SUPPORTING INFORMATION

Hydrothermal Coliquefaction of Anaerobic Digestate with Polyphenolic Extracts from Agricultural Byproducts Producing Nearly Nitrogen-Free Biocrude Oil

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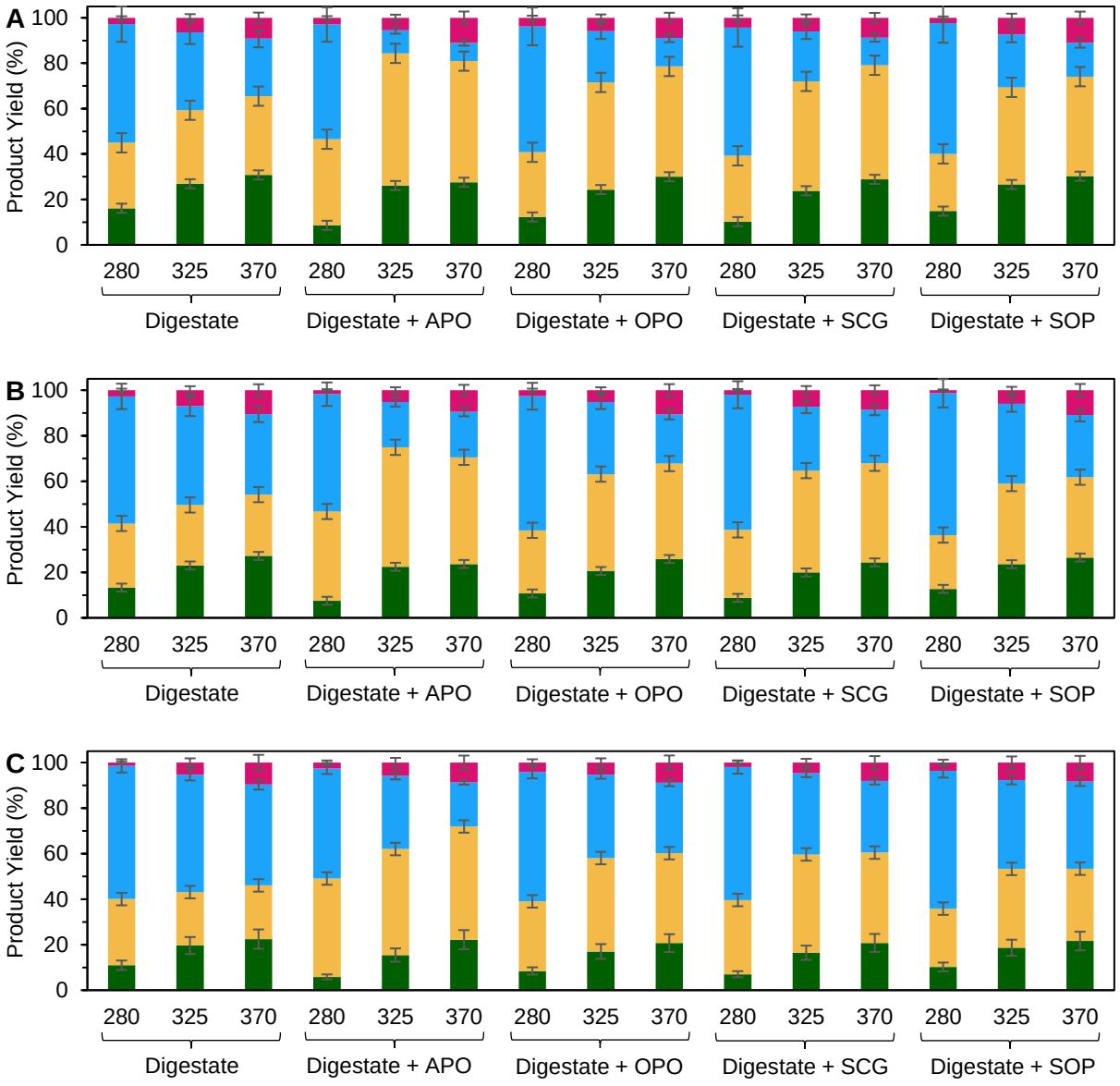


Figure S2. Phosphorus yield in hydrochar (yellow) and aqueous-phase (blue) coproducts from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min with (A) acidic, (B) neutral, and (C) alkaline feedstock pHs.

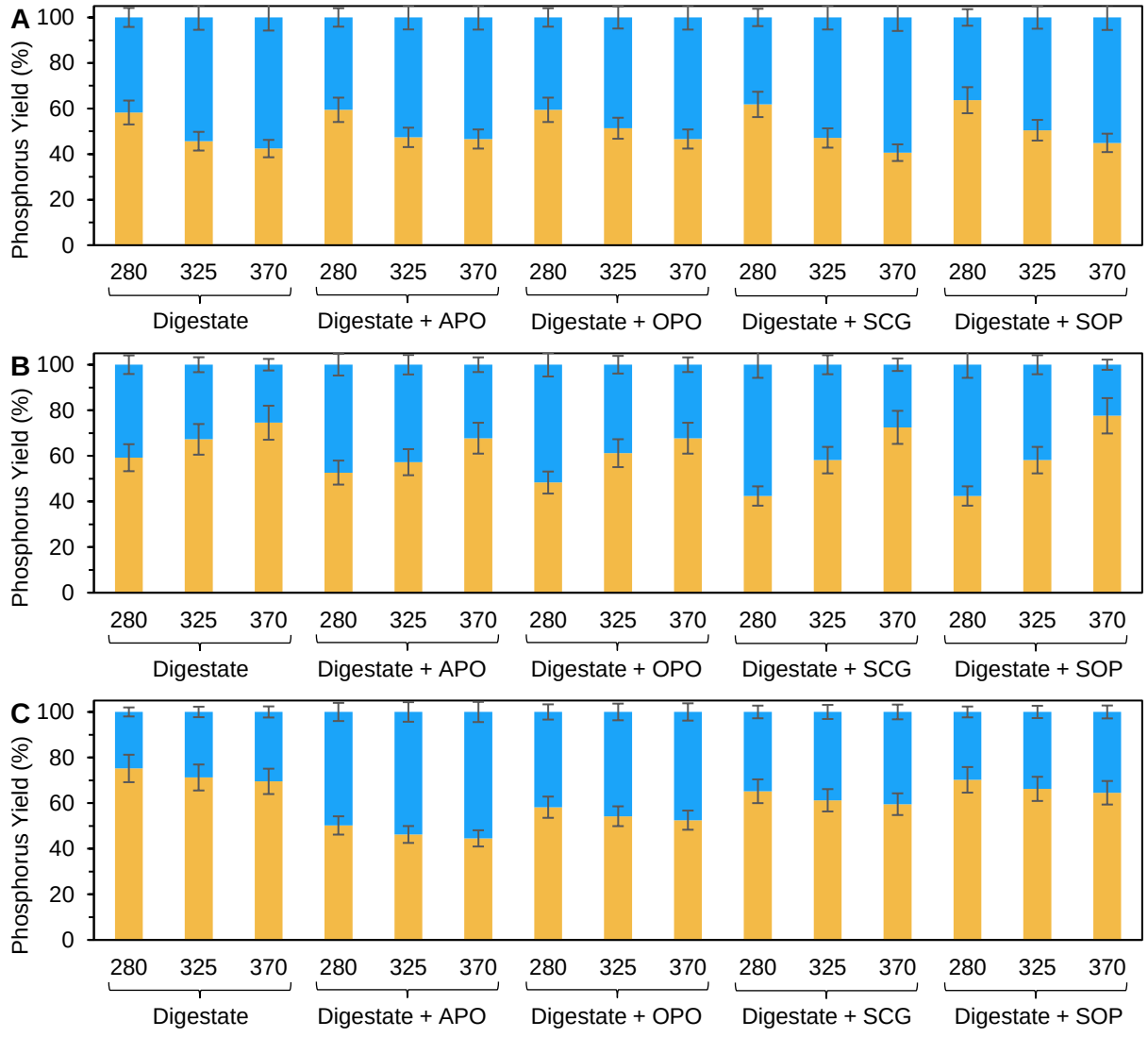


Figure S3. Calcium yield in hydrochar (yellow) and aqueous-phase (blue) coproducts from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min with (A) acidic, (B) neutral, and (C) alkaline feedstock pHs.

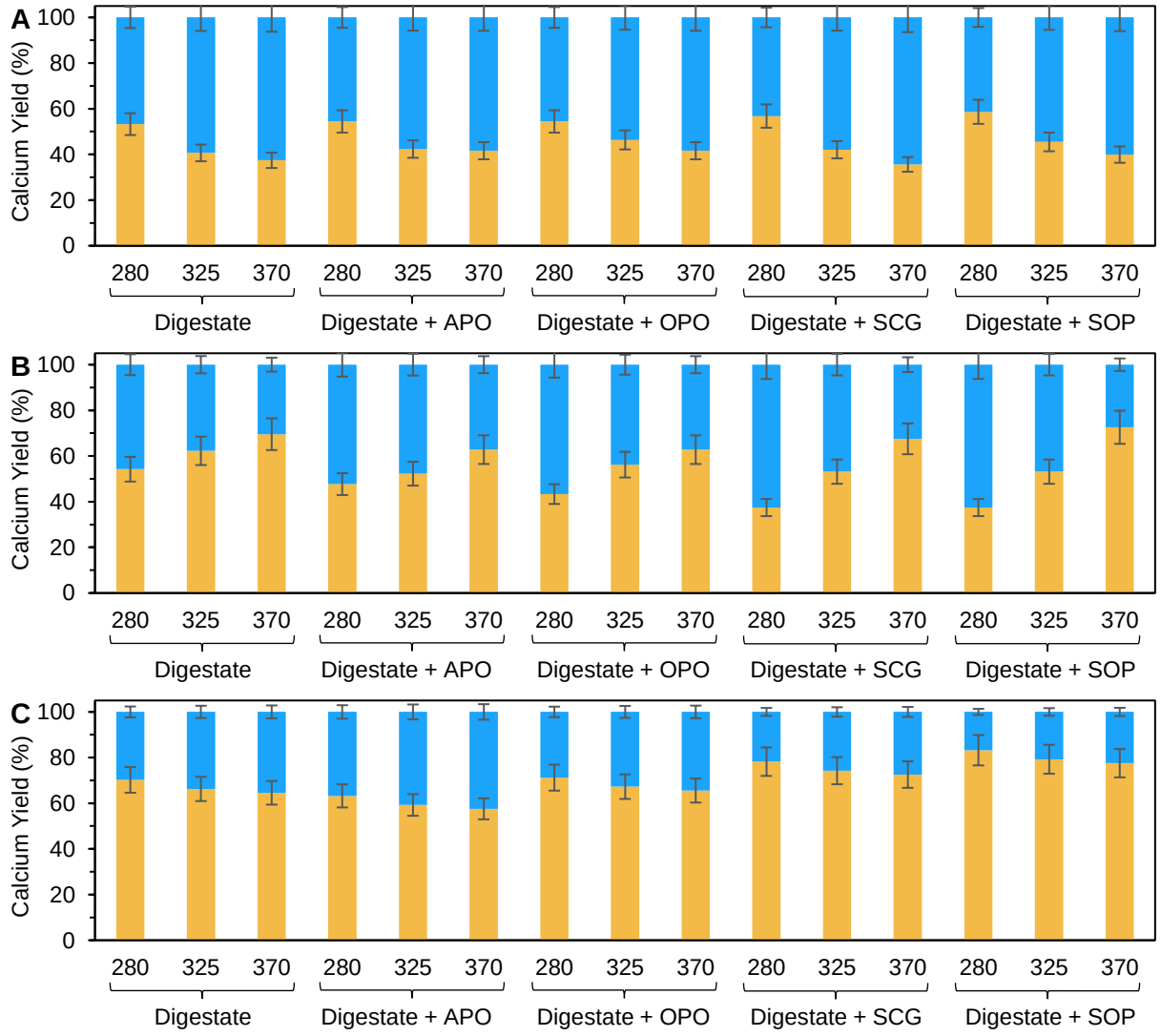


Figure S4. Magnesium yield in hydrochar (yellow) and aqueous-phase (blue) coproducts from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min with (A) acidic, (B) neutral, and (C) alkaline feedstock pHs.

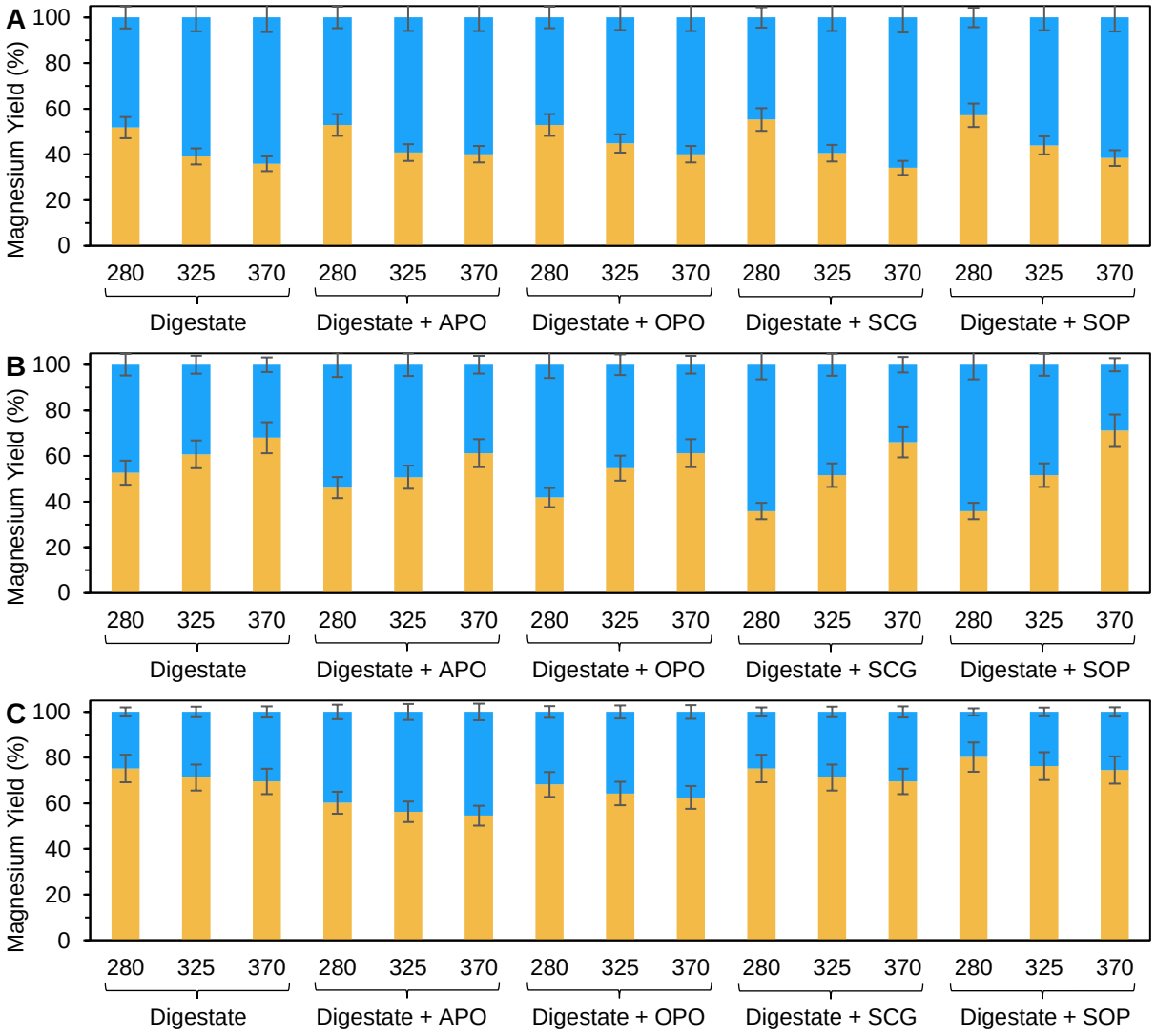


Figure S5. Aluminum yield in hydrochar (yellow) and aqueous-phase (blue) coproducts from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min with (A) acidic, (B) neutral, and (C) alkaline feedstock pHs.

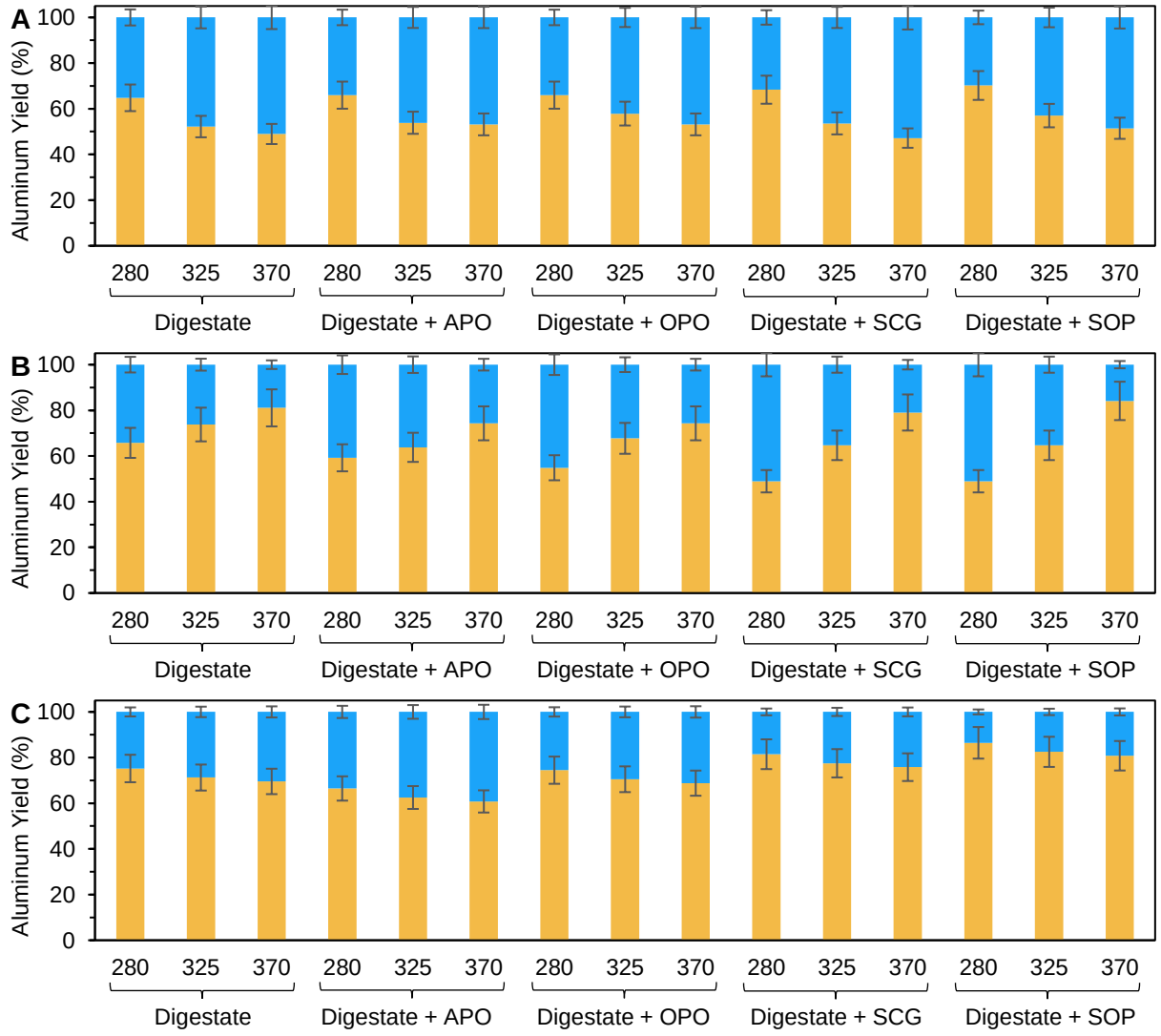


Figure S6. Potassium yield in hydrochar (yellow) and aqueous-phase (blue) coproducts from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min with (A) acidic, (B) neutral, and (C) alkaline feedstock pHs.

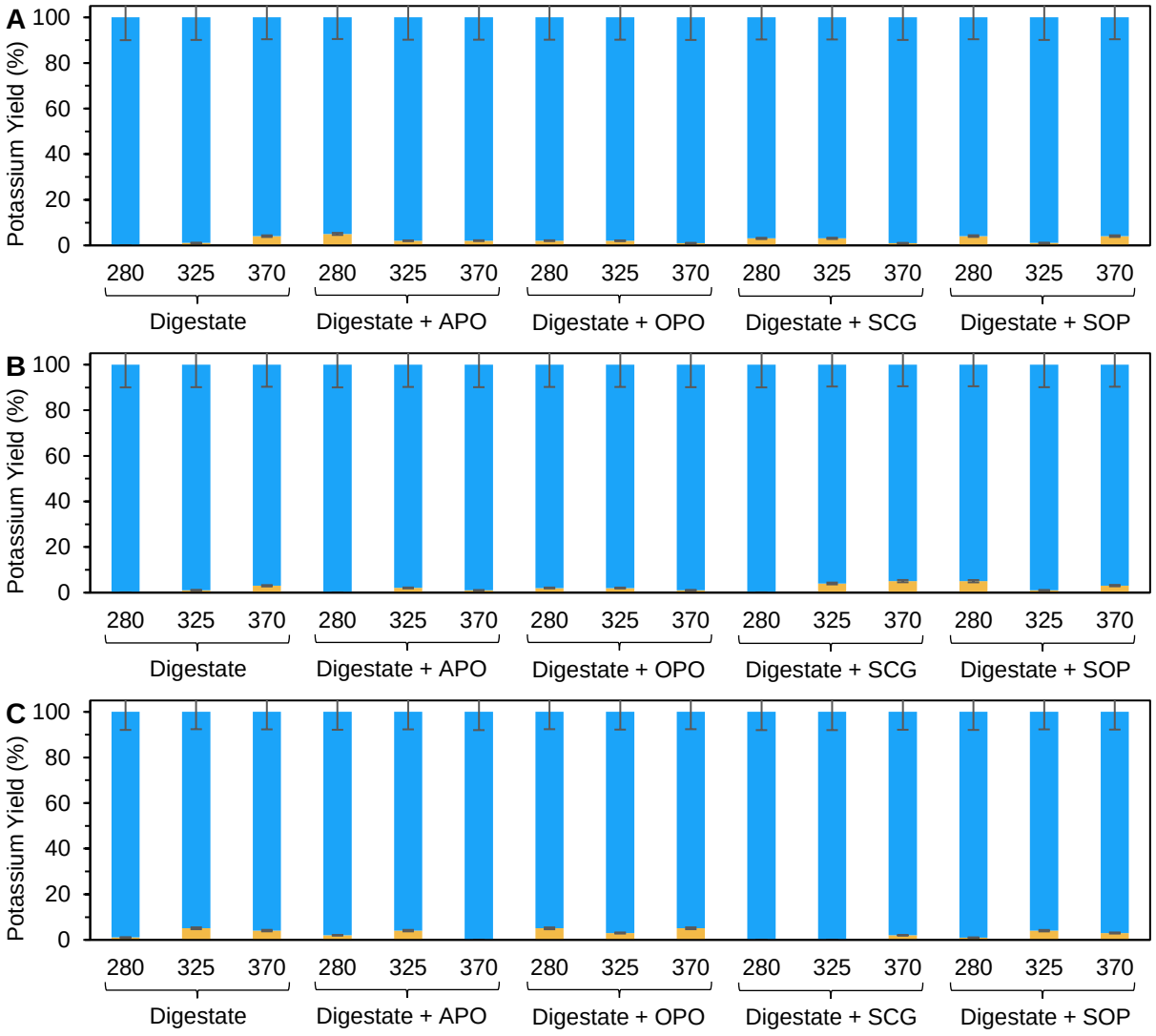
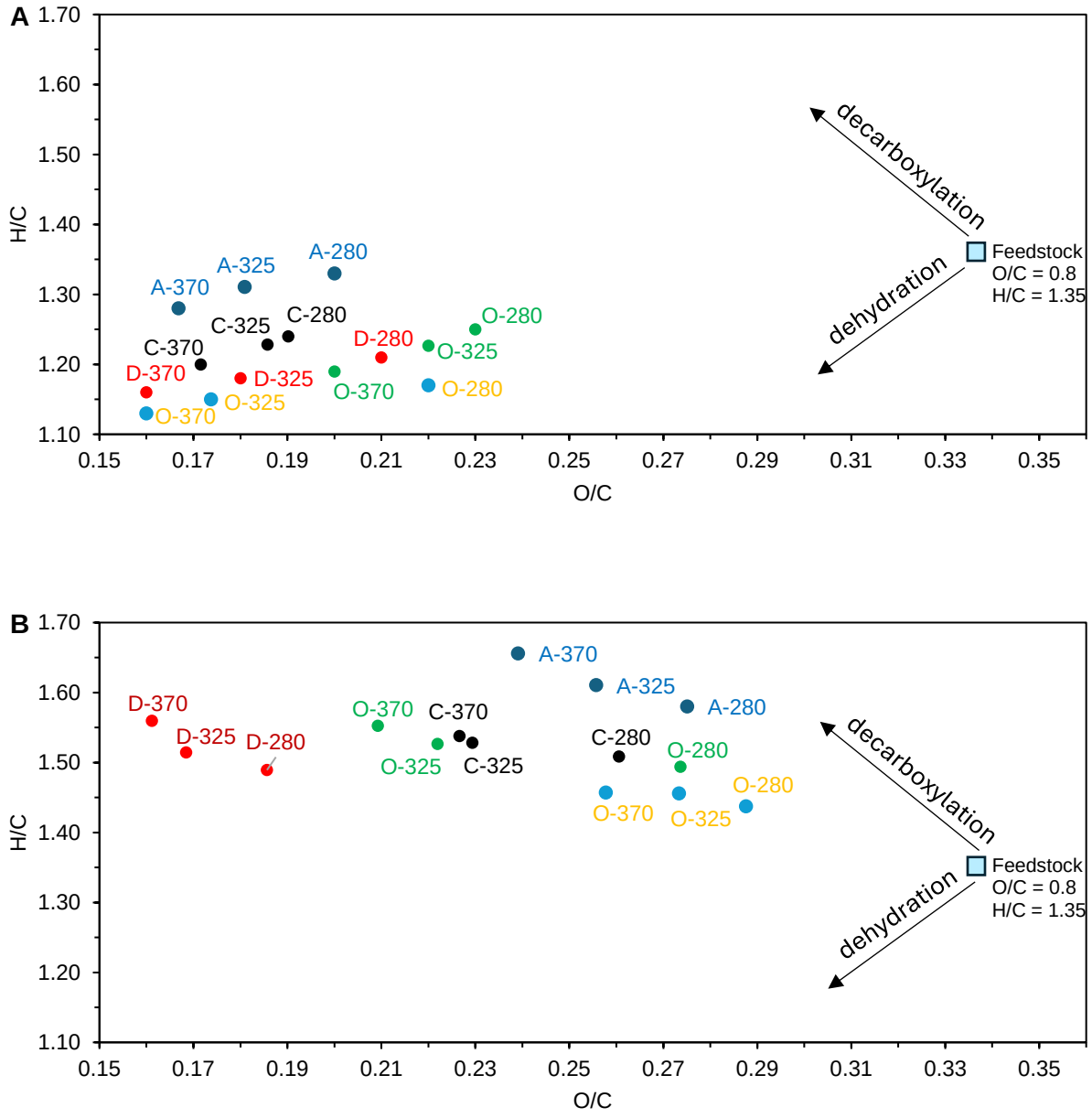


Figure S7. The Van Krevelen diagram indicating the deoxygenation of biocrude from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (blue), olive pomace (green), spent coffee grounds (black), and sweet orange peels (yellow) at 280, 325, and 370 °C for 60 min with (A) acidic, (B) neutral, and (C) alkaline feedstock pHs.



