethylacetoacetate	14.04, 20.55, 30.04, 50.04, 60.04, 61.14, 90.04, 167.64, 200, 172, 176	2.3%
formyl acetate	20, 156.5, 167.66	3.3%
acetic anhydride	21.75, 167.04	5.4%
lactic acid	22.80, 71.25, 185.08	2.6%
acetic acid	25.98, 184.11	9.6%
2-oxovaleric acid	13.4, 17, 35.5, 40, 162, 186.5	4.5%
Subtotal carboxylic acid & ester		*34.3%*
2-methyl pyrazine	21.5, 142, 144, 145, 154	4.6%
pyridazine	127.2, 152	7.2%
5,7-dimethoxyquinoline	55.5, 98, 99.5, 116.5, 118, 130.7, 150.5, 151, 156, 160.5	4.8%
Subtotal N-heterocyclic		*16.6%*
acetaldehyde	30.55, 199.68	8.1%
benzaldehyde	129.08, 129.48, 134.43, 136.47, 192.28	4.2%
Subtotal aldehyde		*12.3%*
Total		100%

Table S21. Chemical composition of HTL-AP from HTL of lignin-rich digestates at pH 8 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
acetamide	22.11, 170.66	4.3%
2-phenethylamine	40.19, 43.60, 126.09, 128.8, 139.3	3.0%
Subtotal amine & amide		*7.3%*
catechol	119.5, 124, 146.2	9.8%
phenol	115.48, 121.09, 129.79, 155.02	10.0%
2-aminophenol	114, 117, 120, 138, 142	9.0%
Subtotal phenols		*28.8%*
benzoic acid	128.49, 129.44, 130.28, 133.83, 172.7	5.6%
acetic acid	25.98, 184.11	13.6%
formic acid	175.91	2.4%
chloropropanoic acid	20.21, 51.76, 178.16	2.6%
2-hydroxy-3-methyl butyric acid	16.55, 19.45, 31.67, 75.04, 176.69	3.0%
levulinic acid	26.8, 29.75, 38, 177.5, 208.1	6.4%
Subtotal carboxylic acid & ester		*33.6%*
5-nitro-4H-1,2,3-triazol-4-one	125.15, 154.03, 216.11	5.0%
4H-1,2,3-triazol-4-one	130.09, 210	6.0%
Subtotal N-heterocyclic		*11.0%*
acetonitrile	1.16, 117.18	5.7%
Subtotal azine & nitrile		*5.7%*
acetaldehyde	30.55, 199.68	4.6%
benzaldehyde	129.08, 129.48, 134.43, 136.47, 192.28	4.3%
salicylaldehyde	117.5, 119.7, 120.8, 134, 136, 161, 196.5	4.7%
Subtotal aldehyde		*13.6%*
Total		100%

Table S22. Chemical composition of HTL-AP from HTL of cellulose-rich digestates at pH 3.5 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
acetamide	22.11, 170.66	6.8%
subtotal amine & amide		*6.8%*
catechol	115.5, 120, 144.5	2.5%
phenol	115.48, 121.09, 129.79, 155.02	5.9%
ethyl-2-methoxyphenol	55.84, 110.89, 114.69, 120.04, 121.49, 146.02, 146.71	2.6%
Subtotal phenols		*11.0%*
glycolic acid	63.93, 182.69	1.8%
acetic acid	25.98, 184.11	12.4%
levulinic acid	28, 30, 38, 178, 207	9.9%
formic acid	175.91	4.1%
Subtotal carboxylic acid & ester		*28.2%*
2-pentanone	13.5, 17.8, 29.7, 45.5, 208	5.6%
2,5-hexanedione	29.65, 34.5, 207.2	7.2%
acetophenone	28.98, 131.04, 131.53, 136.87	7.6%
Subtotal ketone		*20.4%*
pyrrole	107.5, 118	7.1%
Subtotal N-heterocyclic		*7.1%*
malononitrile	9.8, 169.93	5.5%

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
Subtotal azine & nitrile		*5.5%*
furan-2-ylmethanol	57.5, 108, 110.5, 143, 155	6.3%
4-acetyl-anisole	26, 55.2, 114, 130.5, 163.5, 195.6	5.0%
Subtotal furans, ether, & O-heterocyclic		*11.3%*
3-butenal	13.71, 15.69, 45.82, 202.8	3.5%
glyoxal	28.62, 190.4, 194.74	2.2%
2,2-dimethyl-3-oxobutanal	19.1, 26.3, 60, 201.2, 207.5	1.0%
acetaldehyde	30.55, 199.68	3.0%
Subtotal aldehyde		*9.7%*
Total		100%