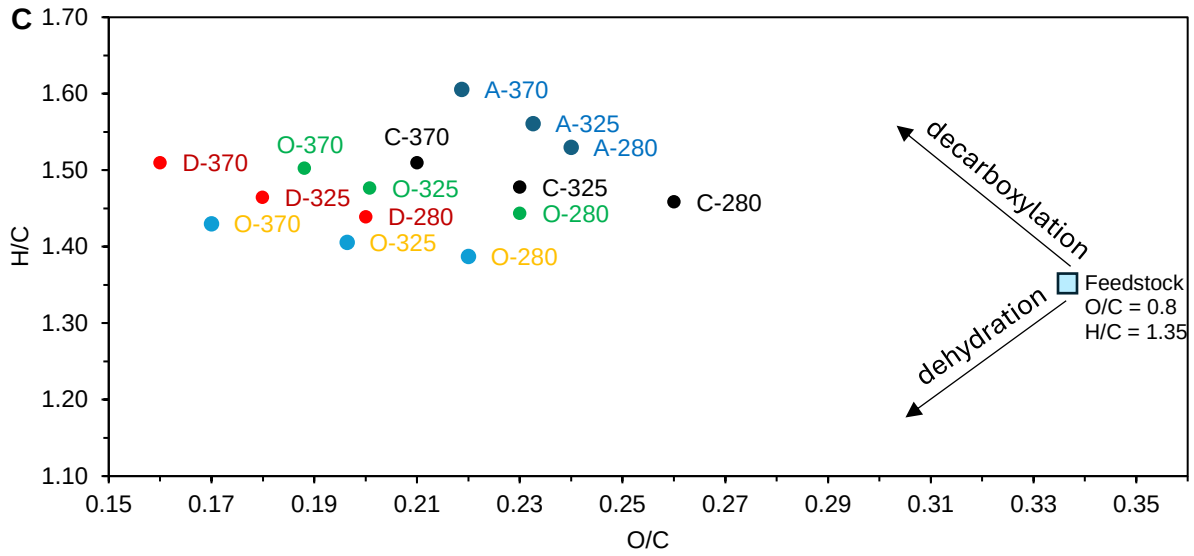


Figure S8. The reaction pathways involving ferulic acid, methylglyoxal, acetoin, and ammonia under acid catalysis. The blue and brown colors indicate that the corresponding compounds were detected in the aqueous and solid phases, respectively.

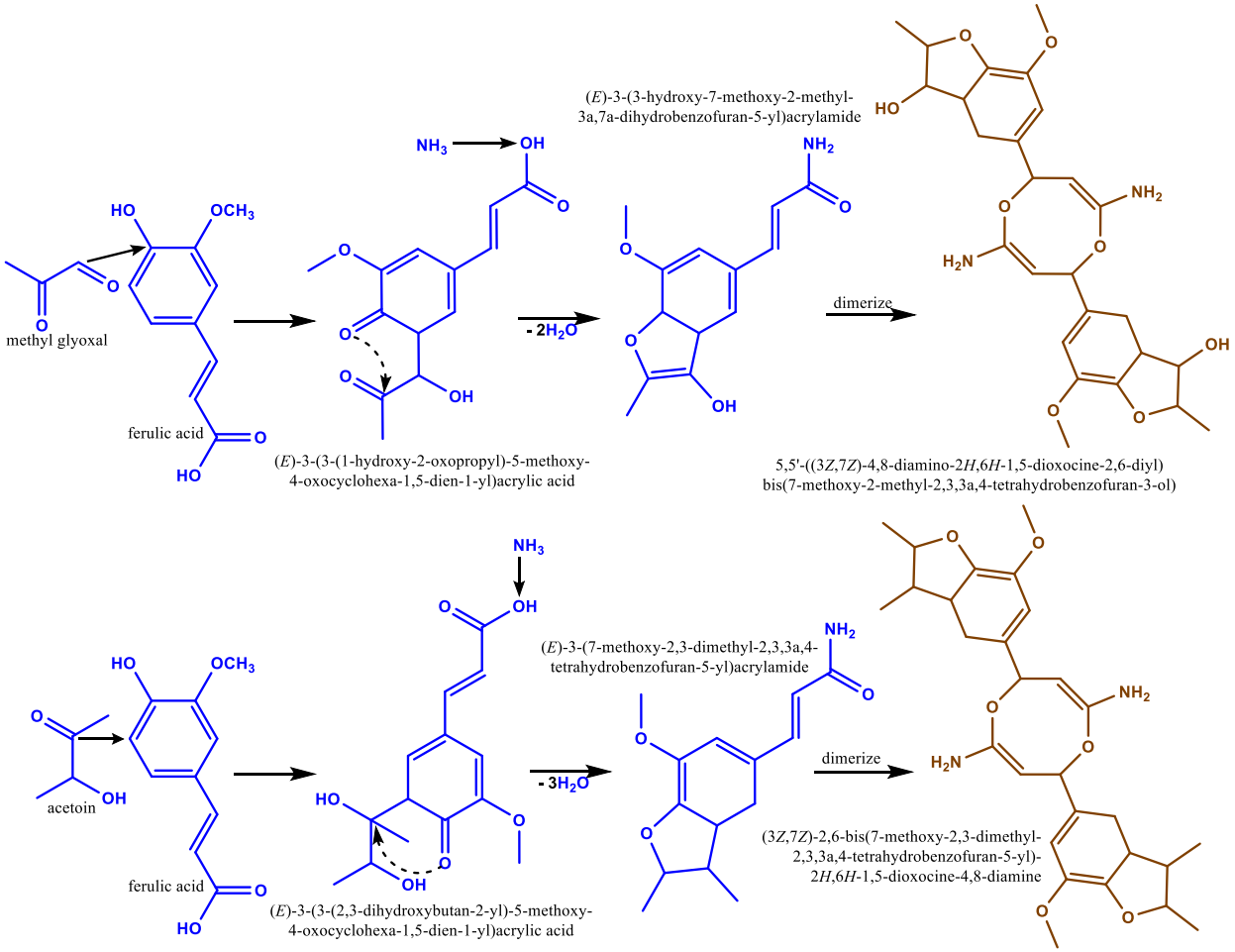


Figure S9. The reaction pathways involving ferulic acid, methylglyoxal, acetoin, and ammonia under alkali catalysis. The blue and brown colors indicate that the corresponding compounds were detected in the aqueous and solid phases, respectively.

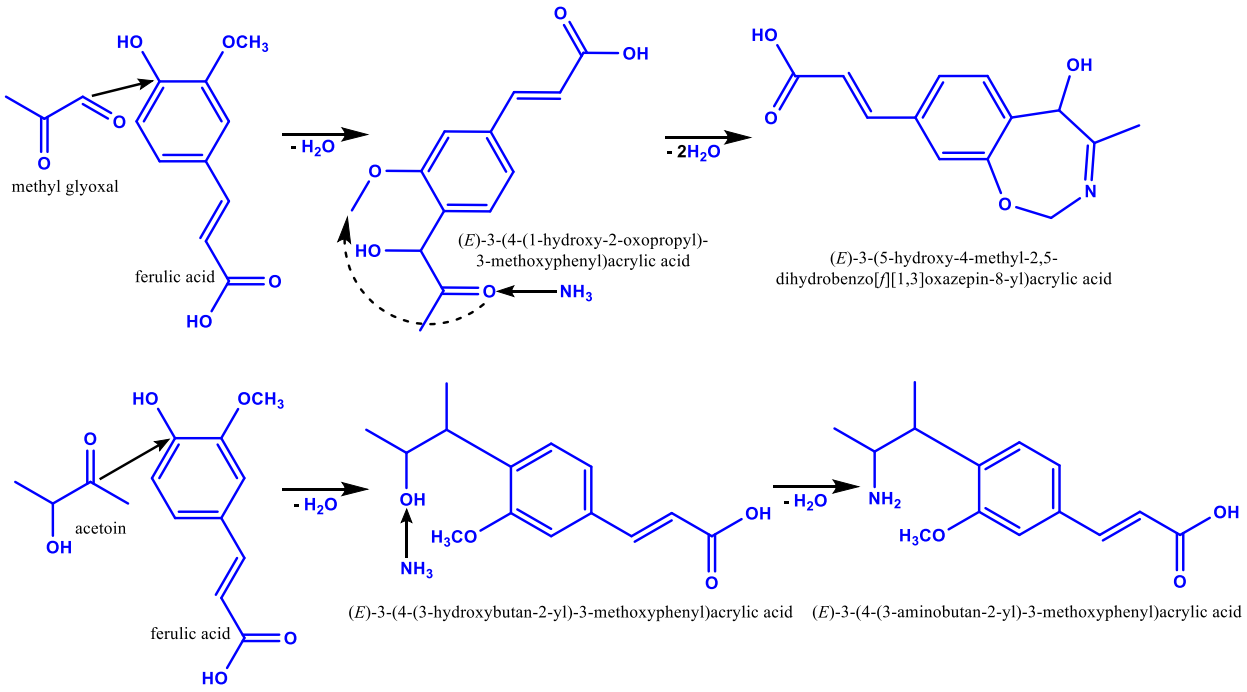


Figure S10. The reaction pathways involving caffeic acid, methylglyoxal, acetoin, and ammonia under acid catalysis. The blue and brown colors indicate that the corresponding compounds were detected in the aqueous and solid phases, respectively.

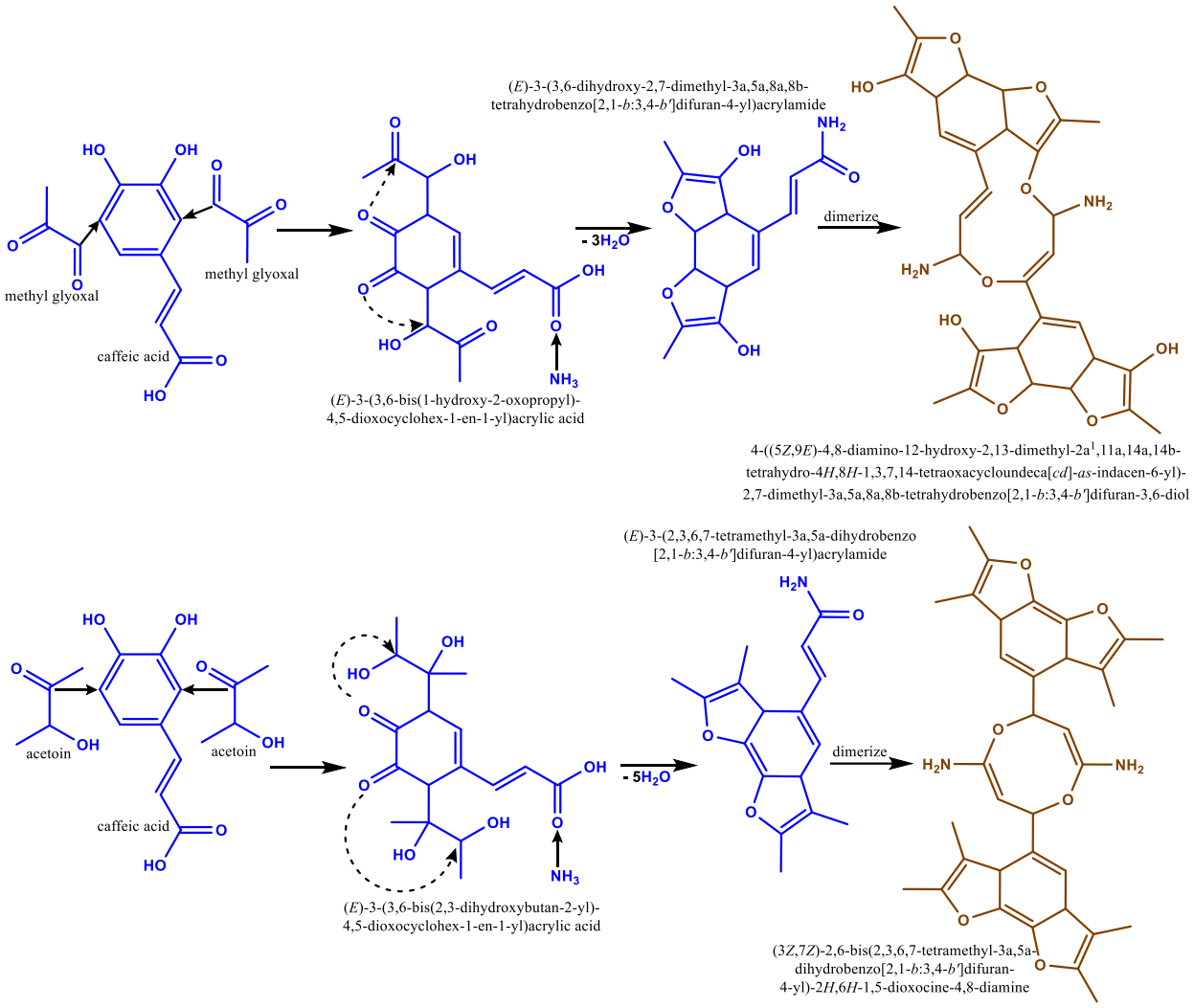


Figure S11. The reaction pathways involving caffeic acid, methylglyoxal, acetoin, and ammonia under alkali catalysis. The blue and brown colors indicate that the corresponding compounds were detected in the aqueous and solid phases, respectively.

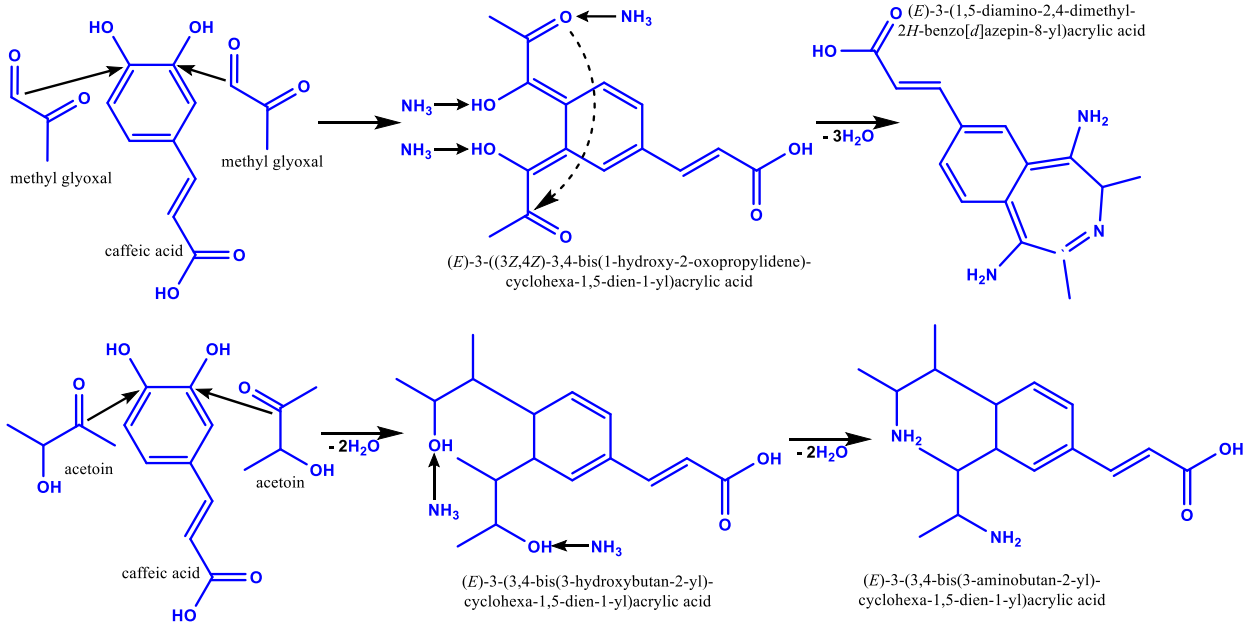


Figure S12. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of epicatechin (○), methylglyoxal (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

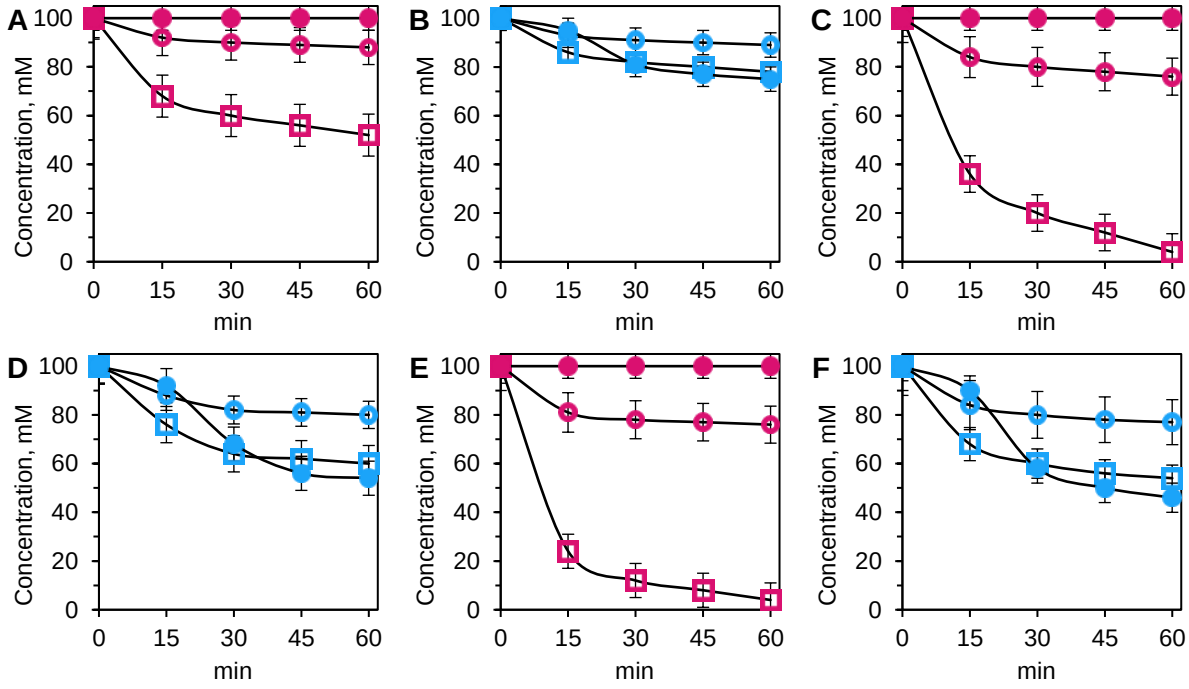


Figure S13. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of epicatechin (○), acetoin (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

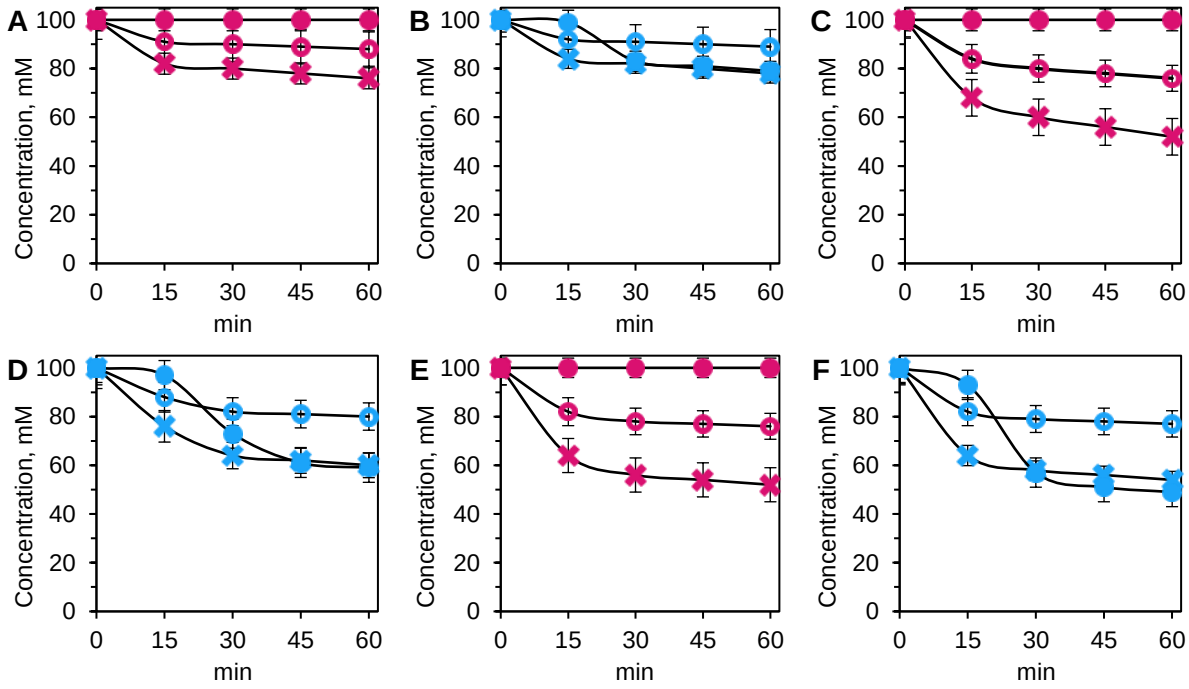


Figure S14. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of quercetin (○), methylglyoxal (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

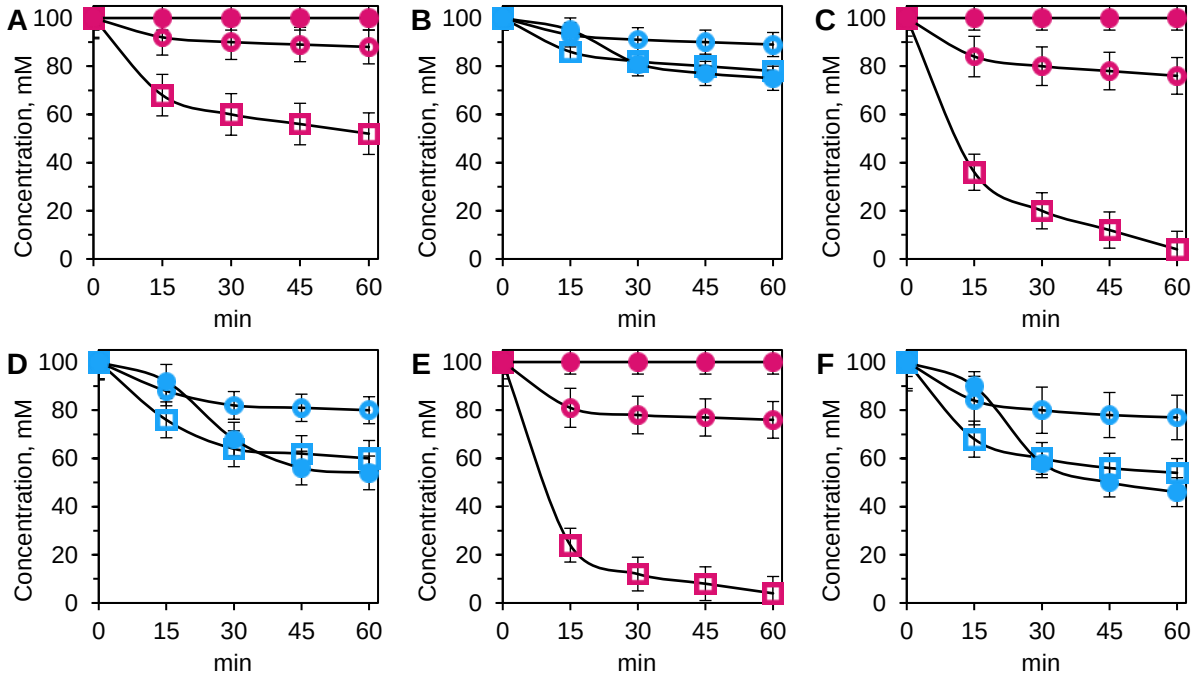


Figure S15. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of quercetin (○), acetoin (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

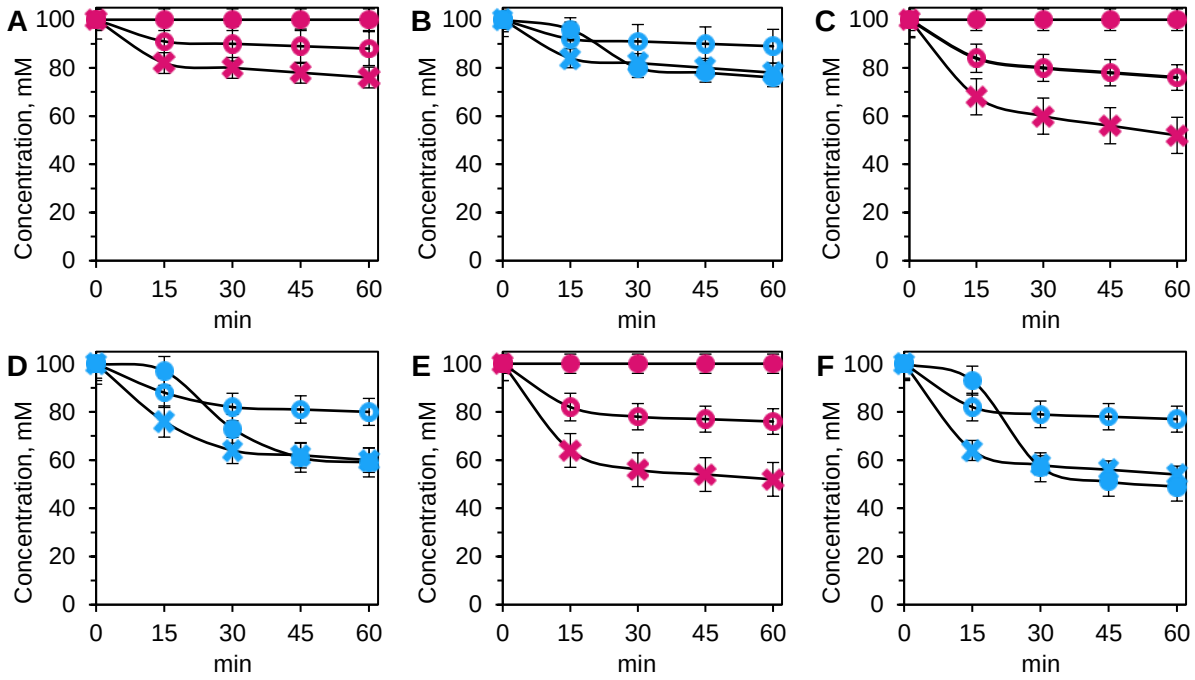


Figure S16. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of caffeic acid (○), methylglyoxal (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

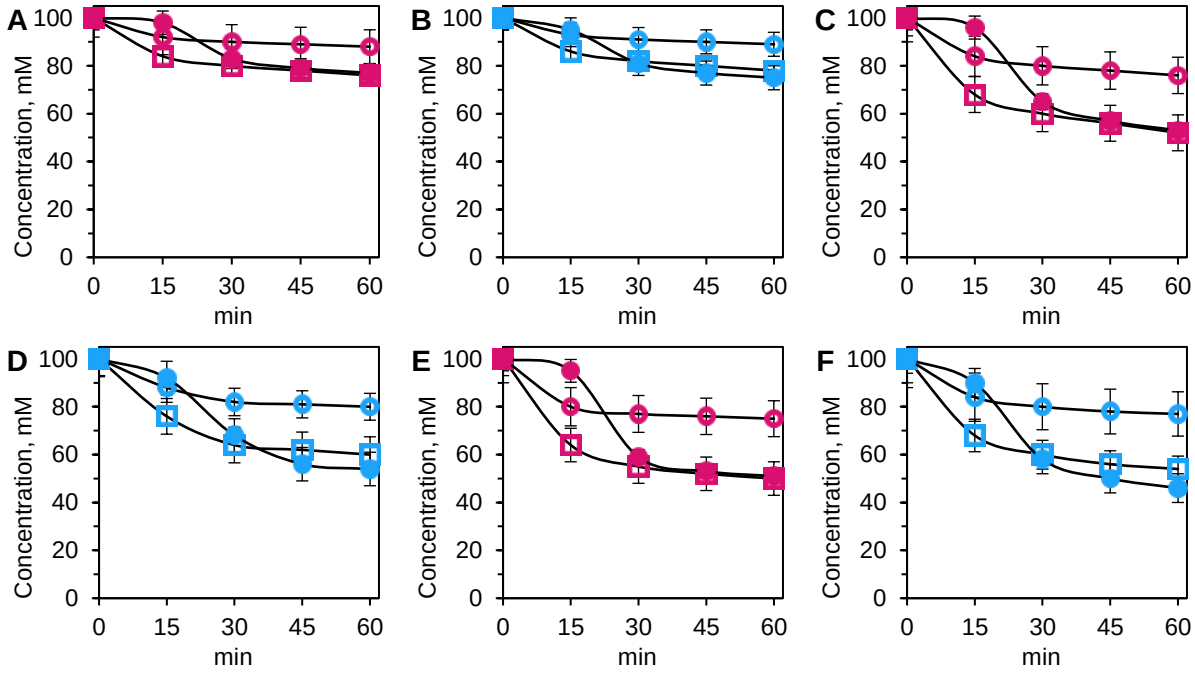


Figure S17. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of caffeic acid (○), acetoin (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

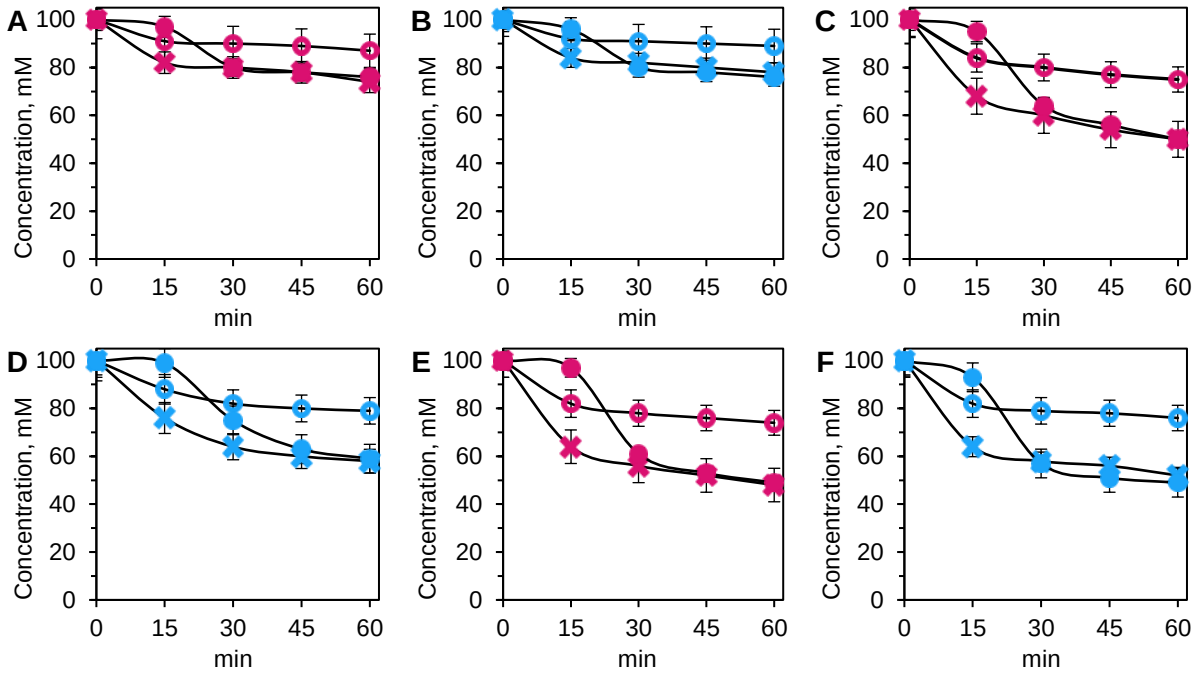


Figure S18. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of ferulic acid (○), methylglyoxal (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

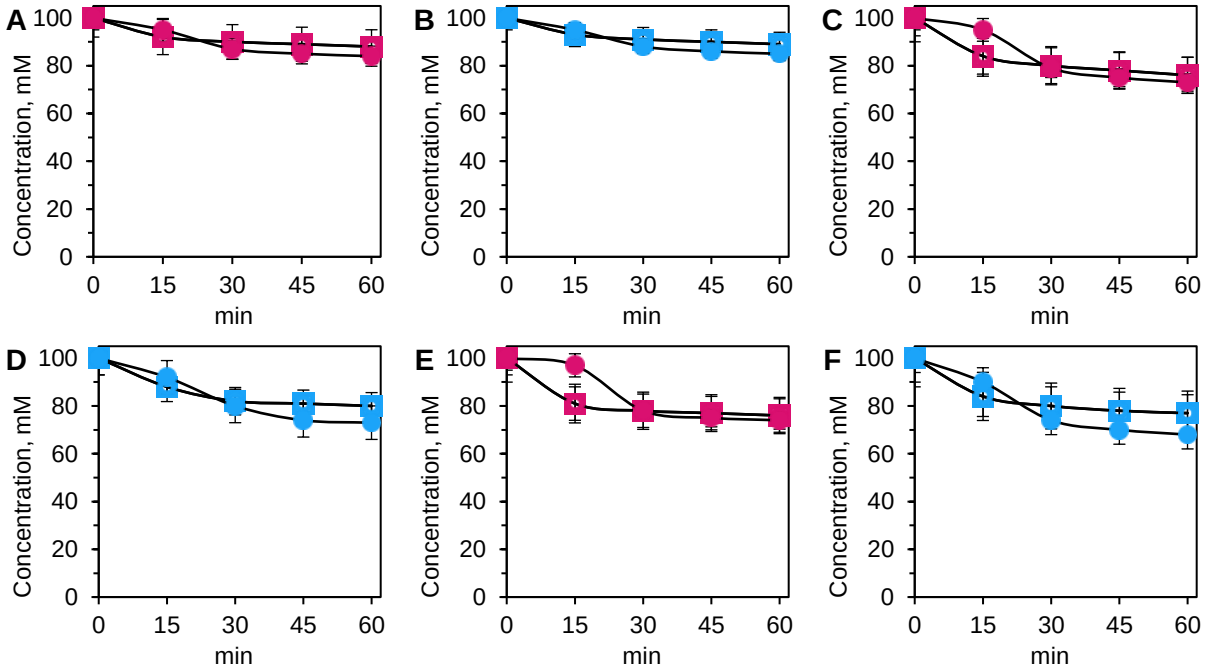


Figure S19. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of ferulic acid (○), acetoin (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

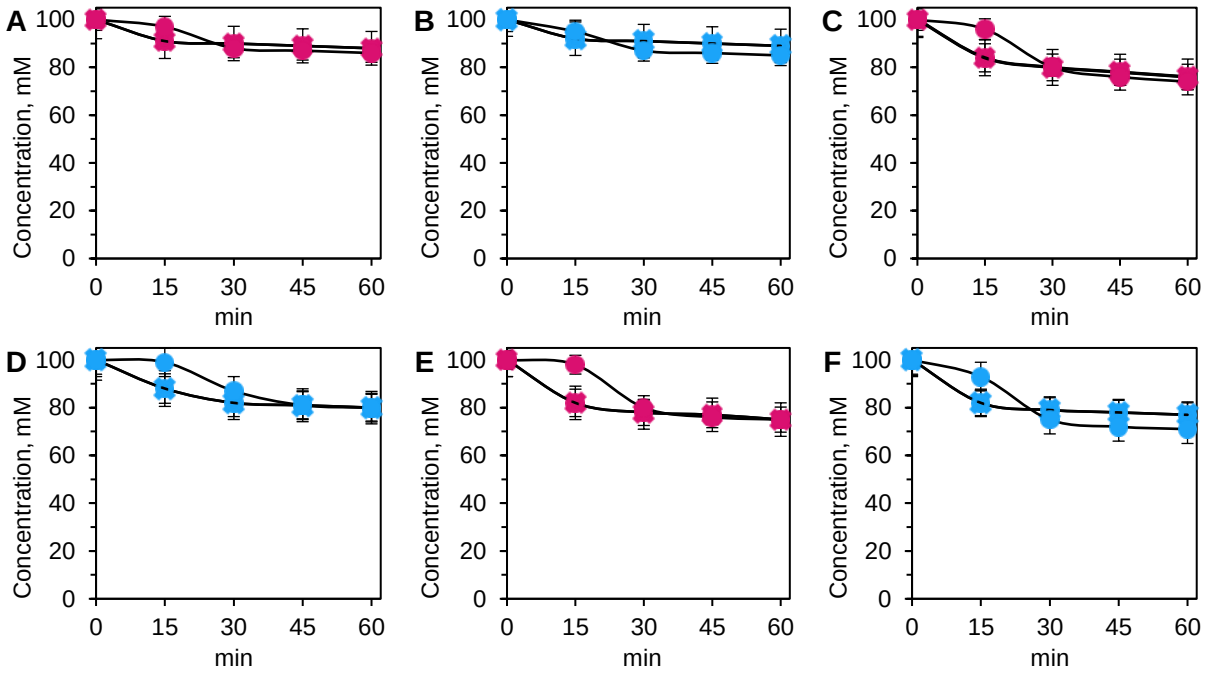


Figure S20. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of gallic acid (○), methylglyoxal (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

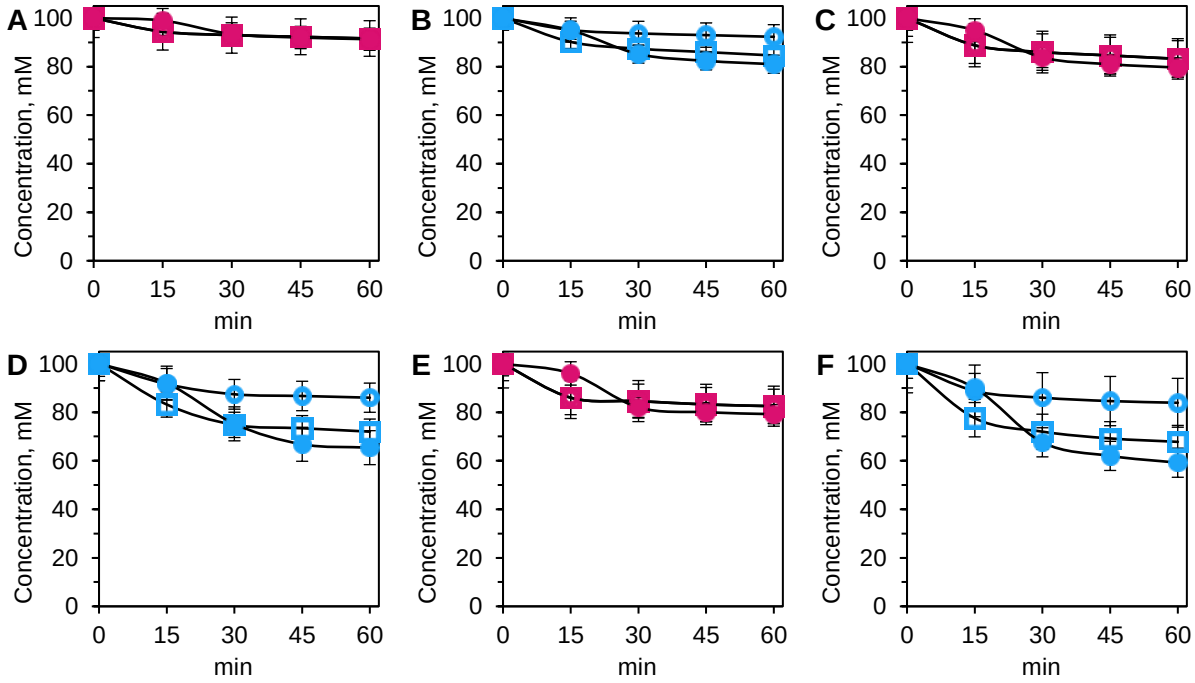


Figure S21. The time evolution of experimental (markers) and calculated (solid line) concentration of HTL of equimolar mixture of gallic acid (○), acetoin (□), and NH_3-N (●) at 280 (A–B), 325 (C–D), and 370 (E–F) °C under acid (red) and alkali (blue) catalyzed conditions.

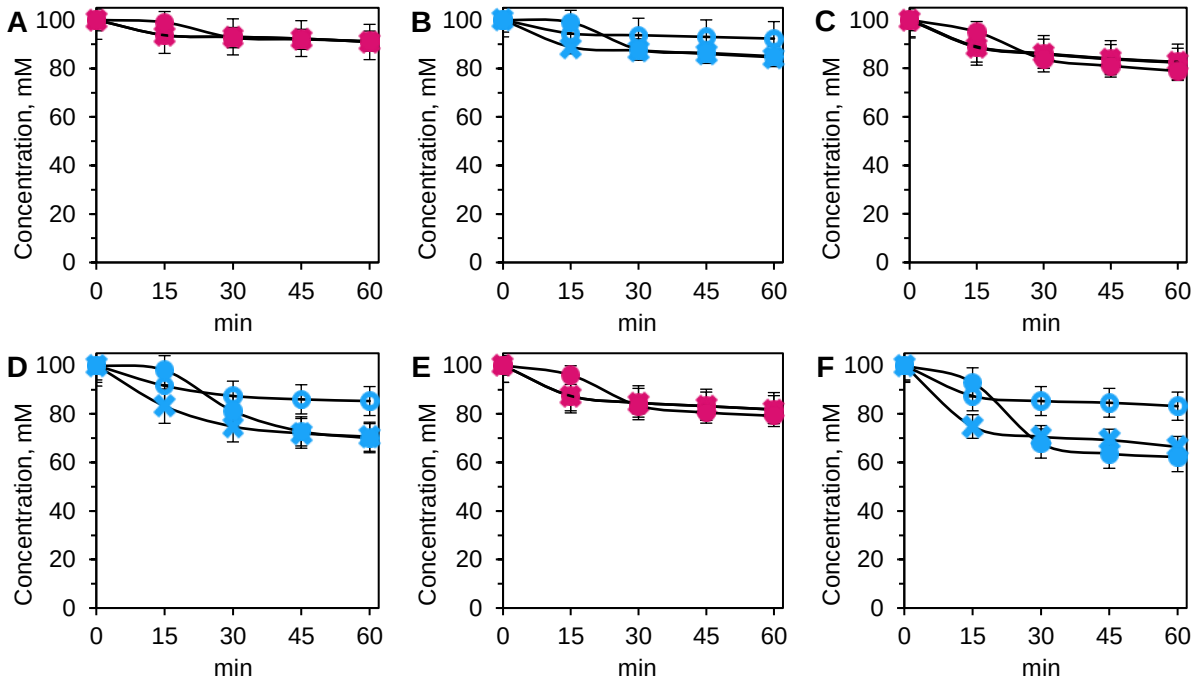
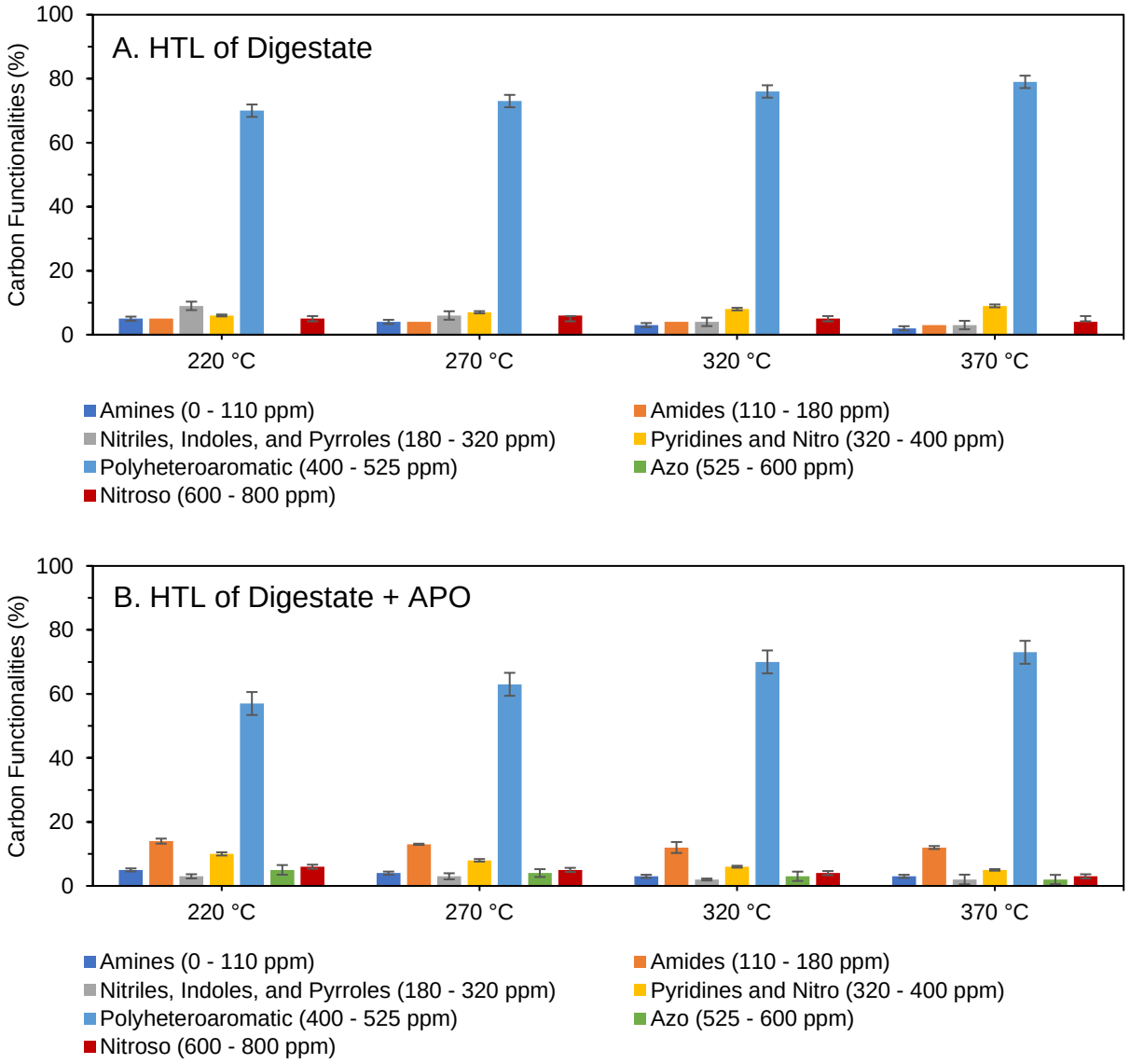
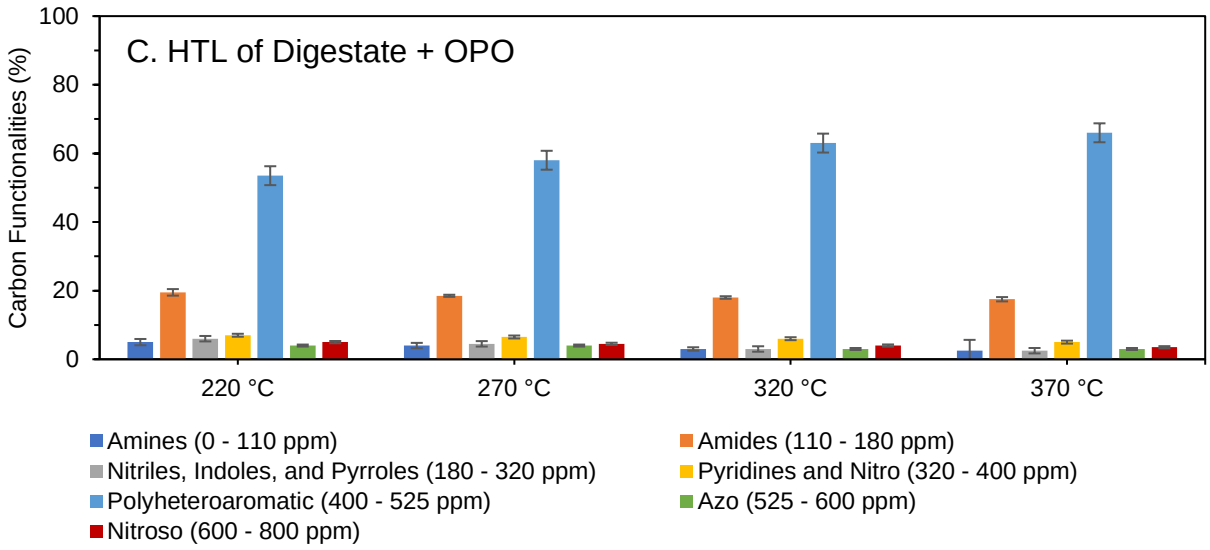
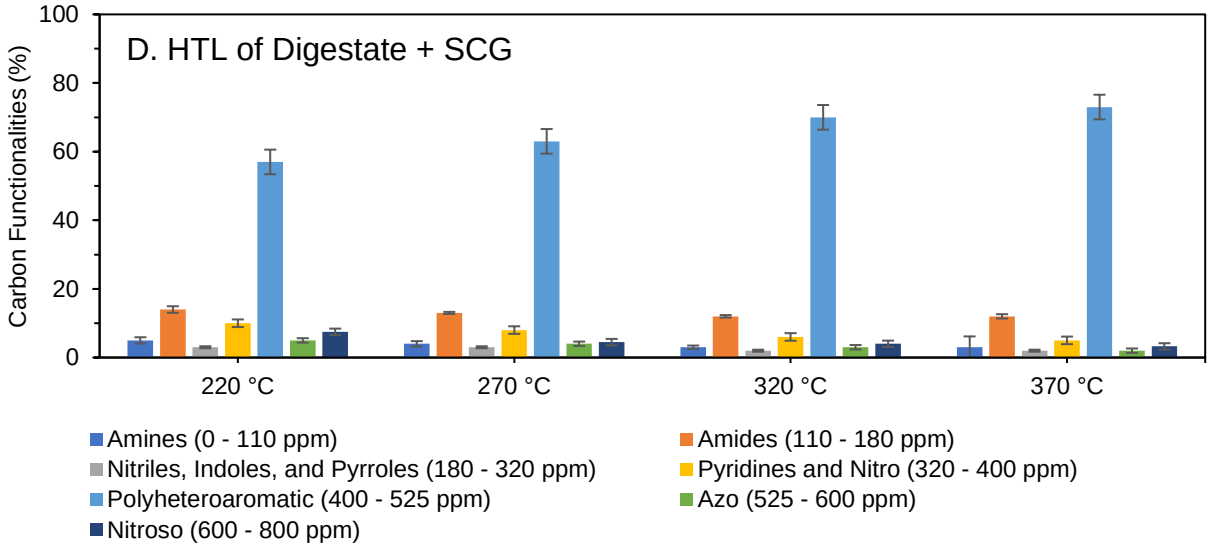


Figure S22. The solid-state ^{15}N-NMR of hydrochar produced from HTL of (A) digestate and its mixtures with polyphenolic extract from (B) apple pomace, (C) olive pomace, (D) spent coffee grounds, and (E) sweet orange peels at 370 °C under acid catalysis.




C. HTL of Digestate + OPO
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Amines (0 - 110 ppm)
Amides (110 - 180 ppm)
Nitriles, Indoles, and Pyrroles (180 - 320 ppm)
Pyridines and Nitro (320 - 400 ppm)
Polyheteroaromatic (400 - 525 ppm)
Azo (525 - 600 ppm)
Nitroso (600 - 800 ppm)


D. HTL of Digestate + SCG
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Amines (0 - 110 ppm)
Amides (110 - 180 ppm)
Nitriles, Indoles, and Pyrroles (180 - 320 ppm)
Pyridines and Nitro (320 - 400 ppm)
Polyheteroaromatic (400 - 525 ppm)
Azo (525 - 600 ppm)
Nitroso (600 - 800 ppm)