Table S23. Chemical composition of HTL-AP from HTL of cellulose-rich digestates at pH 3.5 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
acetamide	22.11, 170.66	7.2%
Subtotal amine & amide		*7.2%*
2-aminophenol	114, 117, 120, 138, 142	3.4%
resorcinol	103.45, 108.79, 131.59, 158.77	2.9%
hydroquinone	111.82, 124.74, 158.02, 178.29	3.7%
phenol	115.48, 121.09, 129.79, 155.02	5.1%
Subtotal phenols		*15.1%*
acetic acid	25.98, 184.11	10.4%
levulinic acid	28, 30, 38, 178, 207	4.8%
formyl acetate	20, 156.5, 167.66	5.2%
benzoic acid	128.49, 129.4, 130.28, 133.83, 172.7	7.5%
Subtotal carboxylic acid & ester		*27.9%*
acetoin	19.54, 24.94, 73.16	3.9%
2,5-hexanedione	29.65, 34.5, 207.2	4.8%
acetophenone	28.98, 131.04, 131.53, 136.87	5.4%
2-pentanone	13.5, 17.8, 29.7, 45.5, 208	2.2%
Subtotal ketone		*16.3%*
3-aminopyrazole	67.5, 94, 133.45, 155	6.6%
Subtotal N-heterocyclic		*6.6%*
furan-2-ylmethanol	56.85, 107.5, 110.36, 142.3, 154.5	6.5%
4-acetyl-anisole	26, 55.2, 114, 130.5, 163.5, 195.6	4.8%
Subtotal furans, ether, & O-heterocyclic		*11.3%*
2-methyl-butanal	11, 13.02, 23.77, 47.5, 205	5.6%
2-oxo-propanal oxime	25.7, 150, 198.5	4.8%
acetaldehyde	30.55, 199.68	5.2%
Subtotal aldehyde		*15.6%*
Total		100%

Table S24. Chemical composition of HTL-AP from HTL of cellulose-rich digestates at pH 8 and 320 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
acrylamide	129, 131, 171	6.4%
Subtotal amine & amide		*6.4%*
phenol	115.48, 121.09, 129.79, 155.02	10.2%
2-aminophenol	114, 117, 120, 138, 142	8.6%
resorcinol	103.45,108.79, 131.59, 158.77	4.3%
p-cresol	21.7, 117.7, 133, 156	5.0%
Subtotal phenols		*28.1%*
benzoic acid	128.49, 129.4, 130.28, 133.83, 172.7	5.4%
2-(2-methoxyphenyl)-acetic acid	35.65, 55.04, 110.54, 120.04, 124.04, 128.69, 130.14, 156.74, 172.5	4.3%
acetic acid	25.98, 184.11	10.3%
nicotinic acid	123.71, 126.66, 136.9, 150.21, 153.18, 166.23	3.7%
lactic acid	22.8, 71.25, 185.08	3.5%
2,3-dihydroxy-2-methyl-succinic acid	16.65, 37.5, 38.25, 172, 176.51	2.3%
Subtotal carboxylic acid & ester		*29.5%*
butanone	8.89, 30.03, 38.44, 211.47	5.0%
Subtotal ketone		*5.0%*
3-methylpyridine	18.24, 122.5, 133.5, 137, 143.4, 150.5	4.9%
3-cyanopyridine	110.04, 117.64, 123.25, 139.9, 152.5	6.0%
2-methyl pyrazine	21.5, 142, 144, 145, 154	3.5%
1H-pyrazole	104.65, 134.05	2.2%
pyridazine	127.2, 152	4.5%
Subtotal N-heterocyclic		*21.1%*
methyl glyoxal	23, 27, 89.5, 91, 101.62, 207.84	2.6%
acetaldehyde	30.55, 199.68	7.3%
Subtotal aldehyde		*9.9%*
Total		100%

Table S25. Chemical composition of HTL-AP from HTL of cellulose-rich digestates at pH 8 and 360 ºC based on liquid-state ^{13}C NMR analysis.

Detected compounds	Chemical shift (ppm)	Relative spectral area percentage
nicotinamide	123.29, 129.7, 135.07, 148.65, 151.78, 166.49	4.3%
acetamide	22.11, 170.66	4.2%
Subtotal amine & amide		8.5%
phenol	115.48, 121.09, 129.79, 155.02	18.8%
catechol	115.5, 120, 144.5	10.0%
Subtotal phenols		*28.8%*
nicotinic acid	123.71, 126.66, 136.9, 150.21, 153.18, 166.23	5.2%
picolinic acid	124.6, 127.25, 137.5, 144, 144.85, 165.86	3.6%
benzoic acid	128.49, 129.44, 130.28, 133.83, 172.7	7.5%
acetic acid	25.98, 184.11	10.4%
glutaric acid	25.5, 40, 186.37	4.0%
Subtotal carboxylic acid & ester		*30.7%*
4H-1,2,3-triazol-4-one	130.09, 210	6.0%
5-nitro-4H-1,2,3-triazol-4-one	125.15, 154.03, 216.11	3.0%
piperidine	25.5, 27.8, 47.5	7.7%
Subtotal N-heterocyclic		*16.7%*
acetonitrile	1.16, 117.18	5.5%
Subtotal azine & nitrile		*5.5%*
glyceraldehyde	64.76, 76.5, 92.5	4.8%
acetaldehyde	30.55, 199.68	5.0%
Subtotal aldehyde		*9.8%*
Total		100%