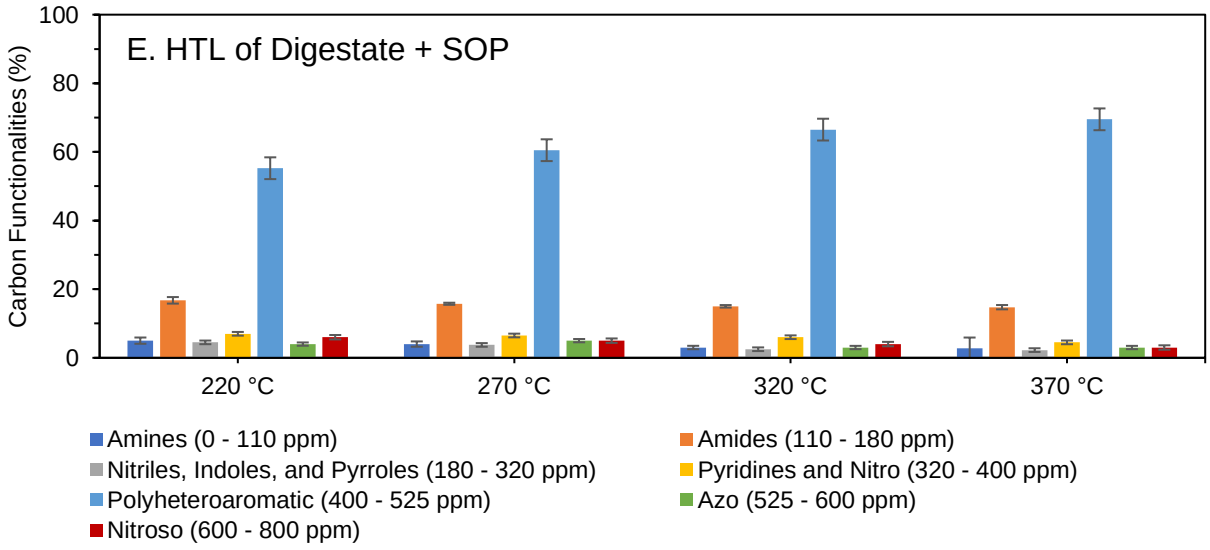
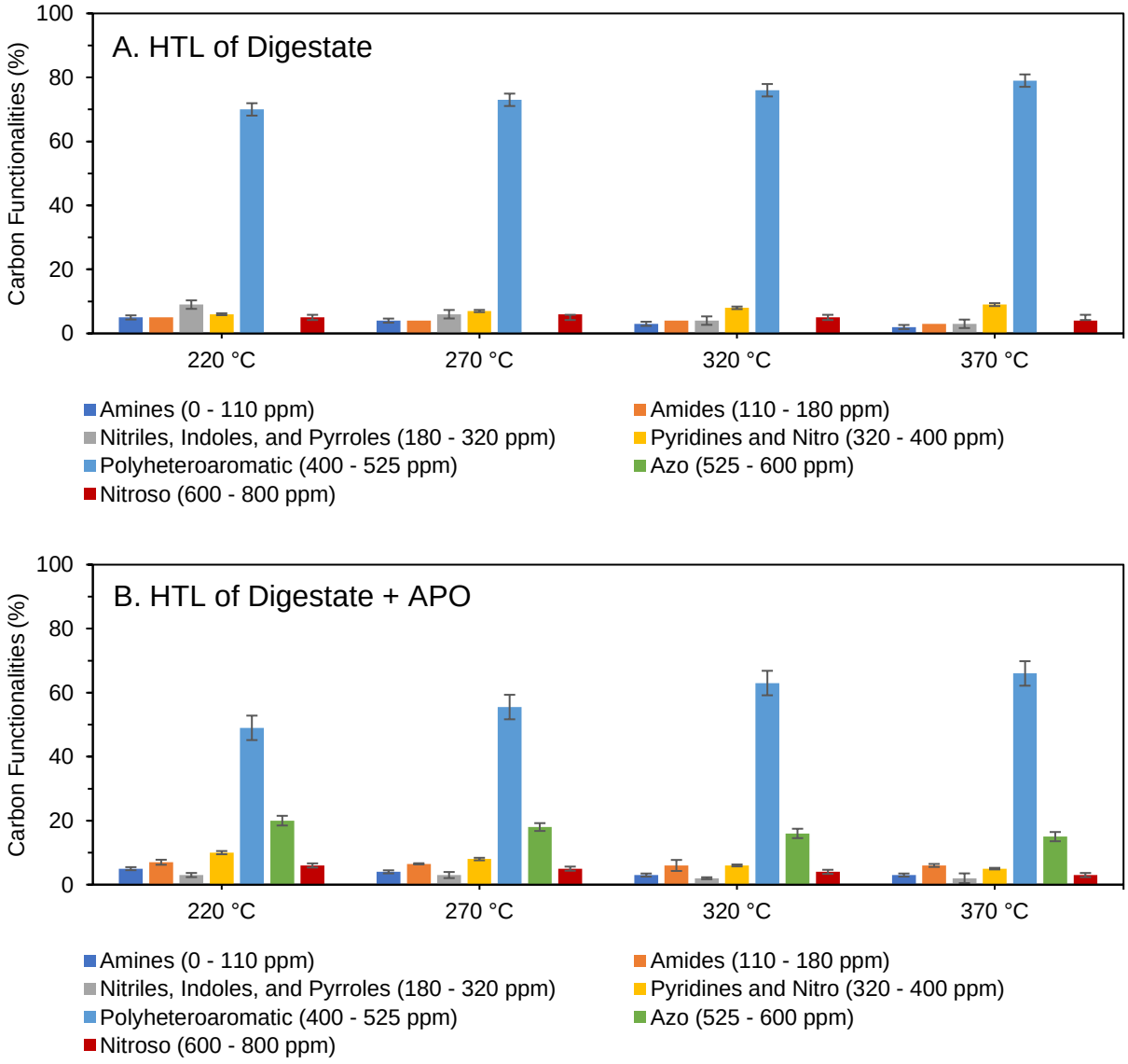
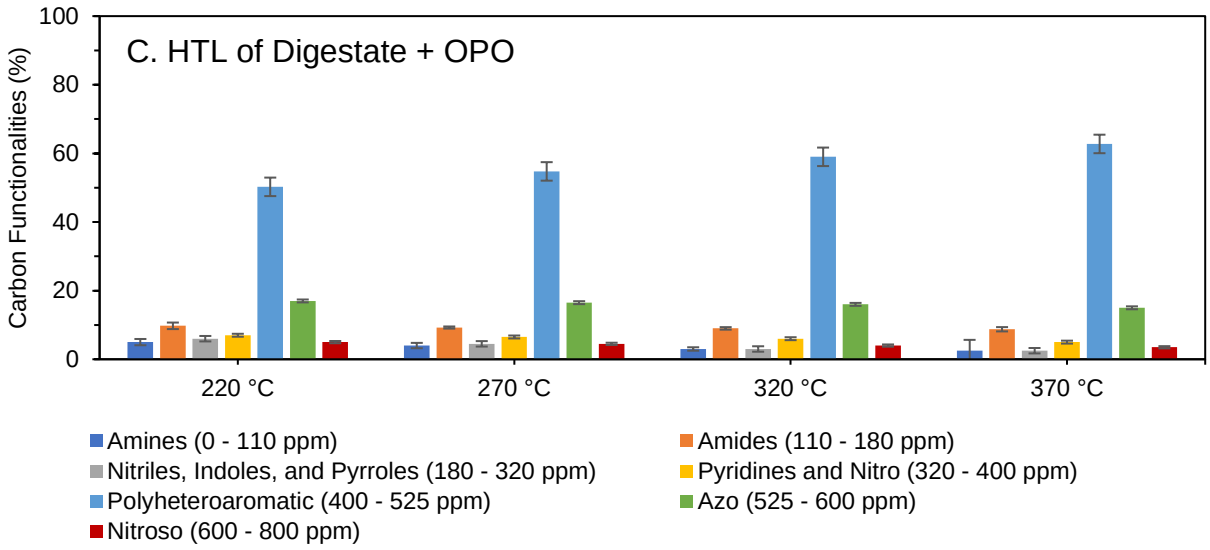
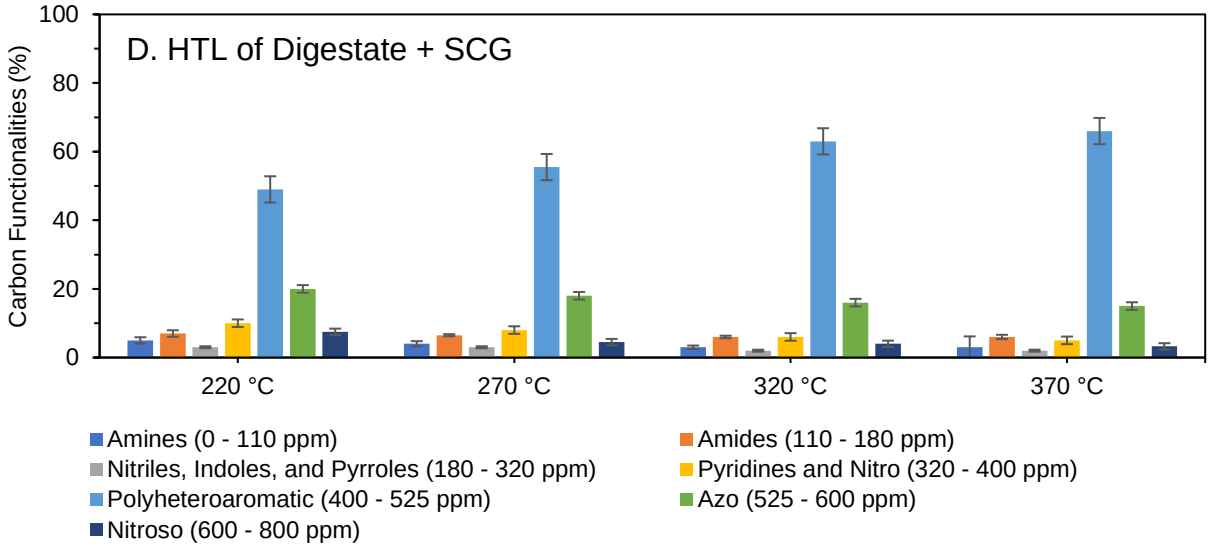

E. HTL of Digestate + SOP
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Amines (0 - 110 ppm)
Amides (110 - 180 ppm)
Nitriles, Indoles, and Pyrroles (180 - 320 ppm)
Pyridines and Nitro (320 - 400 ppm)
Polyheteroaromatic (400 - 525 ppm)
Azo (525 - 600 ppm)
Nitroso (600 - 800 ppm)

Figure S23. The solid-state ^{15}N-NMR of hydrochar produced from HTL of (A) digestate and its mixtures with polyphenolic extract from (B) apple pomace, (C) olive pomace, (D) spent coffee grounds, and (E) sweet orange peels at 370 °C under alkali catalysis.




C. HTL of Digestate + OPO
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Amines (0 - 110 ppm)
Amides (110 - 180 ppm)
Nitriles, Indoles, and Pyrroles (180 - 320 ppm)
Pyridines and Nitro (320 - 400 ppm)
Polyheteroaromatic (400 - 525 ppm)
Azo (525 - 600 ppm)
Nitroso (600 - 800 ppm)


D. HTL of Digestate + SCG
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Amines (0 - 110 ppm)
Amides (110 - 180 ppm)
Nitriles, Indoles, and Pyrroles (180 - 320 ppm)
Pyridines and Nitro (320 - 400 ppm)
Polyheteroaromatic (400 - 525 ppm)
Azo (525 - 600 ppm)
Nitroso (600 - 800 ppm)

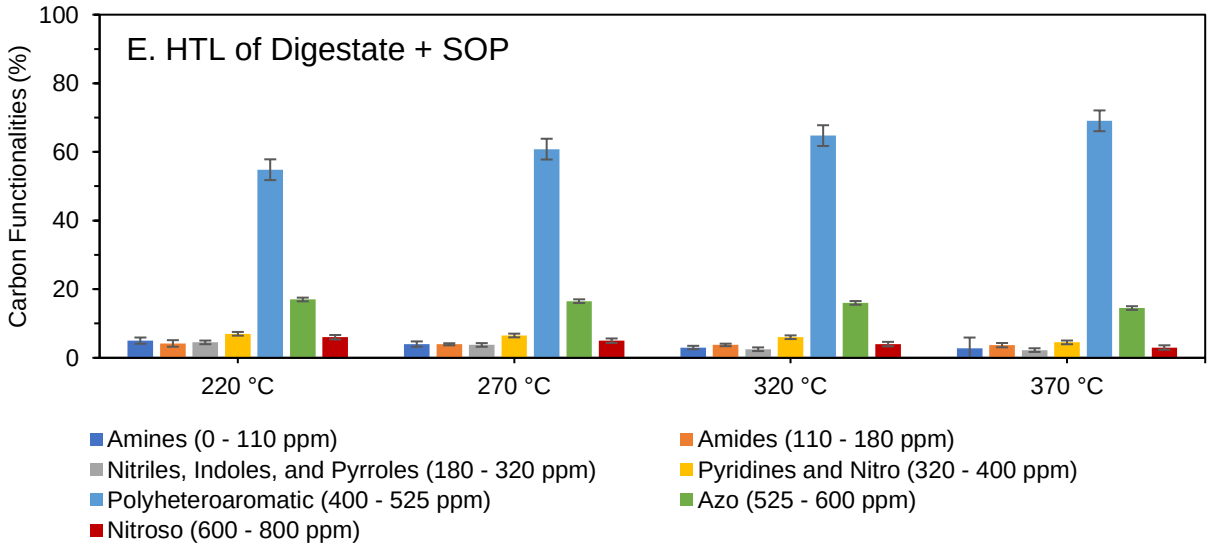
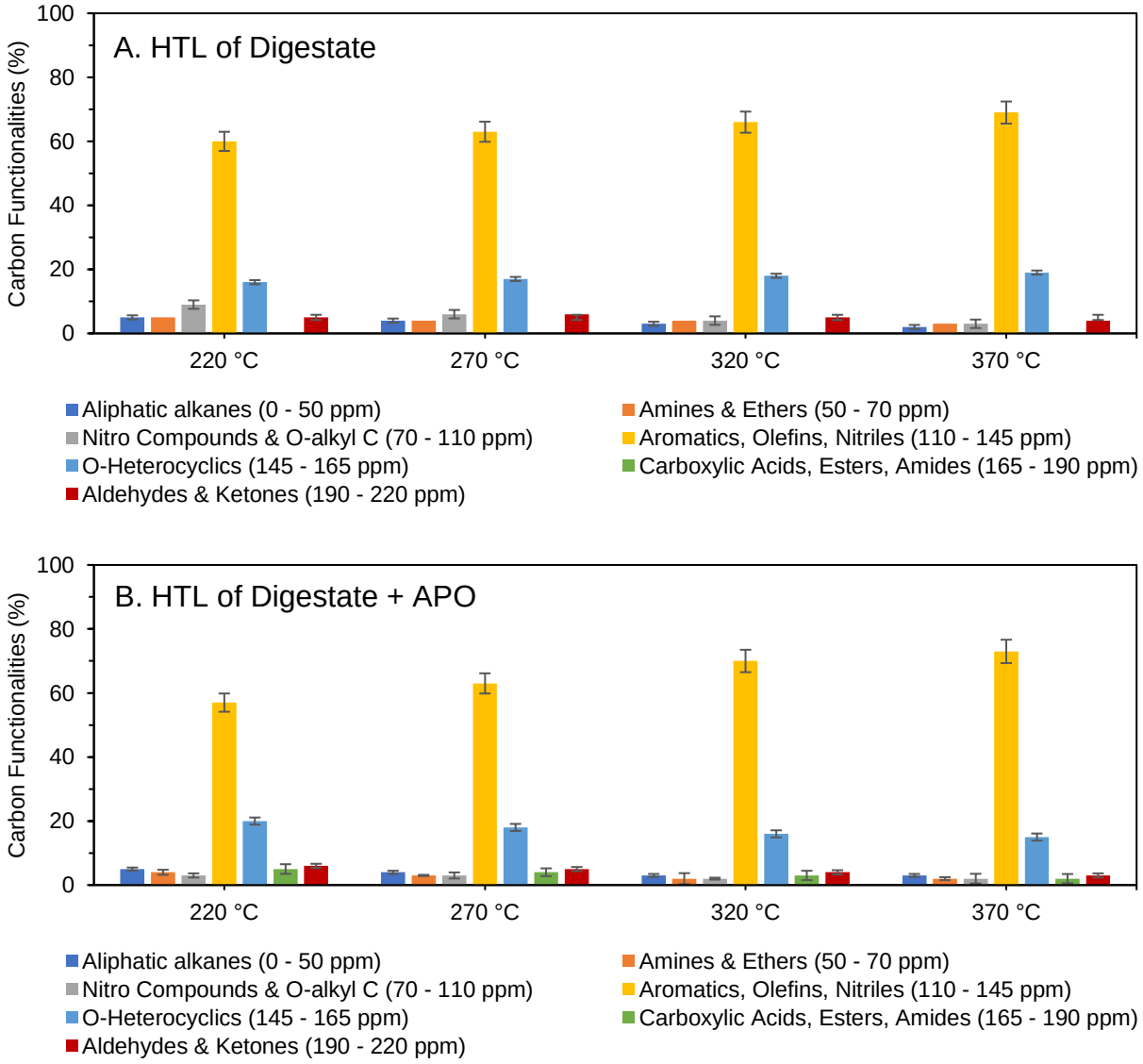

E. HTL of Digestate + SOP
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Amines (0 - 110 ppm)
Amides (110 - 180 ppm)
Nitriles, Indoles, and Pyrroles (180 - 320 ppm)
Pyridines and Nitro (320 - 400 ppm)
Polyheteroaromatic (400 - 525 ppm)
Azo (525 - 600 ppm)
Nitroso (600 - 800 ppm)

Figure S24. The solid-state ^{13}C-NMR of hydrochar produced from HTL of (A) digestate and its mixtures with polyphenolic extract from (B) apple pomace, (C) olive pomace, (D) spent coffee grounds, and (E) sweet orange peels at 370 °C under acid catalysis.



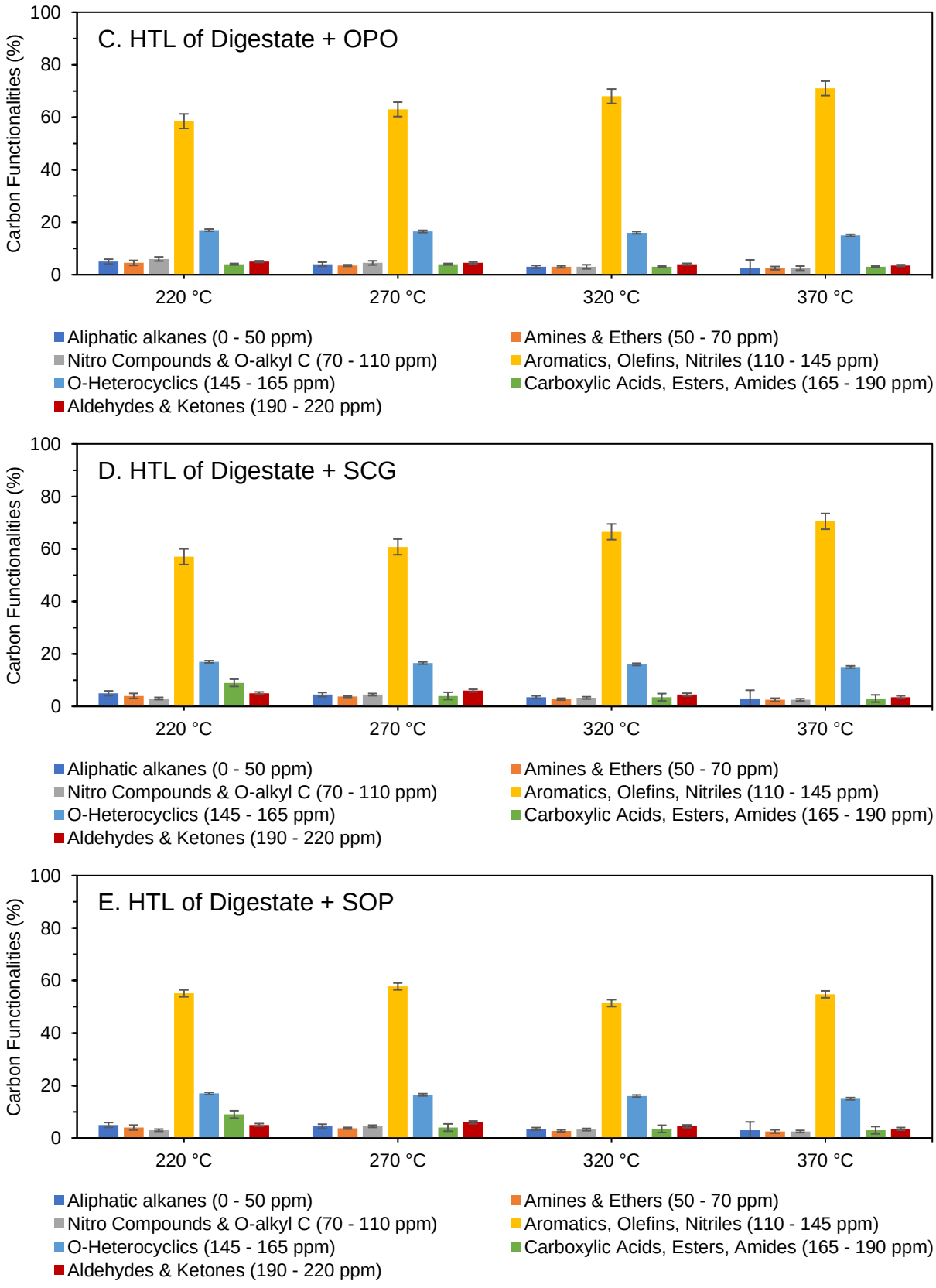
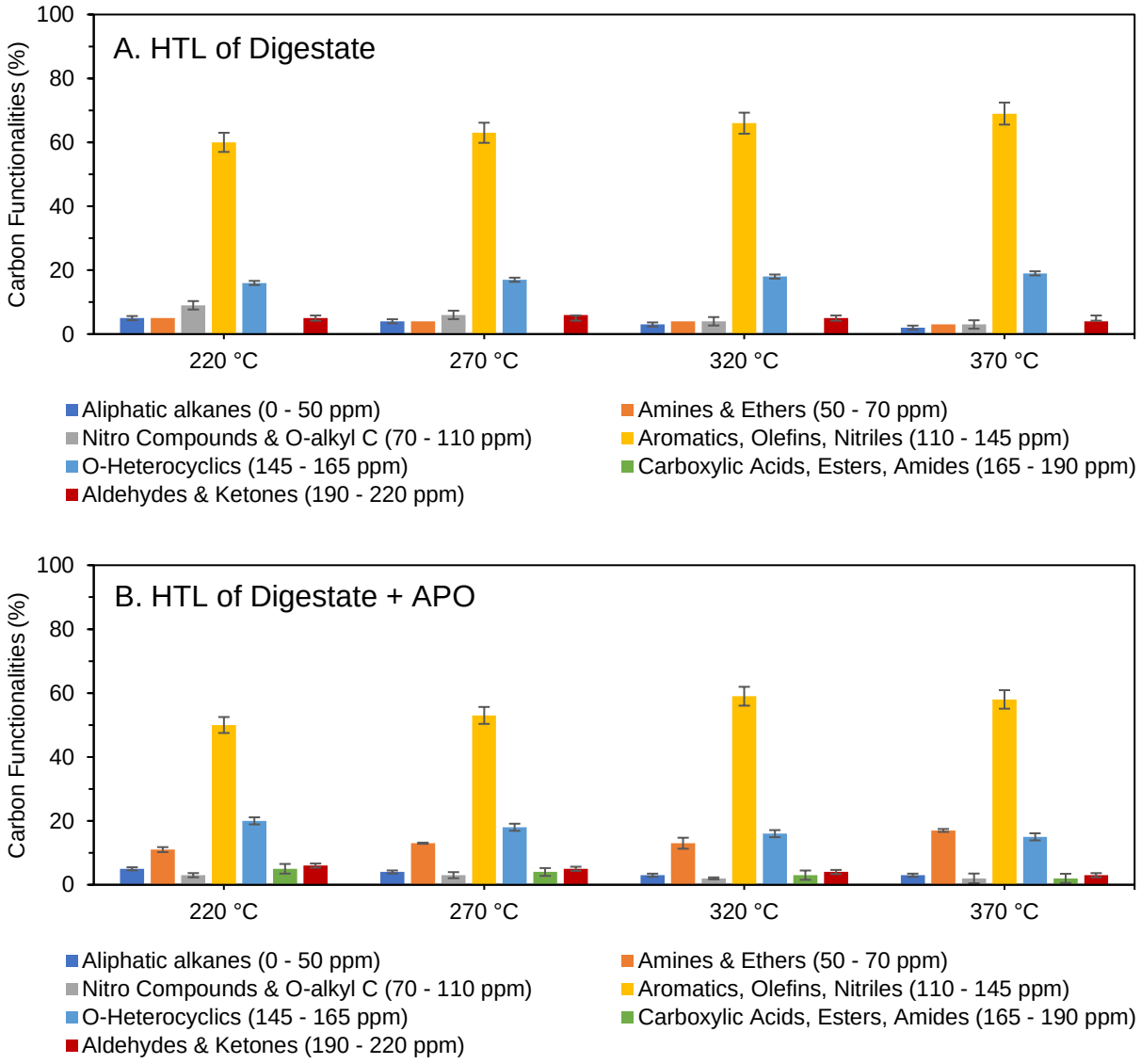

C. HTL of Digestate + OPO
D. HTL of Digestate + SCG
E. HTL of Digestate + SOP
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Aliphatic alkanes (0 - 50 ppm)
Amines & Ethers (50 - 70 ppm)
Nitro Compounds & O-alkyl C (70 - 110 ppm)
Aromatics, Olefins, Nitriles (110 - 145 ppm)
O-Heterocyclics (145 - 165 ppm)
Carboxylic Acids, Esters, Amides (165 - 190 ppm)
Aldehydes & Ketones (190 - 220 ppm)

Figure S25. The solid-state ^{13}C-NMR of hydrochar produced from HTL of (A) digestate and its mixtures with polyphenolic extract from (B) apple pomace, (C) olive pomace, (D) spent coffee grounds, and (E) sweet orange peels at 370 °C under alkali catalysis.



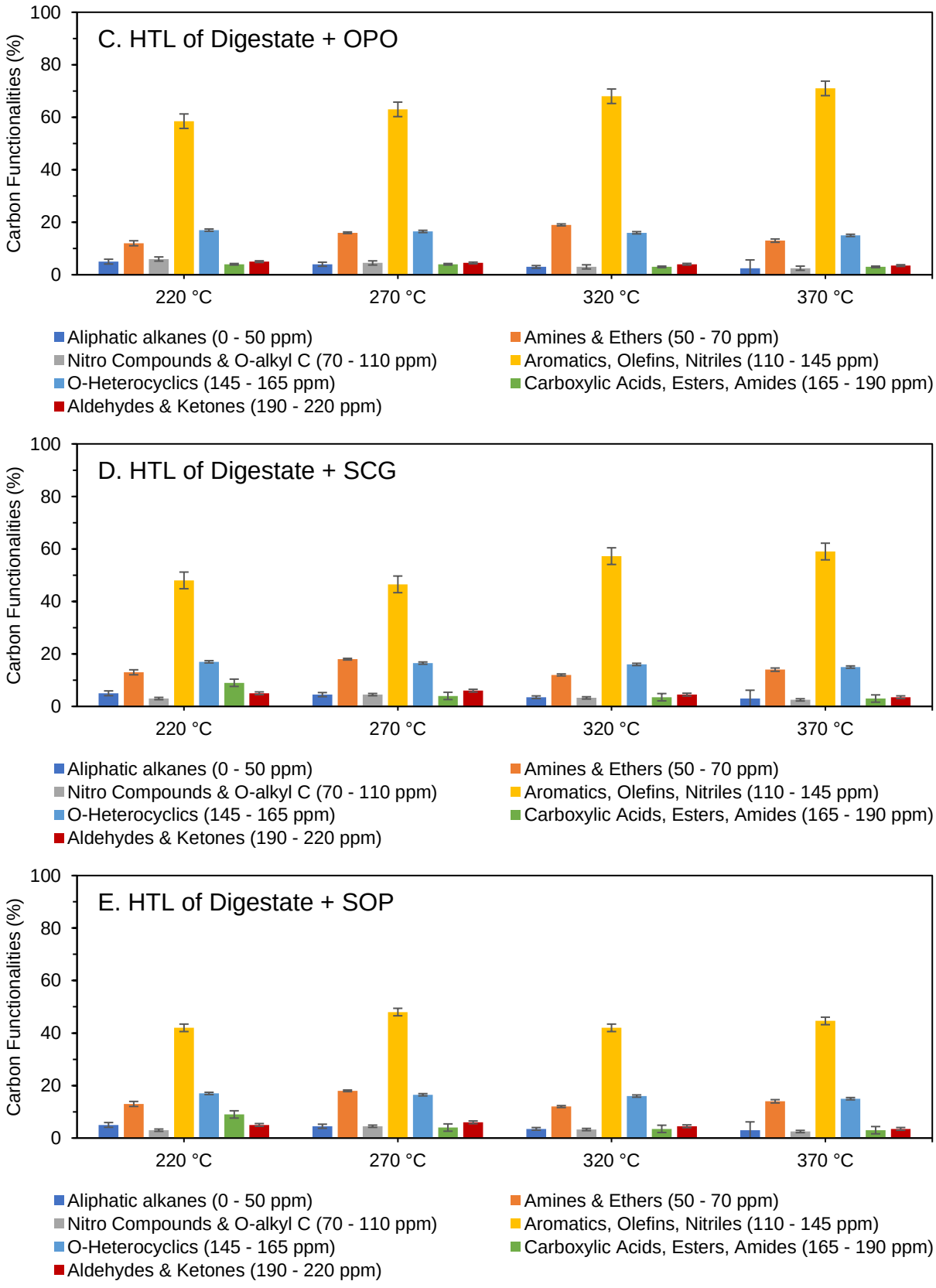

C. HTL of Digestate + OPO
D. HTL of Digestate + SCG
E. HTL of Digestate + SOP
Carbon Functionalities (%)
100
80
60
40
20
0
220 °C
270 °C
320 °C
370 °C
Aliphatic alkanes (0 - 50 ppm)
Amines & Ethers (50 - 70 ppm)
Nitro Compounds & O-alkyl C (70 - 110 ppm)
Aromatics, Olefins, Nitriles (110 - 145 ppm)
O-Heterocyclics (145 - 165 ppm)
Carboxylic Acids, Esters, Amides (165 - 190 ppm)
Aldehydes & Ketones (190 - 220 ppm)

Figure S26. The atom numbering of significant polyphenols: epicatechin, quercetin, caffeic acid, ferulic acid, and gallic acid.

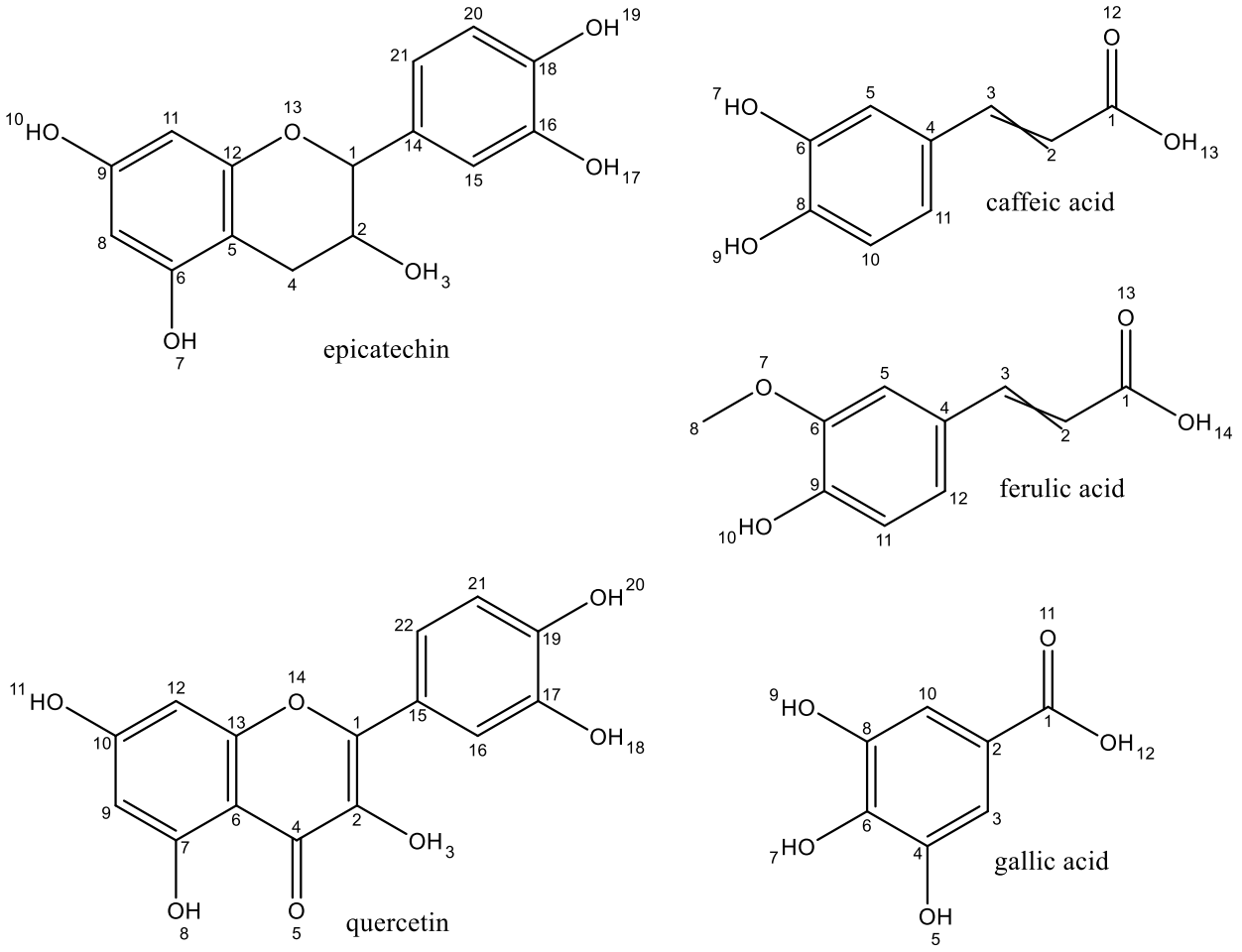


Figure S27. The final pH of the aqueous-phase coproduct from HTL of digestate and its mixtures with polyphenols extracts from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min with (A) acidic (pH 3); (B) neutral (pH 7); and (C) alkaline (pH 11) feedstock pHs.

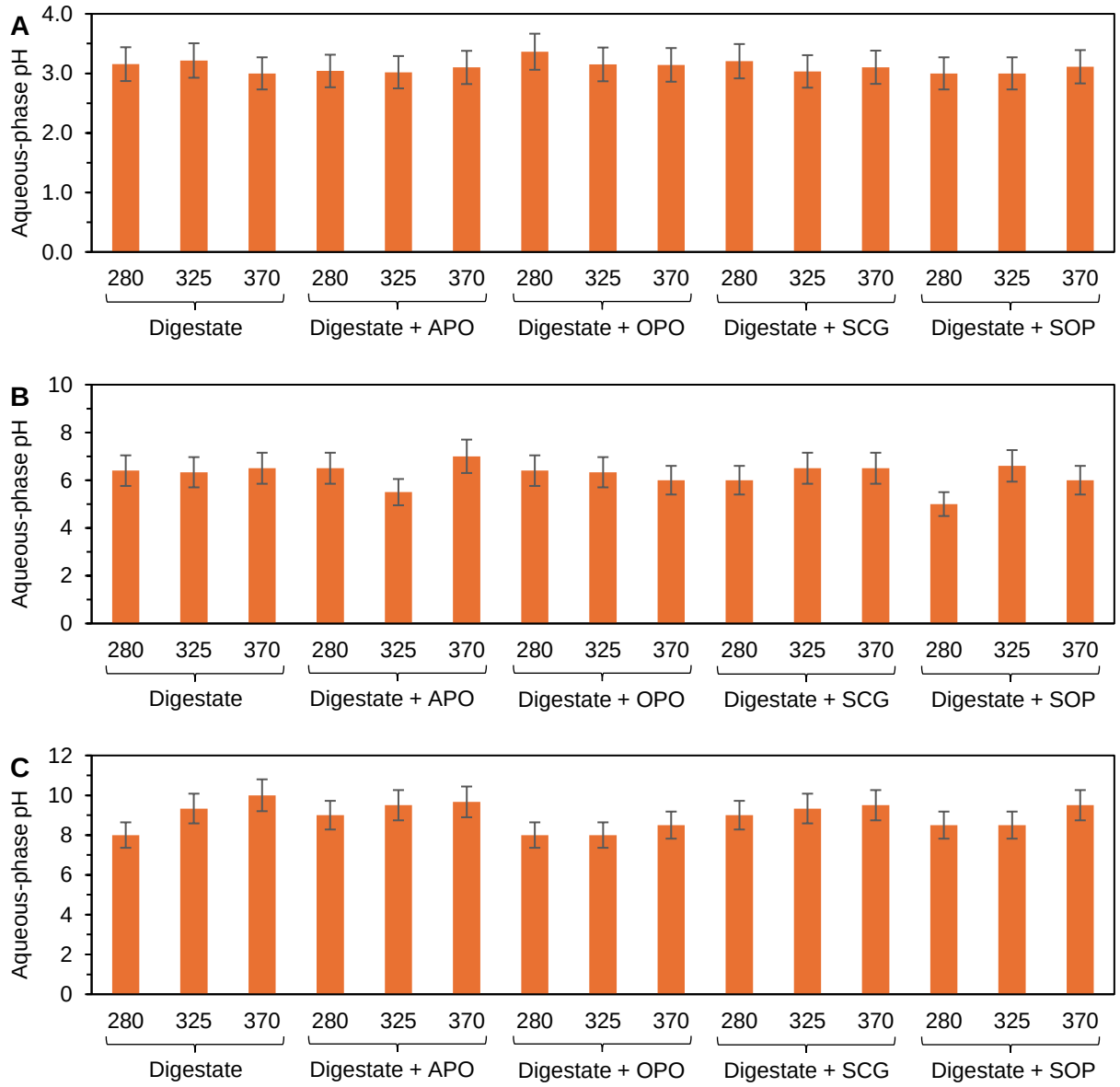


Table S1. Limitations of previous studies on *in situ* heteroatom removal of HTL-derived biocrude.

Previous studies	Summary
Lu et al. [1]	The *in situ* catalytic DO and DN have demonstrated success in reducing the oxygen content of biocrude to 15–25 wt% by promoting decarboxylation and dehydration of biocrude constituents (e.g., esters, furans, and ketones) into aliphatic hydrocarbons using solid heterogeneous catalysts based on transition metals, e.g., Ni-doped hydrotalcite and Fe–Co/ZSM-5. However, the nitrogen removal is not so significant (i.e., 5–7 wt%) since the catalyzed denitrogenation occurs via direct deamination of mostly amino acids yielding NH_3 that readily reacts with reducing sugars, aldehydes, and carboxylic acid radicals producing N-heterocycles and amides in biocrude.
Du et al. [2] Wang et al. [3] Cui et al. [4]	The *in situ* HDO and HDN initiated by a series of catalytic decarbonylation and WGS reactions to provide hydrogen only reduce the nitrogen content in biocrude to 2–4 wt% despite much higher yield of hydrocarbon, i.e., 80–90%. The employment of noble metal catalysts (e.g., Ru, Pt, Cu, and Ce) supported by silica, alumina, and various clay minerals in this effort has four shortcomings. The first one is the higher selectivity of deoxygenation over denitrogenation. The second one is the competitive adsorption of CO by the catalyst and hydrochar surfaces, compromising the acquired yield of hydrogen available for HDO and HDN reactions. The third one is the quick catalyst deactivation due to the poisoning of acidic active sites of the catalyst by basic nitrogen-containing compounds, e.g., pyridines and amines. The fourth one is the recoverability and reusability of the catalyst because it is mixed with the hydrochar formed during HTL, reducing the economic attractiveness of HTL commercial operations.

Previous studies	Summary
Li et al. [5] Han et al. [6] Mahesh et al. [7]	The *in situ* HDO and HDN aided by hydrogen-donor solvents (e.g., formic acid, glycerol, ethylene glycol, and isopropyl alcohol) is the least promising despite the improved yield of biocrude (i.e., 55–65%) and the lowered oxygen content of biocrude, i.e., 15–20%. The utilization of formic acid as a H-donor yields a substantial amount of CO_2 as a result of formic acid dehydrogenation, leading to the requirement of additional unit processes to capture CO_2. Meanwhile, the use of alcohols as H-donors produces biocrude with higher nitrogen content. The higher nitrogen content is due to the formation of α-dicarbonyls/α-hydroxycarbonyls derived from aldehydes (e.g., glyceraldehyde and acetaldehyde), which are produced after dehydrogenation of alcohols. The α-dicarbonyls/α-hydroxycarbonyls are key precursors for N-heterocycles formation via the Maillard, Paal-Knorr, and Debus-Radziszewski reactions.

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Table S2. Physicochemical characteristics of anaerobically digested sewage sludge including the employed characterization methods (see the references on the next page).

Parameters	Value	Methods
pH	7.15 ± 0.22	Electrometric[8]
NH_3-N (mg/l)	4290 ± 19.65	ASTM D1426-15[9]
DM (%FM)	88.95 ± 2.05	Drying at 105 ºC[8]
Ash Content (%DM)	25.21 ± 3.11	ASTM E1131-20[10]
Proximate Analysis (%DM)		
Lignin	20.24 ± 3.86	The Van Soest's detergent fiber analysis[11] : - acid detergent lignin (ADL)[12] - acid detergent fiber (ADF)[12]
Cellulose	22.69 ± 1.67	- neutral detergent fiber (NDF)[12] Lignin = ADL Cellulose = (ADF – ADL)
Hemicellulose	8.95 ± 1.05	Hemicellulose = (NDF – ADL)
Soluble sugars	-	Luff-Schoorl[13]
Lipid	0.59 ± 0.37	Drying and Soxhlet extraction[8]
Protein	3.72 ± 0.92	N_{org} × 6.25; $N_{org\ is}$ the difference between total Kjeldahl nitrogen[8] and NH_3-N[9]
Organic acids	0.64 ± 0.15	Distillation and titration method[8] The organic acid for digestate was assumed as acetic acid.
Ultimate Analysis (%DM)		
C	43.90 ± 1.70	ASTM D5373-21[14]
H	4.18 ± 0.42	
N	1.83 ± 0.56	
O	40.22 ± 1.93	
P	1.21 ± 0.40	SMT extraction protocol[15] and molybdate blue method[8]
K	1.57 ± 0.67	SMT extraction protocol[15] and turbidimetric tetraphenylborate method[16]
Ca	4.09 ± 0.34	SMT extraction protocol[15] and oxalate method[17]
Mg	1.15 ± 0.81	SMT extraction protocol[15] and Calmagite method[18]
Cl	1.25 ± 0.16	SMT extraction protocol[15] and mercury(II) thiocyanate method[19]
Al	3.57 ± 0.58	SMT extraction protocol[15] and aluminon method[20]

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17 R. W. Wells, *Am. J. Clin. Pathol.*, 1948, **18**, 576–578.

18 M. F. Ryan and H. Barbour, *Ann. Clin. Biochem.*, 1998, **35**, 449–459.

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20 C. J. Van Nieuwenburg and G. Uitenbroek, *Anal. Chim. Acta*, 1948, **2**, 88–91.

Table S3. Description of methods characterizing the polyphenolic extract and hydrochar.

Analytical Methods	Procedures
UPLC–Q–Exactive Orbitrap/MS analysis of polyphenolic extract	The samples were eluted with solvents A (0.1 % formic acid in ultrapure water) and B (0.1 % formic acid in methanol). The gradient was the following: 0–3 min 5 to 15% B, 3–11 min 15 to 30% B, 11–15 min 30 to 50% B, 15–21 min 50 to 90% B, 21–22 min 90 to 5% B. The flow rate of the mobile phase, column temperature, injection volume, and capillary voltage were set at 0.3 mL/min, 40 °C, 5 μL, and 3200 V, respectively. The mass spectra were recorded in negative ion mode from 80 to 1200 m/z. Identification of corresponding polyphenols was conducted by comparing their spectra and retention times with those of externally injected reference compounds. For quantification, external calibration curves were prepared for each standard. For compounds whose standards were not available, identification was performed using the mass of the parent ion and typical MS fragmentation pattern with references.
Solid-state ^{13}C-NMR of hydrochar	The direct-polarization magic-angle spinning (DP-MAS) ^{13}C SS-NMR was carried out on a 500 MHz Bruker Avance II NMR spectrometer, with a 4 mm triple resonance probe, 200 MHz operating frequency, 90° pulse length of 2 μs, 20 s recycle delay, 13 kHz MAS rate, and 1024 number of transients. The two-pulse phase-modulated proton-decoupling technique was used to obtain high-resolution spectra. The reference compound was adamantane-d16 (≥98%, Sigma-Aldrich) with respect to tetramethylsilane (Sigma-Aldrich). The NMR spectra was analyzed using MNova 14.2.3 from MestreLab.
Solid-state ^{15}N-NMR of hydrochar	The ^{15}N NMR was performed on a Tecmag Apollo Spectrometer equipped with a 4 mm HXY MAS Chemagnetics probe operating at a ^{15}N frequency of ∼29.90 MHz. The cross-polarization (CP) from ^{1}H to ^{15}N nuclei with heteronuclear decoupling (i.e., ^{15}N CP-MAS at a MAS frequency of 5 kHz), 5 μs π/2 ^{1}H and 6.5 μs π/2 ^{15}N excitation pulses, eight-step phase cycling, a recycle delay of 2 s, and TPPM ^{1}H–^{15}N heteronuclear decoupling was employed during the spectra acquisition. The acquired ^{15}N NMR spectra were referenced to ammonia at 0 ppm. The NMR spectra was analyzed using MNova 14.2.3 from MestreLab.

Table S4. Pearson correlation analysis on the relationship of reaction temperature, feedstock pH, and polyphenols composition with the yield of carbon and nitrogen and biocrude elemental content. The red color indicates a negative correlation whereas the black color indicates a positive correlation.

Response Variables	Temperature	Feedstock pH	Total Polyphenol	Total Tannin	Total Flavonoid	Gallic Acid	Caffeic Acid	Ferulic Acid	Epicatechin	Quercetin
C_{Oil}	280	3	0.87	0.89	0.79	0.93	0.90	0.98	0.88	0.87
		7	0.87	0.89	0.79	0.93	0.90	0.10	0.88	0.87
		11	0.87	0.89	0.79	0.93	0.90	0.98	0.88	0.87
	325	3	0.77	0.59	0.74	0.65	0.63	0.66	0.68	0.67
		7	0.77	0.59	0.74	0.65	0.63	0.66	0.68	0.67
		11	0.77	0.59	0.74	0.65	0.63	0.66	0.68	0.67
	370	3	0.81	0.90	0.70	0.93	0.90	0.94	0.86	0.85
		7	0.81	0.90	0.70	0.93	0.90	0.94	0.86	0.85
		11	0.81	0.90	0.70	0.93	0.90	0.94	0.86	0.85
C_{Char}	280	3	0.68	0.76	0.61	0.80	0.77	0.90	0.73	0.72
		7	0.68	0.76	0.60	0.80	0.76	0.13	0.72	0.71
		11	0.66	0.74	0.58	0.79	0.75	0.89	0.70	0.69
	325	3	0.97	0.97	0.93	0.99	0.98	0.99	0.98	0.98
		7	0.97	0.97	0.93	0.98	0.98	0.99	0.98	0.98
		11	0.97	0.96	0.92	0.98	0.97	0.99	0.98	0.97
	370	3	0.97	0.98	0.91	0.99	0.99	0.98	0.98	0.98
		7	0.96	0.97	0.91	0.99	0.98	0.99	0.98	0.97
		11	0.96	0.97	0.91	0.99	0.98	0.99	0.98	0.97
C_{AqP}	280	3	0.13	0.00	0.13	0.03	0.01	0.24	0.06	0.07
		7	0.07	0.19	0.04	0.24	0.19	0.64	0.14	0.13
		11	0.48	0.60	0.46	0.61	0.59	0.75	0.55	0.55
	325	3	0.86	0.95	0.81	0.93	0.94	0.91	0.92	0.92
		7	0.90	0.97	0.83	0.98	0.97	0.97	0.94	0.94
		11	0.91	0.98	0.87	0.97	0.97	0.94	0.96	0.96

Response Variables	Temperature	Feedstock pH	Total Polyphenol	Total Tannin	Total Flavonoid	Gallic Acid	Caffeic Acid	Ferulic Acid	Epicatechin	Quercetin
	370	3	0.97	0.99	0.94	0.98	0.99	0.92	0.99	1.00
		7	0.98	0.95	0.99	0.94	0.96	0.93	0.98	0.98
		11	0.97	0.95	0.95	0.96	0.96	0.98	0.97	0.97
C_{Gas}	280	3	0.56	0.36	0.54	0.45	0.40	0.51	0.46	0.44
		7	0.37	0.55	0.25	0.48	0.52	0.85	0.45	0.46
		11	0.45	0.35	0.60	0.27	0.35	0.19	0.43	0.45
	325	3	0.53	0.48	0.52	0.56	0.51	0.76	0.51	0.50
		7	0.48	0.48	0.62	0.41	0.47	0.45	0.51	0.53
		11	0.13	0.02	0.11	0.10	0.02	0.29	0.05	0.03
	370	3	0.11	0.35	0.07	0.26	0.31	0.15	0.23	0.25
		7	0.51	0.53	0.34	0.62	0.55	0.65	0.50	0.48
		11	0.75	0.75	0.64	0.73	0.75	0.54	0.74	0.74
ER_{Oil}	280	3	0.78	0.89	0.72	0.90	0.89	0.93	0.85	0.84
		7	0.87	0.89	0.79	0.93	0.90	0.10	0.88	0.87
		11	0.87	0.89	0.79	0.93	0.90	0.98	0.88	0.87
	325	3	0.77	0.59	0.74	0.65	0.63	0.66	0.68	0.67
		7	0.77	0.59	0.74	0.65	0.63	0.66	0.68	0.67
		11	0.77	0.59	0.74	0.65	0.63	0.66	0.68	0.67
	370	3	0.81	0.90	0.70	0.93	0.90	0.94	0.86	0.85
		7	0.81	0.90	0.70	0.93	0.90	0.94	0.86	0.85
		11	0.81	0.90	0.70	0.93	0.90	0.94	0.86	0.85
N_{Oil}	280	3	0.93	0.91	0.91	0.88	0.91	0.76	0.93	0.94
		7	0.98	0.96	0.94	0.95	0.97	0.57	0.98	0.98
		11	0.89	0.90	0.80	0.95	0.91	0.98	0.90	0.89
	325	3	0.93	0.91	0.91	0.87	0.91	0.75	0.93	0.94
		7	0.97	0.95	0.94	0.92	0.95	0.82	0.97	0.97
		11	0.98	0.98	0.92	0.99	0.99	0.93	0.99	0.99
	370	3	0.93	0.91	0.91	0.88	0.91	0.76	0.93	0.94
		7	0.96	0.96	0.93	0.94	0.96	0.84	0.97	0.98

Response Variables	Temperature	Feedstock pH	Total Polyphenol	Total Tannin	Total Flavonoid	Gallic Acid	Caffeic Acid	Ferulic Acid	Epicatechin	Quercetin
		11	0.93	0.98	0.85	0.99	0.98	0.98	0.96	0.95
N_{Char}	280	3	0.90	0.95	0.84	0.96	0.95	0.99	0.93	0.92
		7	0.67	0.76	0.60	0.80	0.76	0.13	0.72	0.71
		11	0.66	0.74	0.58	0.79	0.75	0.89	0.70	0.69
	325	3	0.36	0.39	0.30	0.48	0.41	0.67	0.38	0.36
		7	0.97	0.97	0.93	0.98	0.98	0.99	0.98	0.98
		11	0.97	0.96	0.92	0.98	0.97	0.99	0.98	0.97
	370	3	0.64	0.59	0.66	0.52	0.58	0.32	0.62	0.64
		7	0.96	0.97	0.91	0.99	0.98	0.99	0.98	0.97
		11	0.96	0.97	0.91	0.99	0.98	0.99	0.97	0.97
N_{AqP}	280	3	0.09	0.02	0.15	0.07	0.01	0.28	0.06	0.08
		7	0.62	0.55	0.64	0.49	0.55	0.82	0.59	0.61
		11	0.89	0.80	0.84	0.81	0.82	0.72	0.85	0.84
	325	3	0.82	0.78	0.81	0.73	0.78	0.56	0.81	0.82
		7	0.84	0.81	0.83	0.76	0.81	0.60	0.83	0.85
		11	0.97	0.93	0.91	0.95	0.95	0.89	0.96	0.95
	370	3	0.87	0.83	0.86	0.78	0.82	0.63	0.86	0.87
		7	0.92	0.92	0.87	0.89	0.91	0.75	0.92	0.93
		11	0.83	0.91	0.73	0.94	0.92	0.95	0.87	0.86
N_{Gas}	280	3	0.56	0.36	0.54	0.45	0.40	0.51	0.46	0.44
		7	0.37	0.55	0.25	0.48	0.52	0.85	0.45	0.46
		11	0.45	0.35	0.60	0.27	0.35	0.19	0.43	0.45
	325	3	0.53	0.48	0.52	0.56	0.51	0.76	0.51	0.50
		7	0.48	0.48	0.62	0.41	0.47	0.45	0.51	0.53
		11	0.13	0.02	0.11	0.10	0.02	0.29	0.05	0.03
	370	3	0.11	0.35	0.07	0.26	0.31	0.15	0.23	0.25
		7	0.51	0.53	0.34	0.62	0.55	0.65	0.50	0.48
		11	0.75	0.75	0.64	0.73	0.75	0.54	0.74	0.74
%C	280	3	0.39	0.43	0.38	0.34	0.41	0.10	0.42	0.44

Response Variables	Temperature	Feedstock pH	Total Polyphenol	Total Tannin	Total Flavonoid	Gallic Acid	Caffeic Acid	Ferulic Acid	Epicatechin	Quercetin
		7	0.90	0.83	0.95	0.84	0.84	0.01	0.89	0.89
		11	0.26	0.47	0.20	0.38	0.43	0.19	0.37	0.39
	325	3	0.91	0.94	0.80	0.97	0.95	0.93	0.93	0.92
		7	0.16	0.37	0.11	0.27	0.33	0.07	0.27	0.28
		11	0.80	0.71	0.80	0.67	0.71	0.52	0.76	0.77
	370	3	0.98	0.96	0.94	0.98	0.97	0.98	0.98	0.97
		7	0.76	0.67	0.66	0.75	0.70	0.75	0.71	0.69
		11	0.55	0.47	0.71	0.42	0.47	0.50	0.54	0.56
%H	280	3	0.66	0.76	0.60	0.79	0.76	0.89	0.72	0.71
		7	0.04	0.11	0.14	0.18	0.11	0.51	0.03	0.01
		11	0.52	0.64	0.45	0.68	0.64	0.80	0.59	0.58
	325	3	0.39	0.45	0.39	0.50	0.45	0.69	0.43	0.42
		7	0.43	0.38	0.42	0.47	0.41	0.68	0.41	0.39
		11	0.82	0.84	0.78	0.88	0.85	0.97	0.84	0.83
	370	3	0.19	0.26	0.18	0.31	0.26	0.53	0.23	0.22
		7	0.46	0.50	0.42	0.57	0.51	0.75	0.49	0.47
		11	0.44	0.46	0.48	0.49	0.47	0.69	0.47	0.46
%O	280	3	0.98	0.90	0.98	0.90	0.92	0.85	0.96	0.96
		7	0.99	0.94	0.99	0.92	0.94	0.42	0.98	0.98
		11	0.84	0.74	0.79	0.81	0.77	0.87	0.80	0.78
	325	3	0.94	0.93	0.88	0.90	0.93	0.78	0.94	0.94
		7	0.68	0.78	0.63	0.70	0.76	0.51	0.74	0.75
		11	0.76	0.83	0.64	0.88	0.84	0.92	0.79	0.78
	370	3	0.90	0.87	0.88	0.83	0.87	0.69	0.89	0.90
		7	0.68	0.72	0.70	0.63	0.70	0.46	0.71	0.73
		11	0.67	0.77	0.48	0.80	0.77	0.70	0.70	0.69
%N	280	3	0.93	0.91	0.91	0.87	0.91	0.75	0.93	0.94
		7	0.97	0.96	0.94	0.94	0.96	0.59	0.97	0.98
		11	0.84	0.87	0.74	0.92	0.89	0.96	0.86	0.84

Response Variables	Temperature	Feedstock pH	Total Polyphenol	Total Tannin	Total Flavonoid	Gallic Acid	Caffeic Acid	Ferulic Acid	Epicatechin	Quercetin
	325	3	0.93	0.91	0.91	0.87	0.91	0.75	0.93	0.94
		7	0.96	0.95	0.93	0.92	0.95	0.82	0.97	0.97
		11	0.97	0.99	0.90	1.00	0.99	0.94	0.99	0.98
	370	3	0.93	0.91	0.91	0.88	0.91	0.76	0.93	0.94
		7	0.96	0.96	0.92	0.94	0.96	0.84	0.97	0.98
		11	0.91	0.97	0.83	0.99	0.97	0.97	0.95	0.94
O/C_{Oil}	280	3	0.99	0.90	0.98	0.91	0.91	0.89	0.95	0.95
		7	0.99	0.93	1.00	0.92	0.94	0.34	0.98	0.98
		11	0.71	0.63	0.64	0.72	0.66	0.81	0.67	0.65
	325	3	0.94	0.94	0.89	0.92	0.94	0.80	0.95	0.95
		7	0.65	0.76	0.60	0.68	0.73	0.48	0.71	0.72
		11	0.86	0.94	0.75	0.96	0.94	0.95	0.90	0.89
	370	3	0.91	0.88	0.89	0.84	0.88	0.71	0.90	0.91
		7	0.57	0.62	0.60	0.52	0.60	0.35	0.61	0.63
		11	0.56	0.67	0.36	0.71	0.67	0.60	0.59	0.58
H/C_{Oil}	280	3	0.48	0.55	0.42	0.61	0.56	0.77	0.52	0.50
		7	0.48	0.55	0.42	0.61	0.56	0.39	0.52	0.50
		11	0.48	0.55	0.42	0.61	0.56	0.77	0.52	0.50
	325	3	0.60	0.65	0.56	0.70	0.66	0.85	0.63	0.62
		7	0.60	0.65	0.56	0.70	0.66	0.85	0.63	0.62
		11	0.60	0.65	0.56	0.70	0.66	0.85	0.63	0.62
	370	3	0.29	0.36	0.28	0.41	0.36	0.62	0.33	0.32
		7	0.29	0.36	0.28	0.41	0.36	0.62	0.33	0.32
		11	0.29	0.36	0.28	0.41	0.36	0.62	0.33	0.32
N/C_{Oil}	280	3	0.93	0.91	0.91	0.87	0.91	0.75	0.93	0.94
		7	0.97	0.96	0.93	0.94	0.96	0.59	0.97	0.98
		11	0.85	0.88	0.74	0.93	0.90	0.96	0.87	0.85
	325	3	0.93	0.91	0.91	0.87	0.91	0.75	0.93	0.94
		7	0.96	0.95	0.93	0.93	0.95	0.82	0.97	0.97

Response Variables	Temperature	Feedstock pH	Total Polyphenol	Total Tannin	Total Flavonoid	Gallic Acid	Caffeic Acid	Ferulic Acid	Epicatechin	Quercetin
		11	0.97	0.99	0.90	0.99	0.99	0.93	0.99	0.99
	370	3	0.93	0.91	0.91	0.88	0.91	0.76	0.93	0.94
		7	0.96	0.96	0.93	0.94	0.96	0.84	0.97	0.98
		11	0.92	0.97	0.84	0.99	0.98	0.98	0.95	0.95

Table S5. Chromatographic composition of the gas-phase coproduct produced from HTL of digestate and its four mixtures with polyphenolic extract from apple pomace (APO), olive pomace (OPO), spent coffee grounds (SCG), and sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min.

Feedstocks	Gaseous Compounds	Gas composition (mol%)								
		Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
		280	325	370	280	325	370	280	325	370
Pure Digestate	CO_2	98.0	97.3	96.5	98.5	95.1	94.6	93.3	94.2	95.5
	CO	1.2	2.3	1.7	1.6	1.3	1.5	2.2	2.8	1.7
	H_2	0.8	0.3	1.8	-0.1	3.6	3.9	4.5	3.0	2.8
Digestate + APO	CO_2	96.5	97.1	96.6	96.4	97.1	95.0	93.5	95.5	98.0
	CO	2.1	2.1	1.8	2.4	1.8	1.3	1.8	1.3	1.9
	H_2	1.4	0.8	1.6	1.2	1.1	3.8	4.7	3.2	0.2
Digestate + OPO	CO_2	94.6	94.4	93.9	97.6	96.1	95.4	96.3	93.8	93.3
	CO	2.3	2.2	1.1	2.7	2.7	2.8	2.7	1.4	1.4
	H_2	3.0	3.4	5.0	-0.3	1.3	1.8	1.0	4.8	5.3
Digestate + SCG	CO_2	96.2	94.7	95.5	98.1	97.3	94.5	97.5	97.6	93.9
	CO	1.5	2.4	2.5	2.3	1.3	1.2	2.6	1.3	1.7
	H_2	2.4	2.9	2.0	-0.3	1.4	4.3	-0.1	1.1	4.4
Digestate + SOP	CO_2	94.7	96.1	95.1	94.1	97.8	94.3	95.2	95.8	94.6
	CO	2.4	1.8	2.7	2.7	2.7	1.3	2.3	2.8	2.3
	H_2	2.9	2.1	2.2	3.2	-0.5	4.4	2.5	1.5	3.1

Table S6. XRD phase composition of hydrochar from HTL of pure digestate at 280, 325, and 370 °C for 60 min.

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
Calcite	10.1	7.9	6.8	10.4	12.5	11.5	12.6	15.4	13.9
Nesquehonite	12.1	9.9	8.1	11.3	11.7	11.4	13.5	14.2	14.2
Brushite	12.2	9.8	8.4	13.8	11.7	13.5	17.1	13.2	15.8
Wavellite	11.2	9.6	7.2	3.4	3.47	2.33	3.47	3.4	3.2
Monetite		3.6	5.6						
Magnesite		4.5	7.0		2.6	3.4		3.3	3.8
Variscite		7.8	9.4						
Hydroxyapatite					4.3	7.2		5.1	8.5
A-type carbonated apatite					4.8	5.5		6.0	6.7
1-methyl-5,8,12,13-tetrahydro-1H-tripyrrolo-[3″,4″:3′,4′;3‴,4‴:5′,6′;3⁗,2⁗:7′,8′]-cycloocta-[1′,2′:3,4]-pyrrolo-[2,1-b]oxazol-13-amine	13.1	12.7	12.1						
(Z)-1,13-diimino-2,5,9,12,13,14,14a,14b-octahydro-1H,7H-azepino[1′,2′:3,4]imidazo[1,5-a]-azocine-3,11-dicarbonitrile	9.2	8.7	7.6						
ethyl-1′,3′,3′-trimethyl-8-nitrospiro[chromene-2,2′-indoline]-5′-carboxylate				11.4	11.6	12.1	6.7	6.7	7.0
(E)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene				7.38	7.74	7.92	9.2	9.2	7.2
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one				9.26	8.46	8.31	9.6	9.6	7.3
3-amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2H-benzo[e][1,2]oxazin-6(5H)-one				13.3	13.5	13.7	8.3	8.3	7.1
4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one				19.7	7.56	3.1	19.6	5.6	5.4
6-methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	10.1	9.0	8.8						
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one	9.2	7.8	7.6						
alizarin	13.0	8.4	11.3						

Table S7. XRD phase composition of hydrochar from HTL of digestate mixture with polyphenolic extract from apple pomace at 280, 325, and 370 °C for 60 min.

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
Calcite	4.9	4.1	4.3	11.1	13.4	12.2	13.3	16.3	15.0
Nesquehonite	6.2	4.9	3.8	12.0	12.5	12.1	14.5	15.2	15.2
Brushite	5.9	4.6	4.1	14.7	12.4	14.5	18.3	14.0	16.8
Wavellite	6.0	5.4	3.9	3.9	4.0	2.7	3.6	5.3	5.3
Monetite		5.7	7.0						
Magnesite		3.2	7.5		6.6	0.3		6.2	0.5
Variscite		4.2	1.7						
Hydroxyapatite					10.3	11.5		6.5	5.7
A-type carbonated apatite					9.7	8.7		6.6	6.3
5,5'-((3Z,7Z)-4,8-diamino-2H,6H-1,5-dioxocine-2,6-diyl)bis(7-methoxy-2-methyl-2,3,3a,4-tetrahydrobenzofuran-3-ol)	6.5	6.2	5.4						
(3Z,7Z)-2,6-bis(7-methoxy-2,3-dimethyl-2,3,3a,4-tetrahydrobenzofuran-5-yl)-2H,6H-1,5-dioxocine-4,8-diamine	7.1	6.8	6.2						
4-((5Z,9E)-4,8-diamino-12-hydroxy-2,13-dimethyl-2a1,11a,14a,14b-tetrahydro-4H,8H-1,3,7,14-tetraoxacycloundeca[cd]-as-indacen-6-yl)-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-3,6-diol	1.2	0.7	-0.1						
(3Z,7Z)-2,6-bis(2,3,6,7-tetramethyl-3a,5a-dihydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2H,6H-1,5-dioxocine-4,8-diamine	3.7	3.5	2.8						
6,14-diamino-1,9-dimethyl-1,2a1,6,8a,8a1,9,14,16a-octahydro-2λ^3,7,8,10λ^3,15,16-hexaoxacyclododeca[1,2,3-cd:7,8,9-c'd']diindene-3,4,11,12-tetraol	8.7	8.3	7.5						
3'-(6,7-dihydroxy-2,3-dimethyl-3a,7a-dihydrobenzofuran-4-yl)-8,8',9,9'-tetramethyl-3,3',4,4',7a,7'a,10a,10'a-octahydro-[3,7'-bibenzofuro[6,7-f][1,2,5,4]trioxazepine]-7-carboxamide	7.3	6.8	6.0						
8-(3,6-dihydroxy-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2,5-dimethyl-3a,3b,6a,9,10,10b-hexahydro-8H-difuro[2,3-f:2',3'-h]chromene-3,6,9-triol	3.2	2.8	2.0						
2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-3,4,9a,9b-tetrahydro-2H-furo[2,3-h]chromene-3,5-diol	3.8	3.5	2.7						
3,5-dihydroxy-2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-2,3,9a,9b-tetrahydro-4H-furo[2,3-h]chromen-4-one	5.2	4.9	4.0						
1-methyl-5,8,12,13-tetrahydro-1H-tripyrrolo-[3″,4″:3′,4′;3‴,4‴:5′,6′;3⁗,2⁗:7′,8′]-cycloocta-[1′,2′:3,4]-pyrrolo-[2,1-b]oxazol-13-amine	6.7	4.6	7.2						
(Z)-1,13-diimino-2,5,9,12,13,14,14a,14b-octahydro-1H,7H-azepino[1′,2′:3,4]imidazo[1,5-a]-azocine-3,11-dicarbonitrile	5.6	6.6	9.9						
ethyl-1′,3′,3′-trimethyl-8-nitrospiro[chromene-2,2′-				9.2	6.9	10.2	5.4	5.1	6.6

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
indoline]-5′-carboxylate									
(E)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene				5.4	5.2	6.7	7.0	7.4	5.8
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one				8.3	5.2	6.4	7.0	8.1	5.1
3-amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2H-benzo[e][1,2]oxazin-6(5H)-one				8.9	6.6	8.0	6.2	6.5	4.1
4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one				26.5	7.0	6.6	24.6	2.9	13.6
6-methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	5.4	4.6	4.1						
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one	4.7	4.7	4.5						
alizarin	7.8	3.9	5.5						

Table S8. XRD phase composition of hydrochar from HTL of digestate mixture with polyphenolic extract from olive pomace at 280, 325, and 370 °C for 60 min.

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
Calcite	6.4	4.3	3.3	11.9	14.4	13.1	14.3	17.4	16.2
Nesquehonite	6.8	5.3	4.2	12.7	13.5	12.9	15.4	16.4	16.4
Brushite	7.2	5.0	4.5	15.6	13.3	15.4	19.5	15.1	18.0
Wavellite	6.3	4.5	3.5	4.6	4.8	3.2	4.3	6.1	6.2
Monetite		5.3	5.5						
Magnesite		3.4	6.6		5.2	0.2		7.5	0.4
Variscite		6.4	1.9						
Hydroxyapatite					5.6	5.7		6.7	7.2
A-type carbonated apatite					7.7	7.5		5.5	6.5
5,5'-((3Z,7Z)-4,8-diamino-2H,6H-1,5-dioxocine-2,6-diyl)bis(7-methoxy-2-methyl-2,3,3a,4-tetrahydrobenzofuran-3-ol)	5.1	4.9	4.1						
(3Z,7Z)-2,6-bis(7-methoxy-2,3-dimethyl-2,3,3a,4-tetrahydrobenzofuran-5-yl)-2H,6H-1,5-dioxocine-4,8-diamine	6.3	5.8	5.0						
4-((5Z,9E)-4,8-diamino-12-hydroxy-2,13-dimethyl-2a1,11a,14a,14b-tetrahydro-4H,8H-1,3,7,14-tetraoxacycloundeca[cd]-as-indacen-6-yl)-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-3,6-diol	7.8	7.5	6.6						
(3Z,7Z)-2,6-bis(2,3,6,7-tetramethyl-3a,5a-dihydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2H,6H-1,5-dioxocine-4,8-diamine	5.2	4.9	4.1						
6,14-diamino-1,9-dimethyl-1,2a1,6,8a,8a1,9,14,16a-octahydro-2λ^3,7,8,10λ^3,15,16-hexaoxacyclododeca[1,2,3-cd:7,8,9-c'd']diindene-3,4,11,12-tetraol	7.1	6.8	5.9						
3'-(6,7-dihydroxy-2,3-dimethyl-3a,7a-dihydrobenzofuran-4-yl)-8,8',9,9'-tetramethyl-	1.5	1.1	0.3						

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
3,3',4,4',7a,7'a,10a,10'a-octahydro-[3,7'-bibenzofuro[6,7-f][1,2,5,4]trioxazepine]-7-carboxamide									
8-(3,6-dihydroxy-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2,5-dimethyl-3a,3b,6a,9,10,10b-hexahydro-8H-difuro[2,3-f:2',3'-h]chromene-3,6,9-triol	2.8	2.6	1.7						
2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-3,4,9a,9b-tetrahydro-2H-furo[2,3-h]chromene-3,5-diol	3.2	3.0	2.1						
3,5-dihydroxy-2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-2,3,9a,9b-tetrahydro-4H-furo[2,3-h]chromen-4-one	6.3	6.1	5.2						
1-methyl-5,8,12,13-tetrahydro-1H-tripyrrolo-[3″,4″:3′,4′;3‴,4‴:5′,6′;3⁗,2⁗:7′,8′]-cycloocta-[1′,2′:3,4]-pyrrolo-[2,1-b]oxazol-13-amine	4.1	2.0	2.7						
(Z)-1,13-diimino-2,5,9,12,13,14,14a,14b-octahydro-1H,7H-azepino[1′,2′:3,4]imidazo[1,5-a]-azocine-3,11-dicarbonitrile	4.7	8.4	16.9						
ethyl-1′,3′,3′-trimethyl-8-nitrospiro[chromene-2,2′-indoline]-5′-carboxylate				7.6	7.7	8.5	5.9	5.4	4.4
(E)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene				5.7	6.2	6.1	8.2	5.5	6.1
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one				8.3	6.5	6.4	6.7	8.1	5.9
3-amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2H-benzo[e][1,2]oxazin-6(5H)-one				8.4	8.0	7.4	4.5	4.9	4.4
4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one				25.3	7.1	13.6	21.3	1.3	8.4
6-methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	6.0	4.4	5.0						
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one	5.0	4.0	4.5						
Alizarin	8.2	4.5	6.4						

Table S9. XRD phase composition of hydrochar from HTL of digestate mixture with polyphenolic extract from spent coffee grounds at 280, 325, and 370 °C for 60 min.

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
Calcite	5.2	4.1	3.3	12.7	15.3	14.0	15.3	18.4	17.3
Nesquehonite	6.2	5.9	4.4	13.5	14.6	13.9	16.3	17.7	17.4
Brushite	7.2	5.6	4.0	16.7	14.3	16.4	20.8	16.0	19.4
Wavellite	6.0	5.7	3.5	5.4	5.6	3.8	5.0	7.1	7.3
Monetite		3.5	5.6						
Magnesite		6.2	6.6		6.5	0.3		6.2	0.4
Variscite		7.5	1.6						
Hydroxyapatite					5.2	7.2		7.4	7.8
A-type carbonated apatite					7.5	6.3		5.7	6.7

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
5,5'-((3Z,7Z)-4,8-diamino-2H,6H-1,5-dioxocine-2,6-diyl)bis(7-methoxy-2-methyl-2,3,3a,4-tetrahydrobenzofuran-3-ol)	5.4	5.0	4.3						
(3Z,7Z)-2,6-bis(7-methoxy-2,3-dimethyl-2,3,3a,4-tetrahydrobenzofuran-5-yl)-2H,6H-1,5-dioxocine-4,8-diamine	1.1	0.6	0.0						
4-((5Z,9E)-4,8-diamino-12-hydroxy-2,13-dimethyl-2a1,11a,14a,14b-tetrahydro-4H,8H-1,3,7,14-tetraoxacycloundeca[cd]-as-indacen-6-yl)-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-3,6-diol	6.3	5.8	5.0						
(3Z,7Z)-2,6-bis(2,3,6,7-tetramethyl-3a,5a-dihydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2H,6H-1,5-dioxocine-4,8-diamine	2.7	2.3	1.5						
6,14-diamino-1,9-dimethyl-1,2a1,6,8a,8a1,9,14,16a-octahydro-2λ^3,7,8,10λ^3,15,16-hexaoxacyclododeca[1,2,3-cd:7,8,9-c'd']diindene-3,4,11,12-tetraol	7.8	7.5	6.6						
3'-(6,7-dihydroxy-2,3-dimethyl-3a,7a-dihydrobenzofuran-4-yl)-8,8',9,9'-tetramethyl-3,3',4,4',7a,7'a,10a,10'a-octahydro-[3,7'-bibenzofuro[6,7-f][1,2,5,4]trioxazepine]-7-carboxamide	4.6	4.3	3.7						
8-(3,6-dihydroxy-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2,5-dimethyl-3a,3b,6a,9,10,10b-hexahydro-8H-difuro[2,3-f:2',3'-h]chromene-3,6,9-triol	4.2	3.8	3.2						
2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-3,4,9a,9b-tetrahydro-2H-furo[2,3-h]chromene-3,5-diol	3.5	3.0	2.2						
3,5-dihydroxy-2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-2,3,9a,9b-tetrahydro-4H-furo[2,3-h]chromen-4-one	5.2	4.8	4.1						
1-methyl-5,8,12,13-tetrahydro-1H-tripyrrolo-[3″,4″:3′,4′;3‴,4‴:5′,6′;3⁗,2⁗:7′,8′]-cycloocta-[1′,2′:3,4]-pyrrolo-[2,1-b]oxazol-13-amine	2.7	1.9	2.3						
(Z)-1,13-diimino-2,5,9,12,13,14,14a,14b-octahydro-1H,7H-azepino[1′,2′:3,4]imidazo[1,5-a]-azocine-3,11-dicarbonitrile	15.0	10.0	24.6						
ethyl-1′,3′,3′-trimethyl-8-nitrospiro[chromene-2,2′-indoline]-5′-carboxylate				5.4	6.9	7.2	3.6	4.0	3.7
(E)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene				7.0	7.3	7.1	7.8	8.2	5.5
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one				6.8	6.8	5.8	9.0	2.0	5.9
3-amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2H-benzo[e][1,2]oxazin-6(5H)-one				7.5	6.3	7.7	4.1	4.9	4.0
4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one				25	3.8	10.3	18.2	2.4	4.8
6-methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	4.7	4.6	4.3						
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-	5.2	3.8	3.7						

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
pyrano[3,2-g]chromen-2-one									
alizarin	7.0	4.1	5.8						

Table S10. XRD phase composition of hydrochar from HTL of digestate mixture with polyphenolic extract from sweet orange peels (SOP) at 280, 325, and 370 °C for 60 min.

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
Calcite	6.0	3.7	4.3	13.6	16.2	14.9	16.5	18.7	18.4
Nesquehonite	6.8	6.3	4.8	14.4	15.7	14.7	17.4	18.9	18.6
Brushite	5.9	5.9	4.5	17.8	15.4	17.7	21.4	16.5	19.9
Wavellite	6.0	4.5	3.4	6.3	6.6	4.4	5.7	8.2	8.5
Monetite		5.8	6.0						
Magnesite		4.1	5.8		3.3	0.2		5.6	0.4
Variscite		3.4	1.9						
Hydroxyapatite					6.6	7.7		7.4	5.5
A-type carbonated apatite					7.3	5.2		7.3	5.3
5,5'-((3Z,7Z)-4,8-diamino-2H,6H-1,5-dioxocine-2,6-diyl)bis(7-methoxy-2-methyl-2,3,3a,4-tetrahydrobenzofuran-3-ol)	2.5	2.0	1.4						
(3Z,7Z)-2,6-bis(7-methoxy-2,3-dimethyl-2,3,3a,4-tetrahydrobenzofuran-5-yl)-2H,6H-1,5-dioxocine-4,8-diamine	4.5	4.3	3.6						
4-((5Z,9E)-4,8-diamino-12-hydroxy-2,13-dimethyl-2a1,11a,14a,14b-tetrahydro-4H,8H-1,3,7,14-tetraoxacycloundeca[cd]-as-indacen-6-yl)-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-3,6-diol	1.5	1.2	0.5						
(3Z,7Z)-2,6-bis(2,3,6,7-tetramethyl-3a,5a-dihydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2H,6H-1,5-dioxocine-4,8-diamine	2.8	2.4	1.6						
6,14-diamino-1,9-dimethyl-1,2a1,6,8a,8a1,9,14,16a-octahydro-2λ^3,7,8,10λ^3,15,16-hexaoxacyclododeca[1,2,3-cd:7,8,9-c'd']diindene-3,4,11,12-tetraol	9.5	9.1	8.5						
3'-(6,7-dihydroxy-2,3-dimethyl-3a,7a-dihydrobenzofuran-4-yl)-8,8',9,9'-tetramethyl-3,3',4,4',7a,7'a,10a,10'a-octahydro-[3,7'-bibenzofuro[6,7-f][1,2,5,4]trioxazepine]-7-carboxamide	7.6	7.2	6.4						
8-(3,6-dihydroxy-2,7-dimethyl-3a,5a,8a,8b-tetrahydrobenzo[2,1-b:3,4-b']difuran-4-yl)-2,5-dimethyl-3a,3b,6a,9,10,10b-hexahydro-8H-difuro[2,3-f:2',3'-h]chromene-3,6,9-triol	5.8	5.5	4.7						
2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-3,4,9a,9b-tetrahydro-2H-furo[2,3-h]chromene-3,5-diol	5.4	5.1	4.4						
3,5-dihydroxy-2-(7-hydroxy-2,3-dimethyl-3a,4-dihydrobenzofuran-5-yl)-8,9-dimethyl-2,3,9a,9b-	4.7	4.2	3.4						

Phase composition	Phase composition (wt%)								
	Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	280	325	370	280	325	370	280	325	370
tetrahydro-4H-furo[2,3-h]chromen-4-one									
1-methyl-5,8,12,13-tetrahydro-1H-tripyrrolo-[3″,4″:3′,4′;3‴,4‴:5′,6′;3⁗,2⁗:7′,8′]-cycloocta-[1′,2′:3,4]-pyrrolo-[2,1-b]oxazol-13-amine	3.0	1.6	2.1						
(Z)-1,13-diimino-2,5,9,12,13,14,14a,14b-octahydro-1H,7H-azepino[1′,2′:3,4]imidazo[1,5-a]-azocine-3,11-dicarbonitrile	10.3	10.1	16.9						
ethyl-1′,3′,3′-trimethyl-8-nitrospiro[chromene-2,2′-indoline]-5′-carboxylate				5.4	6.0	7.6	3.8	4.0	3.3
(E)-1,2-dichloro-1,2-bis(5-phenyloxazol-2-yl)ethene				3.8	4.6	5.0	5.2	3.9	3.7
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one				5.5	5.3	4.1	5.1	3.9	3.4
3-amino-4-(3-methoxyphenyl)-3,4,7,8-tetrahydro-2H-benzo[e][1,2]oxazin-6(5H)-one				7.9	7.6	7.7	4.3	4.1	4.0
4-(4-(2-(2,4-dinitrophenoxy)-ethoxy)-3-methoxy-benzylidene-amino)-1,5-dimethyl-2-phenyl-1H-pyrazol-3(2H)-one				25.3	5.4	10.7	20.6	3.5	9.0
6-methoxy-1-(2-oxo-1-phenylethyl)-1H-indole-2-carboxylic acid	5.4	4.4	5.2						
5-hydroxy-4,8-dimethyl-4a,10a-dihydro-2H,6H-pyrano[3,2-g]chromen-2-one	5.5	4.9	3.7						
alizarin	6.7	4.3	6.7						

Table S11. GC-MS composition of biocrude from HTL of pure digestate at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
3-hydroxycyclopent-2-en-1-one	7.60	-13.41	4.1	3.7	3.3	2.7	2.4	2.2	1.8	1.6	1.5
2-methyl-2-cyclopenten-1-one	7.45	-15.01	1.3	1.2	0.9	0.9	0.8	0.6	0.6	0.6	0.4
gamma-butyrolactone	4.47	-16.61	2.4	2.2	1.8	1.6	1.4	1.2			
5-methyl-2-(1-methylethyl)-cyclohexanone	6.11	-5.11	1.3	1.2	0.8	0.9	0.8	0.5			
tetrahydro-2*H*-pyran-2-one	8.19	-21.08	2.4	2.0	1.5	1.6	1.3	1.0			
4a,5,8,8a-tetrahydro-2λ^5-naphthalen-2-one	2.09	-18.84	2.4	2.3	1.9						
(*E*)-1-(hydroxymethylene)-5,8-dihydronaphthalen-2(1*H*)-one	8.64	-17.89	1.2	0.8	0.7						
3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one	1.79	-13.41	1.3	1.9	2.6	3.4	4.5	4.9	3.4	4.5	4.9
furan-2,5-dione	9.09	-12.78	4.1	3.7	3.3	2.8	2.5	2.2	6.5	2.2	2.0
2-methylfuran	7.00	-18.53	2.4	1.9	1.8	1.6	1.3	1.2	1.4	1.2	1.1
isobenzofuran-1,3-dione	6.40	-22.04	3.1	2.9	2.8	2.1	2.0	1.9			
4,6-dihydroxy-2*H*-chromen-2-one	1.04	-22.68	2.4	2.2	2.1	1.6	1.4	1.4			
2-methyl-2-phenyl-oxirane	4.32	-4.15							1.3	2.4	1.1
3-methyl-guaiacol	5.81	-6.71	4.5	4.1	3.6	5.7	5.1	4.5	5.1	4.6	2.1
2-phenyl-acetaldehyde	4.17	-2.87	1.2	0.8	0.6	1.5	1.1	0.7			
2,6-dimethoxy-phenol	4.62	-3.51	1.3	1.2	1.1	1.7	1.4	1.3	1.5	1.3	1.2
4-hydroxy-benzaldehyde	3.87	-5.43	2.2	1.9	1.6	2.7	2.4	1.9			
(phenoxymethyl)-oxirane	8.94	-14.69							6.4	4.1	1.3
2-methoxy-4-vinyloxy-phenol	4.32	-23.00	3.2	2.7	2.3	4.0	3.4	2.9			
1,3,5-benzenetriol	3.28	-17.57	5.5	5.0	4.7	6.8	6.2	5.9	2.1	1.2	2.4
1,3-benzodioxane-5-ol	4.02	-10.86	2.4	3.6	3.9	3.0	4.5	4.8			
5-(1-propenyl)-1,3-benzodioxole	7.15	-18.53	3.4	4.7	5.1	4.3	5.8	6.4			
m-cresol	1.19	-6.71	2.4	2.8	2.9	3.0	3.5	3.6	4.9	5.6	5.8

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
6-hydroxy-4,5-dimethyl-2-oxo-2*H*-chromene-8-carbaldehyde	4.77	-4.15				2.2	2.6	2.7	5.4	6.2	6.4
2,5-dihydroxy-4-methylbenzaldehyde	9.09	-16.61				1.1	1.3	1.7	5.9	6.8	7.0
2-(1*H*-pyrrol-1-yl)acetic acid	5.21	-22.36	3.3	2.7	2.3						
1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazole	8.64	-18.53	3.3	2.8	2.3						
4,5-dimethyl-imidazole	5.81	-11.82	2.3	2.1	1.9						
2-(1*H*-pyrrol-1-yl)acetamide	2.53	-4.15	5.4	4.9	4.5						
1,3,4-trimethyl-2,3-dihydro-1*H*-imidazole	8.19	-18.53	2.3	2.0	1.5						
5-methyloxazole-2-carboxylic acid	6.70	-16.29				6.3	6.8	7.5	7.9	8.2	9.5
2,5-dimethylpyrazine	6.11	-17.89				4.2	4.5	5.0	4.7	4.9	5.5
2-ethenyl-5-methyl-pyrazine	8.34	-17.25				4.4	5.2	5.3	4.9	5.7	5.8
2,8-dimethyl-indolizine	5.36	-11.50				3.3	3.9	4.2	3.6	4.2	4.6
3,6-bis(2-methylpropyl)-piperazine-2,3-dione	3.28	-10.86				3.2	3.3	3.8	3.5	3.6	4.1
2,5-dimethyl-piperidine	6.11	-16.93				3.3	3.9	4.3	3.6	4.3	4.7
terephthalic acid	2.98	-19.80	3.2	2.1	0.8						
benzoic acid	5.66	-10.22	2.1	2.0	1.8						
2-formyl-6-hydroxy-4-methoxy-3-(2-oxopropyl)benzoic acid	6.26	-15.33	2.2	1.3	0.5						
methyl hexadecanoate, ester	6.85	-3.19	1.4	2.6	3.5	2.2	2.4	2.7			
methyl oxtadecanoate, ester	4.02	-7.35	2.4	3.0	4.3	5.1	5.2	5.8			
hexadecanoic acid	7.00	-7.67							3.4	4.2	5.3
octadecanoic acid	4.92	-22.36							5.3	2.1	1.4
butane	3.13	-15.97	3.2	4.4	4.6						
pentane	6.11	-3.83	1.1	1.7	3.9						
toluene	3.43	-18.21	3.4	3.7	4.2						
n-hexadecane	8.04	-21.40				4.4	3.5	1.4	5.5	5.2	5.1
n-octadecane	8.64	-7.03				1.4	2.3	3.2	2.7	5.8	6.0
phenanthrene	3.43	-16.29				3.2	3.3	3.3	4.1	4.7	5.6
anthracene	1.34	-10.86	1.4	2.2	2.9	4.3					

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
1-methylene-1,2,5,8-tetrahydronaphthalene	8.19	-20.76	3.4	3.8	4.0						
terphenyl	2.53	-18.53							4.8	4.9	5.4
chrysene	1.79	-7.35	3.2	3.3	4.4						
perylene	7.00	-12.14	2.2	2.6	3.2						
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S12. GC-MS composition of biocrude from HTL of digestate mixture with polyphenolic extract from apple pomace at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
3-hydroxycyclopent-2-en-1-one	7.60	-13.41	5.1	4.6	4.1	4.1	3.7	3.3	7.0	6.3	5.6
2-methyl-2-cyclopenten-1-one	7.45	-15.01	1.7	1.6	1.1	1.3	1.2	0.9	2.3	2.1	1.5
gamma-butyrolactone	4.47	-16.61	2.9	2.7	2.3	2.4	2.2	1.8			
5-methyl-2-(1-methylethyl)-cyclohexanone	6.11	-5.11	1.6	1.5	1.0	1.3	1.2	0.8			
tetrahydro-2*H*-pyran-2-one	8.19	-21.08	2.9	2.5	1.9	2.4	2.0	1.5			
4a,5,8,8a-tetrahydro-2λ^5-naphthalen-2-one	2.09	-18.84	3.0	2.9	2.3						
(*E*)-1-(hydroxymethylene)-5,8-dihydronaphthalen-2(1*H*)-one	8.64	-17.89	1.5	1.0	0.9						
3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one	1.79	-13.41	1.7	2.4	3.3	5.0	6.7	7.3	12.9	17.2	18.7
furan-2,5-dione	9.09	-12.78	5.2	4.6	4.2	4.1	3.7	3.3	25.0	8.5	7.7
2-methylfuran	7.00	-18.53	3.0	2.4	2.3	2.4	1.9	1.8	5.5	4.4	4.2
isobenzofuran-1,3-dione	6.40	-22.04	3.9	3.7	3.5	3.1	2.9	2.8			
4,6-dihydroxy-2*H*-chromen-2-one	1.04	-22.68	2.9	2.7	2.6	2.4	2.2	2.1			
2-methyl-2-phenyl-oxirane	4.32	-4.15							1.6	3.0	3.6
3-methyl-guaiacol	5.81	-6.71	5.7	5.1	4.5	7.1	6.4	5.7	6.4	5.8	4.7
2-phenyl-acetaldehyde	4.17	-2.87	1.5	1.1	0.7	1.9	1.3	0.9			
2,6-dimethoxy-phenol	4.62	-3.51	1.7	1.4	1.3	2.1	1.8	1.7	1.9	1.6	3.9
4-hydroxy-benzaldehyde	3.87	-5.43	2.7	2.4	1.9	3.4	3.0	2.4			

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
(phenoxymethyl)-oxirane	8.94	-14.69									
2-methoxy-4-vinyloxy-phenol	4.32	-23.00	4.0	3.4	2.9	4.9	4.2	3.7			
1,3,5-benzenetriol	3.28	-17.57	6.8	6.2	5.9	8.5	7.8	7.4			
1,3-benzodioxane-5-ol	4.02	-10.86	3.0	4.5	4.8	3.8	5.6	6.0			
5-(1-propenyl)-1,3-benzodioxole	7.15	-18.53	4.3	5.8	6.4	5.3	7.3	8.0			
m-cresol	1.19	-6.71	3.0	3.5	3.6	3.8	4.4	4.5	6.1	7.0	7.2
6-hydroxy-4,5-dimethyl-2-oxo-2*H*-chromene-8-carbaldehyde	4.77	-4.15					3.2	3.4	6.7	7.7	7.9
2,5-dihydroxy-4-methylbenzaldehyde	9.09	-16.61					1.7	2.1	7.4	8.5	8.7
2-(1*H*-pyrrol-1-yl)acetic acid	5.21	-22.36	0.1	0.2	0.2						
1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazole	8.64	-18.53	0.0	0.1	0.2						
4,5-dimethyl-imidazole	5.81	-11.82	0.0	0.1	0.2						
2-(1*H*-pyrrol-1-yl)acetamide	2.53	-4.15	0.1	0.3	0.4						
1,3,4-trimethyl-2,3-dihydro-1*H*-imidazole	8.19	-18.53	0.1	0.1	0.1						
5-methyloxazole-2-carboxylic acid	6.70	-16.29				2.1	2.3	2.5	2.0	2.0	2.4
2,5-dimethylpyrazine	6.11	-17.89				1.4	1.5	1.7	1.2	1.2	1.4
2-ethenyl-5-methyl-pyrazine	8.34	-17.25				1.5	1.7	1.8	1.2	1.4	1.4
2,8-dimethyl-indolizine	5.36	-11.50				1.1	1.3	1.4	0.9	1.1	1.2
3,6-bis(2-methylpropyl)-piperazine-2,3-dione	3.28	-10.86				1.1	1.1	1.3	0.9	0.9	1.0
2,5-dimethyl-piperidine	6.11	-16.93				1.1	1.3	1.4	0.9	1.1	1.2
terephthalic acid	2.98	-19.80	3.5	2.3	0.9						
benzoic acid	5.66	-10.22	2.3	2.2	2.0						
2-formyl-6-hydroxy-4-methoxy-3-(2-oxopropyl)benzoic acid	6.26	-15.33	2.4	1.5	0.6						
methyl hexadecanoate, ester	6.85	-3.19	1.5	2.8	3.8	2.4	2.6	3.0			
methyl oxtadecanoate, ester	4.02	-7.35	2.6	3.2	4.7	5.6	5.7	6.3			
hexadecanoic acid	7.00	-7.67									

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
octadecanoic acid	4.92	-22.36									
butane	3.13	-15.97	3.5	4.8	5.0						
pentane	6.11	-3.83	1.2	1.9	4.3						
toluene	3.43	-18.21	3.7	4.1	4.6						
n-hexadecane	8.04	-21.40				4.8	3.9	1.5	6.0	5.7	5.6
n-octadecane	8.64	-7.03				1.5	2.5	3.5	3.0	6.4	6.6
phenanthrene	3.43	-16.29				3.5	1.8	4.2	1.3	8.2	5.5
anthracene	1.34	-10.86	1.6	2.4	3.2	4.7					
1-methylene-1,2,5,8-tetrahydronaphthalene	8.19	-20.76	3.4	4.2	4.4						
terphenyl	2.53	-18.53									
chrysene	1.79	-7.35	3.5	1.6	1.8						
perylene	7.00	-12.14	2.4	2.0	1.8						
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S13. GC-MS composition of biocrude from HTL of digestate mixture with polyphenolic extract from olive pomace at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
3-hydroxycyclopent-2-en-1-one	7.60	-13.41	5.3	4.7	4.3	4.3	3.8	3.4	7.3	6.5	5.8
2-methyl-2-cyclopenten-1-one	7.45	-15.01	1.7	1.6	1.1	1.4	1.3	0.9	2.4	2.2	1.6
gamma-butyrolactone	4.47	-16.61	3.1	2.8	2.3	2.4	2.3	1.9			
5-methyl-2-(1-methylethyl)-cyclohexanone	6.11	-5.11	1.7	1.5	1.1	1.3	1.2	0.9			
tetrahydro-2*H*-pyran-2-one	8.19	-21.08	3.1	2.6	2.0	2.4	2.1	1.6			
4a,5,8,8a-tetrahydro-2λ^5-naphthalen-2-one	2.09	-18.84	3.1	3.0	2.4						
(*E*)-1-(hydroxymethylene)-5,8-dihydronaphthalen-2(1*H*)-one	8.64	-17.89	1.6	1.1	1.0						
3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one	1.79	-13.41	1.7	2.4	3.4	5.2	6.9	7.6	13.4	17.8	19.4
furan-2,5-dione	9.09	-12.78	5.4	4.8	4.3	4.3	3.8	3.5	25.9	8.8	8.0
2-methylfuran	7.00	-18.53	3.1	2.5	2.4	2.5	2.0	1.9	5.7	4.6	4.4
isobenzofuran-1,3-dione	6.40	-22.04	4.0	3.8	3.7	3.2	3.0	2.9			
4,6-dihydroxy-2*H*-chromen-2-one	1.04	-22.68	3.1	2.8	2.7	2.4	2.3	2.2			

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
2-methyl-2-phenyl-oxirane	4.32	-4.15									
3-methyl-guaiacol	5.81	-6.71	5.9	5.3	4.7	7.4	6.6	5.9	6.6	6.0	4.9
2-phenyl-acetaldehyde	4.17	-2.87	1.6	1.1	0.7	2.0	1.4	0.9			
2,6-dimethoxy-phenol	4.62	-3.51	1.7	1.5	1.4	2.2	1.9	1.7	1.9	1.7	4.0
4-hydroxy-benzaldehyde	3.87	-5.43	2.8	2.5	2.0	3.6	3.1	2.5			
(phenoxymethyl)-oxirane	8.94	-14.69									
2-methoxy-4-vinyloxy-phenol	4.32	-23.00	4.1	3.5	3.0	5.1	4.4	3.8			
1,3,5-benzenetriol	3.28	-17.57	7.1	6.5	6.1	8.8	8.1	7.7			
1,3-benzodioxane-5-ol	4.02	-10.86	3.1	4.7	5.0	3.9	5.8	6.3			
5-(1-propenyl)-1,3-benzodioxole	7.15	-18.53	4.4	6.1	6.7	5.5	7.6	8.3			
m-cresol	1.19	-6.71	3.2	3.6	3.7	3.9	4.5	4.7	6.3	7.3	7.5
6-hydroxy-4,5-dimethyl-2-oxo-2*H*-chromene-8-carbaldehyde	4.77	-4.15					3.3	3.6	6.9	8.0	8.2
2,5-dihydroxy-4-methylbenzaldehyde	9.09	-16.61					1.8	2.2	3.8	8.8	9.1
2-(1*H*-pyrrol-1-yl)acetic acid	5.21	-22.36	0.1	0.2	0.2						
1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazole	8.64	-18.53	0.1	0.1	0.2						
4,5-dimethyl-imidazole	5.81	-11.82	0.0	0.1	0.2						
2-(1*H*-pyrrol-1-yl)acetamide	2.53	-4.15	0.1	0.3	0.4						
1,3,4-trimethyl-2,3-dihydro-1*H*-imidazole	8.19	-18.53	0.0	0.1	0.1						
5-methyloxazole-2-carboxylic acid	6.70	-16.29				0.9	1.0	1.1	3.2	3.3	3.8
2,5-dimethylpyrazine	6.11	-17.89				0.6	0.7	0.7	1.9	2.0	2.2
2-ethenyl-5-methyl-pyrazine	8.34	-17.25				0.7	0.8	0.8	1.9	2.3	2.3
2,8-dimethyl-indolizine	5.36	-11.50				0.5	0.6	0.6	1.4	1.7	1.8
3,6-bis(2-methylpropyl)-piperazine-2,3-dione	3.28	-10.86				0.5	0.5	0.6	1.4	1.4	1.7
2,5-dimethyl-piperidine	6.11	-16.93				0.5	0.6	0.6	0.5	1.7	1.9
terephthalic acid	2.98	-19.80	3.6	2.4	0.9						
benzoic acid	5.66	-10.22	2.4	2.3	2.1						

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
2-formyl-6-hydroxy-4-methoxy-3-(2-oxopropyl)benzoic acid	6.26	-15.33	2.5	1.5	0.6						
methyl hexadecanoate, ester	6.85	-3.19	1.6	2.9	4.0	2.5	2.7	3.1			
methyl oxtadecanoate, ester	4.02	-7.35	2.7	3.4	4.9	5.8	5.9	6.6			
hexadecanoic acid	7.00	-7.67									
octadecanoic acid	4.92	-22.36									
butane	3.13	-15.97	3.6	5.0	5.2						
pentane	6.11	-3.83	1.3	2.0	4.5						
toluene	3.43	-18.21	3.8	4.3	4.8						
n-hexadecane	8.04	-21.40				5.0	4.0	1.6	6.3	6.0	5.8
n-octadecane	8.64	-7.03				1.5	2.6	3.6	3.1	6.6	6.9
phenanthrene	3.43	-16.29				3.9	3.5	6.5	0.0	3.4	0.8
anthracene	1.34	-10.86	1.6	2.5	3.3	5.7					
1-methylene-1,2,5,8-tetrahydronaphthalene	8.19	-20.76	3.6	4.4	4.6						
terphenyl	2.53	-18.53									
chrysene	1.79	-7.35									
perylene	7.00	-12.14	2.3	0.1	0.1						
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S14. GC-MS composition of biocrude from HTL of digestate mixture with polyphenolic extract from spent coffee ground at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
3-hydroxycyclopent-2-en-1-one	7.60	-13.41	4.7	4.2	3.8	3.8	3.4	3.0	6.5	5.8	5.2
2-methyl-2-cyclopenten-1-one	7.45	-15.01	1.5	1.4	1.0	1.2	1.1	0.8	2.1	2.0	1.4
gamma-butyrolactone	4.47	-16.61	2.7	2.5	2.1	2.2	2.0	1.7			
5-methyl-2-(1-methylethyl)-cyclohexanone	6.11	-5.11	1.5	1.4	0.9	1.2	1.1	0.8			
tetrahydro-2*H*-pyran-2-one	8.19	-21.08	2.7	2.3	1.8	2.2	1.8	1.4			
4a,5,8,8a-tetrahydro-2λ^5-naphthalen-2-one	2.09	-18.84	2.8	2.7	2.1						
(*E*)-1-(hydroxymethylene)-5,8-dihydronaphthalen-2(1*H*)-one	8.64	-17.89	1.4	1.0	0.9						

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one	1.79	-13.41	1.5	2.2	3.0	5.6	7.4	8.1	14.3	19.1	20.8
furan-2,5-dione	9.09	-12.78	4.8	4.2	3.8	4.6	4.1	3.7	27.7	9.5	8.5
2-methylfuran	7.00	-18.53	2.7	2.2	2.1	2.6	2.1	2.0	6.1	4.9	4.7
isobenzofuran-1,3-dione	6.40	-22.04	3.6	3.4	3.3	3.5	3.2	3.1			
4,6-dihydroxy-2*H*-chromen-2-one	1.04	-22.68	2.7	2.5	2.4	2.6	2.4	2.3			
2-methyl-2-phenyl-oxirane	4.32	-4.15									
3-methyl-guaiacol	5.81	-6.71	5.2	4.7	4.2	7.9	7.1	6.3	7.1	6.4	5.2
2-phenyl-acetaldehyde	4.17	-2.87	1.4	1.0	0.7	2.1	1.5	1.0			
2,6-dimethoxy-phenol	4.62	-3.51	1.5	1.3	1.2	2.3	2.0	1.8	2.1	1.8	4.3
4-hydroxy-benzaldehyde	3.87	-5.43	2.5	2.2	1.8	3.8	3.3	2.7			
(phenoxymethyl)-oxirane	8.94	-14.69									
2-methoxy-4-vinyloxy-phenol	4.32	-23.00	3.6	3.1	2.7	4.6	3.9	3.4			
1,3,5-benzenetriol	3.28	-17.57	6.3	5.8	5.4	7.8	7.2	6.8			
1,3-benzodioxane-5-ol	4.02	-10.86	2.8	4.1	4.4	3.5	5.2	5.6			
5-(1-propenyl)-1,3-benzodioxole	7.15	-18.53	3.9	5.4	5.9	4.9	6.7	7.4			
m-cresol	1.19	-6.71	2.8	3.2	3.3	3.5	4.0	4.2	5.6	6.4	6.7
6-hydroxy-4,5-dimethyl-2-oxo-2*H*-chromene-8-carbaldehyde	4.77	-4.15					3.0	3.2	3.5	7.1	7.3
2,5-dihydroxy-4-methylbenzaldehyde	9.09	-16.61					1.6	1.9	3.4	7.8	8.0
2-(1*H*-pyrrol-1-yl)acetic acid	5.21	-22.36	0.1	0.1	0.2						
1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazole	8.64	-18.53	0.1	0.1	0.2						
4,5-dimethyl-imidazole	5.81	-11.82	0.0	0.1	0.2						
2-(1*H*-pyrrol-1-yl)acetamide	2.53	-4.15	0.1	0.3	0.4						
1,3,4-trimethyl-2,3-dihydro-1*H*-imidazole	8.19	-18.53	0.1	0.1	0.1						
5-methyloxazole-2-carboxylic acid	6.70	-16.29				1.1	1.1	1.3	4.0	4.1	4.8
2,5-dimethylpyrazine	6.11	-17.89				0.7	0.7	0.8	2.3	2.5	2.7
2-ethenyl-5-methyl-pyrazine	8.34	-17.25				0.7	0.9	0.9	2.4	2.8	2.9

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
2,8-dimethyl-indolizine	5.36	-11.50				0.5	0.6	0.7	1.8	2.1	2.3
3,6-bis(2-methylpropyl)-piperazine-2,3-dione	3.28	-10.86				0.5	0.5	0.6	1.7	1.8	2.1
2,5-dimethyl-piperidine	6.11	-16.93				0.5	0.7	0.7	1.8	2.2	2.3
terephthalic acid	2.98	-19.80	3.2	2.1	0.8						
benzoic acid	5.66	-10.22	2.1	2.1	1.9						
2-formyl-6-hydroxy-4-methoxy-3-(2-oxopropyl)benzoic acid	6.26	-15.33	2.2	1.4	0.5						
methyl hexadecanoate, ester	6.85	-3.19	1.4	2.6	3.5	2.2	2.4	2.8			
methyl oxtadecanoate, ester	4.02	-7.35	2.4	3.0	4.3	5.2	5.3	5.8			
hexadecanoic acid	7.00	-7.67									
octadecanoic acid	4.92	-22.36									
butane	3.13	-15.97	3.2	4.4	4.6						
pentane	6.11	-3.83	1.2	1.8	4.0						
toluene	3.43	-18.21	3.4	3.8	4.2						
n-hexadecane	8.04	-21.40				4.4	3.5	1.4	2.8	2.6	2.6
n-octadecane	8.64	-7.03				1.4	2.3	3.2	2.7	5.9	6.1
phenanthrene	3.43	-16.29				6.7	7.7	10.6	2.0	5.3	2.1
anthracene	1.34	-10.86	1.4	2.2	2.9	6.3					
1-methylene-1,2,5,8-tetrahydronaphthalene	8.19	-20.76	3.2	3.9	4.1						
terphenyl	2.53	-18.53									
chrysene	1.79	-7.35									
perylene	7.00	-12.14	13.2	11.3	11.2						
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S15. GC-MS composition of biocrude from HTL of digestate mixture with polyphenolic extract from sweet orange peels at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
3-hydroxycyclopent-2-en-1-one	7.60	-13.41	4.7	4.2	3.8	3.8	3.4	3.0	6.5	5.8	5.2
2-methyl-2-cyclopenten-1-one	7.45	-15.01	1.5	1.4	1.0	1.2	1.1	0.8	2.1	2.0	1.4
gamma-butyrolactone	4.47	-16.61	2.7	2.5	2.1	2.2	2.0	1.7			
5-methyl-2-(1-methylethyl)-cyclohexanone	6.11	-5.11	1.5	1.4	0.9	1.2	1.1	0.8			

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
tetrahydro-2*H*-pyran-2-one	8.19	-21.08	2.7	2.3	1.8	2.2	1.8	1.4			
4a,5,8,8a-tetrahydro-2λ^5-naphthalen-2-one	2.09	-18.84	2.8	2.7	2.1						
(*E*)-1-(hydroxymethylene)-5,8-dihydronaphthalen-2(1*H*)-one	8.64	-17.89	1.4	1.0	0.9						
3-methyl-6-(1-methylethyl)-2-cyclohexen-1-one	1.79	-13.41	1.5	2.2	3.0	5.6	7.4	8.1	14.3	19.1	20.8
furan-2,5-dione	9.09	-12.78	4.8	4.2	3.8	4.6	4.1	3.7	27.7	9.5	8.5
2-methylfuran	7.00	-18.53	2.7	2.2	2.1	2.6	2.1	2.0	6.1	4.9	4.7
isobenzofuran-1,3-dione	6.40	-22.04	3.6	3.4	3.3	3.5	3.2	3.1			
4,6-dihydroxy-2*H*-chromen-2-one	1.04	-22.68	2.7	2.5	2.4	2.6	2.4	2.3			
2-methyl-2-phenyl-oxirane	4.32	-4.15									
3-methyl-guaiacol	5.81	-6.71	5.2	4.7	4.2	7.9	7.1	6.3	7.1	6.4	5.2
2-phenyl-acetaldehyde	4.17	-2.87	1.4	1.0	0.7	2.1	1.5	1.0			
2,6-dimethoxy-phenol	4.62	-3.51	1.5	1.3	1.2	2.3	2.0	1.8	2.1	1.8	4.3
4-hydroxy-benzaldehyde	3.87	-5.43	2.5	2.2	1.8	3.8	3.3	2.7			
(phenoxymethyl)-oxirane	8.94	-14.69									
2-methoxy-4-vinyloxy-phenol	4.32	-23.00	3.6	3.1	2.7	4.6	3.9	3.4			
1,3,5-benzenetriol	3.28	-17.57	6.3	5.8	5.4	7.8	7.2	6.8			
1,3-benzodioxane-5-ol	4.02	-10.86	2.8	4.1	4.4	3.5	5.2	5.6			
5-(1-propenyl)-1,3-benzodioxole	7.15	-18.53	3.9	5.4	5.9	4.9	6.7	7.4			
m-cresol	1.19	-6.71	2.8	3.2	3.3	3.5	4.0	4.2	5.6	6.4	6.7
6-hydroxy-4,5-dimethyl-2-oxo-2*H*-chromene-8-carbaldehyde	4.77	-4.15					3.0	3.2	3.5	7.1	7.3
2,5-dihydroxy-4-methylbenzaldehyde	9.09	-16.61					1.6	1.9	3.4	7.8	8.0
2-(1*H*-pyrrol-1-yl)acetic acid	5.21	-22.36	0.1	0.1	0.2						
1,3,4,5-tetramethyl-2,3-dihydro-1*H*-imidazole	8.64	-18.53	0.1	0.1	0.2						
4,5-dimethyl-imidazole	5.81	-11.82	0.0	0.1	0.2						

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
2-(1*H*-pyrrol-1-yl)acetamide	2.53	-4.15	0.1	0.3	0.4						
1,3,4-trimethyl-2,3-dihydro-1*H*-imidazole	8.19	-18.53	0.1	0.1	0.1						
5-methyloxazole-2-carboxylic acid	6.70	-16.29				1.1	1.1	1.3	4.0	4.1	4.8
2,5-dimethylpyrazine	6.11	-17.89				0.7	0.7	0.8	2.3	2.5	2.7
2-ethenyl-5-methyl-pyrazine	8.34	-17.25				0.7	0.9	0.9	2.4	2.8	2.9
2,8-dimethyl-indolizine	5.36	-11.50				0.5	0.6	0.7	1.8	2.1	2.3
3,6-bis(2-methylpropyl)-piperazine-2,3-dione	3.28	-10.86				0.5	0.5	0.6	1.7	1.8	2.1
2,5-dimethyl-piperidine	6.11	-16.93				0.5	0.7	0.7	1.8	2.2	2.3
terephthalic acid	2.98	-19.80	3.2	2.1	0.8						
benzoic acid	5.66	-10.22	2.1	2.1	1.9						
2-formyl-6-hydroxy-4-methoxy-3-(2-oxopropyl)benzoic acid	6.26	-15.33	2.2	1.4	0.5						
methyl hexadecanoate, ester	6.85	-3.19	1.4	2.6	3.5	2.2	2.4	2.8			
methyl oxtadecanoate, ester	4.02	-7.35	2.4	3.0	4.3	5.2	5.3	5.8			
hexadecanoic acid	7.00	-7.67									
octadecanoic acid	4.92	-22.36									
butane	3.13	-15.97	3.2	4.4	4.6						
pentane	6.11	-3.83	1.2	1.8	4.0						
toluene	3.43	-18.21	3.4	3.8	4.2						
n-hexadecane	8.04	-21.40				4.4	3.5	1.4	2.8	2.6	2.6
n-octadecane	8.64	-7.03				1.4	2.3	3.2	2.7	5.9	6.1
phenanthrene	3.43	-16.29				6.7	7.7	10.6	2.0	5.3	2.1
anthracene	1.34	-10.86	1.4	2.2	2.9	6.3					
1-methylene-1,2,5,8-tetrahydronaphthalene	8.19	-20.76	3.2	3.9	4.1						
terphenyl	2.53	-18.53									
chrysene	1.79	-7.35									
perylene	7.00	-12.14	13.2	11.3	11.2						
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S16. GC-MS composition of aqueous-phase coproduct from HTL of pure digestate at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
acetic acid	9.23	-4.47	19.2	13.3	8.9	18.2	14.5	9.0	16.1	11.3	8.8
lactic acid	6.11	-23.00							9.6	4.4	3.5
glycolic acid	9.09	-14.69				8.6	4.2	2.3	9.5	4.6	3.7
formic acid	6.70	-22.04	9.9	4.9	3.3						
succinic acid	1.94	-12.14	1.6	3.3	5.0						
levulinic acid	2.38	-13.41	1.6	2.6	4.7						
acrylic acid	8.49	-3.51	1.7	2.5	4.8	8.2	5.2	3.9	9.7	4.7	2.7
acetamide	7.30	-16.93	1.6	2.3	4.0	9.5	4.8	2.9	9.1	5.2	2.8
furan-2-yl methanol	2.53	-7.03	1.1	2.8	4.0	2.6	2.9	4.5			
furan	2.53	-16.29	1.1	2.2	3.8	1.2	4.0	5.0			
5-hydroxymethylfurfural	1.19	-3.19	1.9	3.6	4.8						
acetaldehyde	7.30	-22.68	2.3	2.9	3.2	1.7	3.6	3.8	2.7	2.2	4.6
formaldehyde	6.55	-16.29	7.6	4.3	2.7	1.8	2.8	4.7	2.0	3.0	4.2
methyl glyoxal	1.79	-10.22	3.0	2.8	3.9	1.4	3.0	4.7	1.4	2.4	4.3
glyoxal	5.96	-19.80	2.6	2.3	2.1	2.9	3.9	3.6	2.7	3.3	4.8
acetol	8.04	-15.33	1.4	2.4	3.3	2.3	2.2	4.5	1.6	3.5	3.3
acetoin	2.53	-21.40	2.5	3.9	4.7	1.5	4.0	4.6	1.8	2.7	3.7
glycolaldehyde	7.45	-4.79	1.5	3.6	3.2	2.9	2.5	4.4	2.2	2.5	4.4
ethylene glycol	2.38	-13.73	2.7	3.2	3.3	2.1	2.1	3.9	2.9	3.9	3.4
1-methyl-1*H*-pyrrole	5.96	-18.84									
pyrrole	1.64	-16.61									
2-methyl-pyrazine	5.96	-3.19				2.9	2.6	3.4	1.7	3.0	3.2
nicotinic acid	4.47	-21.08				2.1	3.8	4.4	1.2	3.2	4.3
2-hydroxybenzaldehyde	2.68	-10.54	4.2	3.4	3.1						
phenol	3.13	-5.11	5.0	2.6	3.1	4.9	2.9	4.6	4.3	2.4	4.4
4-aminophenol	7.89	-13.10	3.7	3.9	0.7	3.6	3.8	0.5	4.9	3.2	1.4
catechol	7.30	-13.73	7.7	14.7	6.7	13.3	20.0	17.4	7.8	28.7	23.7
resorcinol	5.06	-17.57	3.1	3.1	3.3	4.3	3.7	3.2	4.6	2.8	4.7
aniline	2.38	-12.46	4.6	3.8	4.9	4.3	3.5	4.6	4.4	3.4	4.2
propane-1,2-diamine	8.04	-22.68	4.4	3.2	4.4						
butane-2,3-diamine	7.60	-18.53	4.2	2.7	4.2						
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S17. GC-MS composition of aqueous-phase coproduct from HTL of digestate mixture with polyphenolic extract from apple pomace at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
acetic acid	9.23	-4.47	20.2	10.4	9.8	17.1	15.3	8.6	12.1	10.3	9.7
lactic acid	6.11	-23.00							6.3	5.3	3.9
glycolic acid	9.09	-14.69				9.9	5.8	4.0	8.7	4.5	3.2
formic acid	6.70	-22.04	9.3	4.7	3.5						
succinic acid	1.94	-12.14	2.6	2.2	4.7						
levulinic acid	2.38	-13.41	2.7	3.3	3.9						
acrylic acid	8.49	-3.51	2.4	2.3	3.4	7.4	4.5	3.6	7.9	5.8	2.7

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
acetamide	7.30	-16.93	2.7	3.9	3.3	7.8	4.6	2.4	7.2	5.9	2.2
furan-2-yl methanol	2.53	-7.03	1.3	3.4	4.2	2.3	2.5	3.4			
furan	2.53	-16.29	2.8	2.7	4.7	2.7	3.2	3.6			
5-hydroxymethylfurfural	1.19	-3.19	2.8	4.0	3.5						
acetaldehyde	7.30	-22.68	1.4	2.7	4.9	2.9	3.2	3.8	1.7	3.3	4.5
formaldehyde	6.55	-16.29	8.6	5.3	2.2	1.8	3.8	4.9	2.9	2.6	4.3
methyl glyoxal	1.79	-10.22									
glyoxal	5.96	-19.80									
acetol	8.04	-15.33									
acetoin	2.53	-21.40									
glycolaldehyde	7.45	-4.79	1.6	3.6	3.5	2.3	2.1	4.2	2.4	2.3	3.7
ethylene glycol	2.38	-13.73	1.8	3.2	4.9	3.0	3.6	4.5	1.8	3.6	4.3
1-methyl-1*H*-pyrrole	5.96	-18.84									
pyrrole	1.64	-16.61									
2-methyl-pyrazine	5.96	-3.19				2.7	2.5	3.4	2.9	2.8	4.7
nicotinic acid	4.47	-21.08				2.6	3.6	3.8	1.4	3.6	3.9
2-hydroxy-benzaldehyde	2.68	-10.54	4.8	2.6	5.0						
phenol	3.13	-5.11	3.2	2.9	4.0	2.5	2.3	4.2	4.3	2.8	4.8
4-aminophenol	7.89	-13.10	3.6	2.8	0.6	3.1	2.3	0.6	4.7	2.8	0.8
catechol	7.30	-13.73	11.7	28.4	20.7	0.1	11.0	11.5	4.5	11.0	17.8
resorcinol	5.06	-17.57	3.6	2.9	3.1	4.5	3.5	4.1	4.8	2.8	4.7
aniline	2.38	-12.46	4.8	2.4	3.5	4.3	2.5	4.8	4.3	2.6	3.6
propane-1,2-diamine	8.04	-22.68	4.0	2.4	3.3						
butane-2,3-diamine	7.60	-18.53	4.4	3.9	3.4						
(*E*)-3-((3*Z*,4*Z*)-3,4-bis(1-hydroxy-2-oxopropylidene)-cyclohexa-1,5-dien-1-yl)acrylic acid	7.89	-11.82				3.0	2.8	3.4	0.0	3.1	2.7
(*E*)-3-(1,5-diamino-2,4-dimethyl-2*H*-benzo[*d*]azepin-8-yl)acrylic acid	8.94	-7.99				3.5	2.9	2.4	4.0	3.2	2.1
(*E*)-3-(4-(1-hydroxy-2-oxopropyl)-3-methoxyphenyl)acrylic acid	5.81	-18.84				2.4	3.5	3.5	2.2	3.3	2.3
(*E*)-3-(5-hydroxy-4-methyl-2,5-dihydrobenzo[*f*][1,3]oxazepin-8-yl)acrylic acid	5.96	-5.75				2.7	3.8	3.0	3.9	3.8	2.2
(3*Z*,5*Z*)-3,5-bis(1-hydroxy-2-oxopropylidene)-4-oxocyclohex-1-ene-1-	3.72	-9.90				2.9	2.5	3.2	2.8	3.3	3.6

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
carboxylic acid											
4,9-diamino-3,10-dimethyl-3,8*a*-dihydro-5*H*-2,8-(epiethan[2]yl[1]ylidene)benzo[*e*][1,2]oxazine-6-carboxylic acid	5.21	-22.04				3.6	3.3	3.6	3.1	3.7	2.3
4-hydroxy-3,5-bis(3-hydroxybutan-2-yl)cyclohex-1-ene-1-carboxylic acid	5.21	-14.37				2.2	2.7	2.5	2.8	3.9	2.7
(3*Z*,5*Z*)-3,5-bis(3-aminobutan-2-ylidene)-4-hydroxycyclohex-1-ene-1-carboxylic acid	6.70	-15.01				2.9	2.2	3.2	3.4	3.7	3.5
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S18. GC-MS composition of aqueous-phase coproduct from HTL of digestate mixture with polyphenolic extract from olive pomace at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
acetic acid	9.23	-4.47	18.2	11.2	10.0	18.2	14.4	11.0	11.2	14.3	9.9
lactic acid	6.11	-23.00							7.9	4.3	3.0
glycolic acid	9.09	-14.69				7.5	4.7	2.7	7.5	4.5	3.2
formic acid	6.70	-22.04	9.3	5.4	2.6						
succinic acid	1.94	-12.14	1.7	2.3	4.4						
levulinic acid	2.38	-13.41	2.4	2.1	4.9						
acrylic acid	8.49	-3.51	1.8	3.6	4.3	6.3	4.2	3.3	7.2	5.9	2.4
acetamide	7.30	-16.93	2.3	2.9	4.7	9.3	5.4	3.8	8.5	5.3	2.8
furan-2-yl methanol	2.53	-7.03	2.9	2.3	4.5	2.8	3.8	3.7			
furan	2.53	-16.29	2.4	3.0	4.8	2.5	2.2	4.5			
5-hydroxymethylfurfural	1.19	-3.19	1.9	3.5	3.8						
acetaldehyde	7.30	-22.68	1.6	2.2	4.5	1.2	3.5	4.2	2.6	2.7	5.0
formaldehyde	6.55	-16.29	7.8	5.3	2.8	1.7	2.1	3.8	2.4	3.8	4.2
methyl glyoxal	1.79	-10.22									
glyoxal	5.96	-19.80									
acetol	8.04	-15.33									
acetoin	2.53	-21.40									
glycolaldehyde	7.45	-4.79	2.0	2.4	3.1	2.9	2.5	4.9	2.7	3.3	3.5

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
ethylene glycol	2.38	-13.73	2.6	2.2	4.6	2.9	3.8	3.1	2.0	3.8	5.0
1-methyl-1*H*-pyrrole	5.96	-18.84									
pyrrole	1.64	-16.61									
2-methyl-pyrazine	5.96	-3.19				2.2	2.2	3.5	2.3	2.8	3.7
nicotinic acid	4.47	-21.08				1.4	3.9	4.3	1.4	4.0	4.0
2-hydroxy-benzaldehyde	2.68	-10.54	4.2	3.2	3.9						
phenol	3.13	-5.11	4.6	2.2	4.5	3.8	2.2	3.2	3.5	2.5	4.9
4-aminophenol	7.89	-13.10	3.5	3.7	1.3	4.6	3.4	1.8	3.7	3.2	1.6
catechol	7.30	-13.73	14.2	31.5	14.3	3.0	9.5	11.0	6.1	6.8	13.8
resorcinol	5.06	-17.57	4.9	3.6	3.5	3.6	3.2	4.7	4.5	3.5	4.4
aniline	2.38	-12.46	4.4	3.0	3.7	3.4	2.8	3.8	3.2	3.4	3.3
propane-1,2-diamine	8.04	-22.68	3.2	2.5	5.0						
butane-2,3-diamine	7.60	-18.53	4.1	2.2	4.9						
(*E*)-3-((3*Z*,4*Z*)-3,4-bis(1-hydroxy-2-oxopropylidene)-cyclohexa-1,5-dien-1-yl)acrylic acid	7.89	-11.82				2.1	3.7	3.0	2.5	2.5	3.7
(*E*)-3-(1,5-diamino-2,4-dimethyl-2*H*-benzo[*d*]azepin-8-yl)acrylic acid	8.94	-7.99				2.3	3.5	3.7	2.3	2.4	2.8
(*E*)-3-(4-(1-hydroxy-2-oxopropyl)-3-methoxyphenyl)acrylic acid	5.81	-18.84				3.5	3.6	3.7	3.4	3.8	2.6
(*E*)-3-(5-hydroxy-4-methyl-2,5-dihydrobenzo[*f*][1,3]oxazepin-8-yl)acrylic acid	5.96	-5.75				2.8	2.2	2.1	2.7	2.4	3.6
(3*Z*,5*Z*)-3,5-bis(1-hydroxy-2-oxopropylidene)-4-oxocyclohex-1-ene-1-carboxylic acid	3.72	-9.90				2.3	3.4	2.2	3.9	3.3	3.5
4,9-diamino-3,10-dimethyl-3,8*a*-dihydro-5*H*-2,8-(epiethan[2]yl[1]ylidene)benzo[*e*][1,2]oxazine-6-carboxylic acid	5.21	-22.04				2.5	3.8	3.3	2.3	3.9	2.3
4-hydroxy-3,5-bis(3-hydroxybutan-2-yl)cyclohex-1-ene-1-carboxylic acid	5.21	-14.37				3.3	2.4	2.2	3.4	3.8	3.1

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
(3*Z*,5*Z*)-3,5-bis(3-aminobutan-2-ylidene)-4-hydroxycyclohex-1-ene-1-carboxylic acid	6.70	-15.01				3.9	3.7	2.7	3.2	3.9	3.5
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S19. GC-MS composition of aqueous-phase coproduct from HTL of digestate mixture with polyphenolic extract from spent coffee ground at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
acetic acid	9.23	-4.47	20.2	10.4	9.8	18.2	10.2	9.0	16.1	11.3	9.9
lactic acid	6.11	-23.00									
glycolic acid	9.09	-14.69							8.6	4.9	3.5
formic acid	6.70	-22.04	9.3	4.7	3.5	8.2	6.0	2.1			
succinic acid	1.94	-12.14	2.6	2.2	4.7	3.0	3.2	3.9			
levulinic acid	2.38	-13.41	2.7	3.3	3.9	2.8	3.3	4.4			
acrylic acid	8.49	-3.51	2.4	2.3	3.4	1.8	2.2	3.2	7.7	5.7	3.6
acetamide	7.30	-16.93	2.7	3.9	3.3	1.2	3.4	3.4	8.5	4.7	2.6
furan-2-yl methanol	2.53	-7.03	1.3	3.4	4.2	1.5	3.8	4.7	2.4	4.0	3.2
furan	2.53	-16.29	2.8	2.7	4.7	2.6	3.9	4.9	2.8	2.9	3.8
5-hydroxymethylfurfural	1.19	-3.19	2.8	4.0	3.5	1.9	3.0	3.1			
acetaldehyde	7.30	-22.68	1.4	2.7	4.9	1.3	3.5	3.4	2.4	2.4	4.2
formaldehyde	6.55	-16.29	8.6	5.3	2.2	7.3	5.1	3.4	1.3	2.8	3.9
methyl glyoxal	1.79	-10.22									
glyoxal	5.96	-19.80									
acetol	8.04	-15.33									
acetoin	2.53	-21.40									
glycolaldehyde	7.45	-4.79	1.6	3.6	3.5	2.6	3.7	3.2	2.9	3.2	4.1
ethylene glycol	2.38	-13.73	1.8	3.2	4.9	2.8	3.5	4.2	1.9	2.3	4.3
1-methyl-1*H*-pyrrole	5.96	-18.84									
pyrrole	1.64	-16.61									
2-methyl-pyrazine	5.96	-3.19							1.2	3.7	3.5
nicotinic acid	4.47	-21.08							1.7	2.5	3.9
2-hydroxy-benzaldehyde	2.68	-10.54	4.8	2.6	5.0	4.5	3.1	3.6			
phenol	3.13	-5.11	3.2	2.9	4.0	4.8	2.5	3.2	3.8	2.3	4.8
4-aminophenol	7.89	-13.10	3.6	2.8	0.6	3.3	2.3	0.5	4.9	3.8	0.9
catechol	7.30	-13.73	11.7	28.4	20.7	14.1	26.0	23.8	4.0	14.4	11.0
resorcinol	5.06	-17.57	3.6	2.9	3.1	4.0	2.8	3.5	3.4	2.9	4.6
aniline	2.38	-12.46	4.8	2.4	3.5	4.6	3.2	3.8	3.7	2.5	4.8
propane-1,2-diamine	8.04	-22.68	4.0	2.4	3.3	4.7	2.2	4.2			

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
butane-2,3-diamine	7.60	-18.53	4.4	3.9	3.4	4.9	3.2	4.6			
(*E*)-3-((3*Z*,4*Z*)-3,4-bis(1-hydroxy-2-oxopropylidene)-cyclohexa-1,5-dien-1-yl)acrylic acid	7.89	-11.82							2.3	2.4	2.9
(*E*)-3-(1,5-diamino-2,4-dimethyl-2*H*-benzo[*d*]azepin-8-yl)acrylic acid	8.94	-7.99							3.7	3.3	2.4
(*E*)-3-(4-(1-hydroxy-2-oxopropyl)-3-methoxyphenyl)acrylic acid	5.81	-18.84							2.6	3.5	3.2
(*E*)-3-(5-hydroxy-4-methyl-2,5-dihydrobenzo[*f*][1,3]oxazepin-8-yl)acrylic acid	5.96	-5.75							2.9	2.1	2.2
(3*Z*,5*Z*)-3,5-bis(1-hydroxy-2-oxopropylidene)-4-oxocyclohex-1-ene-1-carboxylic acid	3.72	-9.90							2.2	3.2	2.7
4,9-diamino-3,10-dimethyl-3,8*a*-dihydro-5*H*-2,8-(epiethan[2]yl[1]ylidene)benzo[*e*][1,2]oxazine-6-carboxylic acid	5.21	-22.04							3.1	2.5	3.4
4-hydroxy-3,5-bis(3-hydroxybutan-2-yl)cyclohex-1-ene-1-carboxylic acid	5.21	-14.37							2.6	4.0	3.6
(3*Z*,5*Z*)-3,5-bis(3-aminobutan-2-ylidene)-4-hydroxycyclohex-1-ene-1-carboxylic acid	6.70	-15.01							3.3	2.8	3.2
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S20. GC-MS composition of aqueous-phase coproduct from HTL of digestate mixture with polyphenolic extract from sweet orange peels at 280, 325, and 370 °C for 60 min.

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
acetic acid	9.23	-4.47	20.1	14.3	10.8	15.2	12.3	10.0	12.1	12.2	8.7
lactic acid	6.11	-23.00							8.9	4.8	3.5
glycolic acid	9.09	-14.69				8.6	4.7	2.5	9.0	5.5	2.9
formic acid	6.70	-22.04	9.4	5.7	3.9						
succinic acid	1.94	-12.14	1.4	3.2	3.9						
levulinic acid	2.38	-13.41	2.3	2.7	4.8						
acrylic acid	8.49	-3.51	1.2	3.2	3.7	5.4	4.5	2.5	8.9	4.2	3.6
acetamide	7.30	-16.93	2.3	2.9	4.5	9.3	5.1	3.4	8.7	4.9	3.6
furan-2-yl methanol	2.53	-7.03	2.2	3.6	4.7	2.7	2.8	4.4			
furan	2.53	-16.29	2.7	3.7	4.2	2.6	2.3	3.6			
5-hydroxymethylfurfural	1.19	-3.19	2.9	3.2	4.4						
acetaldehyde	7.30	-22.68	2.4	3.9	4.9	1.2	2.6	4.3	2.9	2.3	3.4
formaldehyde	6.55	-16.29	8.2	5.8	4.0	1.2	2.1	4.8	1.6	2.2	3.2
methyl glyoxal	1.79	-10.22									
glyoxal	5.96	-19.80									
acetol	8.04	-15.33									
acetoin	2.53	-21.40									
glycolaldehyde	7.45	-4.79	1.9	2.4	4.6	1.2	2.8	4.2	2.4	2.7	3.3
ethylene glycol	2.38	-13.73	3.0	2.3	4.3	2.5	2.3	3.4	3.0	3.2	3.2
1-methyl-1*H*-pyrrole	5.96	-18.84									
pyrrole	1.64	-16.61									
2-methyl-pyrazine	5.96	-3.19				2.7	2.2	4.2	2.3	3.2	3.6
nicotinic acid	4.47	-21.08				1.2	2.8	5.0	1.1	2.9	4.4
2-hydroxy-benzaldehyde	2.68	-10.54	3.7	2.8	4.5						
phenol	3.13	-5.11	4.9	2.4	3.2	2.6	3.1	3.8	3.3	3.2	4.4
4-aminophenol	7.89	-13.10	3.8	2.8	1.0	4.4	3.5	1.9	4.8	3.6	1.4
catechol	7.30	-13.73	11.7	21.8	12.1	4.8	18.2	10.6	3.7	14.1	19.5
resorcinol	5.06	-17.57	3.3	3.7	4.2	4.2	2.9	3.3	3.7	3.1	4.7
aniline	2.38	-12.46	4.4	3.7	4.5	3.9	2.2	3.9	4.0	3.2	3.9
propane-1,2-diamine	8.04	-22.68	4.4	2.6	4.4						
butane-2,3-diamine	7.60	-18.53	3.9	3.4	3.6						
(*E*)-3-((3*Z*,4*Z*)-3,4-bis(1-hydroxy-2-oxopropylidene)-cyclohexa-1,5-dien-1-yl)acrylic acid	7.89	-11.82				3.7	2.2	2.4	3.4	3.9	3.2
(*E*)-3-(1,5-diamino-2,4-dimethyl-2*H*-benzo[*d*]azepin-8-yl)acrylic acid	8.94	-7.99				2.4	2.7	3.4	3.0	2.9	3.7

Chemical Compounds	Calibration Factor		Relative composition (wt%)								
			Feedstock pH 3			Feedstock pH 7			Feedstock pH 11		
	Slope (x 10^5)	Intercept	280	325	370	280	325	370	280	325	370
(*E*)-3-(4-(1-hydroxy-2-oxopropyl)-3-methoxyphenyl)acrylic acid	5.81	-18.84				3.6	3.0	3.7	3.5	2.5	2.4
(*E*)-3-(5-hydroxy-4-methyl-2,5-dihydrobenzo[*f*][1,3]oxazepin-8-yl)acrylic acid	5.96	-5.75				3.6	4.0	3.8	3.7	3.7	2.8
(3*Z*,5*Z*)-3,5-bis(1-hydroxy-2-oxopropylidene)-4-oxocyclohex-1-ene-1-carboxylic acid	3.72	-9.90				3.2	3.7	2.4	1.4	3.4	2.2
4,9-diamino-3,10-dimethyl-3,8*a*-dihydro-5*H*-2,8-(epiethan[2]yl[1]ylidene)benzo[*e*][1,2]oxazine-6-carboxylic acid	5.21	-22.04				2.3	2.6	3.9	2.1	3.5	3.8
4-hydroxy-3,5-bis(3-hydroxybutan-2-yl)cyclohex-1-ene-1-carboxylic acid	5.21	-14.37				3.9	2.3	2.5	2.6	2.3	2.4
(3*Z*,5*Z*)-3,5-bis(3-aminobutan-2-ylidene)-4-hydroxycyclohex-1-ene-1-carboxylic acid	6.70	-15.01				3.7	3.3	2.4	0.0	2.6	2.2
Total			100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table S21. Reaction parameters of four reaction steps of acid- and alkali-catalyzed HTL of methylglyoxal (MGO) / acetoin (ACO), NH_4OAc, and polyphenols (EPI–epicatechin, QUE–quercetin, FRA–ferulic acid, CFA–caffeic acid, and GLA–gallic acid). The reaction order followed the reaction pathways in Figures 3–4, Figures 6–7, and Figures S8–S11. *E* and Δ*H* are in kJ/mol.

Feedstock Mixtures	pH	Step 1				Step 2				Step 3				Step 4			
		A	*E*	Δ*H*	SSE	*A*	*E*	Δ*H*	SSE	*A*	*E*	Δ*H*	SSE	*A*	*E*	Δ*H*	SSE
MGO, EPI, NH_4OAc	3	0.29	40.9	-268.4	9.4E-03	2.03	178.5	365.8	6.6E-03	6.08	362.5	-	4.0E-03	18.25	452.3	-	1.1E-03
	11	0.42	43.1	103.2	5.7E-03	2.97	190.0	211.6	4.5E-03	14.84	388.1	217.1	7.4E-03	44.53	477.0	-148.7	3.5E-03
ACO, EPI, NH_4OAc	3	0.06	33.9	-59.9	9.6E-03	0.39	149.4	593.0	4.1E-03	1.16	299.8	-	1.6E-03	4.65	379.1	-	7.1E-03
	11	0.27	41.4	277.9	4.3E-03	1.64	185.3	211.6	3.2E-03	4.93	375.2	-	9.0E-03	14.78	461.6	-	4.4E-03
MGO, QUE, NH_4OAc	3	0.29	40.6	-344.0	4.7E-03	1.45	180.4	365.8	8.6E-03	7.26	359.6	-	5.9E-03	36.30	459.8	-	9.3E-03
	11	0.55	44.1	27.7	7.3E-03	3.82	193.3	211.6	3.1E-03	19.08	399.4	217.1	9.4E-03	95.41	496.3	-148.7	2.0E-03
ACO, QUE, NH_4OAc	3	0.06	34.3	-135.5	4.4E-03	0.38	154.8	593.0	9.7E-03	1.91	304.7	-	8.8E-03	5.72	389.0	-	2.7E-03
	11	0.33	42.0	202.4	4.0E-03	1.95	189.0	211.6	5.0E-03	5.86	373.0	-	3.2E-03	29.28	472.1	-	6.5E-03
MGO, FRA, NH_4OAc	3	0.06	34.4	-67.1	2.5E-03	0.42	153.8	91.4	4.4E-03	1.27	301.3	177.6	5.8E-03	6.33	387.3	-528.5	2.9E-03
	11	0.05	34.4	-2.5	6.3E-03	0.36	154.0	-	6.3E-03	1.46	312.1	217.1	8.6E-03	4.37	384.9	-193.0	5.4E-03
ACO, FRA, NH_4OAc	3	0.06	34.3	-43.6	3.1E-03	0.35	155.6	85.7	2.6E-03	1.06	303.2	177.6	4.1E-03	4.26	380.7	-765.3	3.6E-03
	11	0.06	35.2	176.7	7.5E-03	0.37	158.3	92.2	6.1E-03	1.11	314.7	-	7.5E-03	4.45	386.1	-	8.4E-03
MGO, CFA, NH_4OAc	3	0.20	39.5	-134.2	8.4E-03	1.19	176.0	182.9	1.1E-03	5.94	356.1	177.6	4.5E-03	29.70	441.2	-231.5	5.9E-03
	11	0.42	43.1	382.7	9.1E-03	2.54	188.6	184.3	5.7E-03	12.72	382.3	217.1	9.0E-03	63.62	473.6	-148.7	9.1E-03
ACO, CFA, NH_4OAc	3	0.14	37.5	-87.2	4.8E-03	0.82	165.3	380.2	2.9E-03	4.08	332.5	177.6	9.0E-03	20.38	415.6	-395.2	1.7E-03
	11	0.34	42.3	277.9	4.3E-03	2.36	191.1	184.3	7.0E-03	11.81	372.6	-	2.4E-03	47.23	468.0	-	1.5E-03
MGO, GLA, NH_4OAc	3	0.03	32.6	-39.9	1.8E-03	0.18	147.2	15.9	2.3E-03	0.73	291.8	177.6	5.8E-03	2.19	369.8	-356.4	2.1E-03
	11	0.07	37.4	549.7	2.2E-03	0.45	166.9	184.3	3.9E-03	1.34	334.3	217.1	7.0E-03	4.01	419.8	-223.4	2.3E-03
ACO, GLA, NH_4OAc	3	0.02	31.0	-16.4	4.6E-03	0.12	136.4	152.3	5.0E-03	0.35	280.3	177.6	6.4E-03	1.06	352.2	-301.3	2.3E-03
	11	0.07	37.0	39.7	6.8E-03	0.47	163.7	184.3	8.6E-03	2.35	333.6	-	4.0E-03	11.74	405.7	-	4.4E-03

Table S22. The estimated and measured (i.e., by DSC) Δ*H* values for the acid-catalyzed and alkali-catalyzed HTL of methylglyoxal (MGO) / acetoin (ACO), NH_4OAc, and polyphenols (EPI–epicatechin, QUE–quercetin, FRA–ferulic acid, CFA–caffeic acid, and GLA–gallic acid). The DSC measurement indicated the peak(s) for positive Δ*H* or valley(s) for negative Δ*H*. The comparison can be made based on the acquired estimated values with the observed sequential peaks/valleys.

Feedstock Mixtures	pH	Estimated values				Measured by DSC			
		Step 1	Step 2	Step 3	Step 4	Peak/Valley 1	Peak/Valley 2	Peak/Valley 3	Peak/Valley 4
MGO, EPI, NH_4OAc	3	-268.4	365.8	-	-	-273.8	372.2	-	-
	11	103.2	211.6	217.1	-148.7	96.8	223.6	190.6	-164.7
ACO, EPI, NH_4OAc	3	-59.9	593.0	-	-	-59.9	548.5	-	-
	11	277.9	211.6	-	-	304.7	232.1	-	-
MGO, QUE, NH_4OAc	3	-344.0	365.8	-	-	-344.0	394.6	-	-
	11	27.7	211.6	217.1	-148.7	29.2	195.9	197.6	-160.1
ACO, QUE, NH_4OAc	3	-135.5	593.0	-	-	-152.2	550.9	-	-
	11	202.4	211.6	-	-	202.4	224.3	-	-
MGO, FRA, NH_4OAc	3	-67.1	91.4	177.6	-528.5	-60.3	91.4	196.8	-587.3
	11	-2.5	-	217.1	-193.0	-2.5	217.1	-193.0	-
ACO, FRA, NH_4OAc	3	-43.6	85.7	177.6	-765.3	-38.0	77.8	171.4	-765.3
	11	176.7	92.2	-	-	188.8	82.0	-	-
MGO, CFA, NH_4OAc	3	-134.2	182.9	177.6	-231.5	-134.2	173.6	177.6	-231.5
	11	382.7	184.3	217.1	-148.7	338.4	175.3	217.1	-148.7
ACO, CFA, NH_4OAc	3	-87.2	380.2	177.6	-395.2	-88.8	380.2	201.9	-425.7
	11	277.9	184.3	-	-	273.1	170.8	-	-
MGO, GLA, NH_4OAc	3	-39.9	15.9	177.6	-356.4	-37.3	16.8	187.5	-378.1
	11	549.7	184.3	217.1	-223.4	549.7	184.3	202.8	-223.4
ACO, GLA, NH_4OAc	3	-16.4	152.3	177.6	-301.3	-15.8	139.2	165.8	-301.3
	11	39.7	184.3	-	-	38.6	194.8	-	-