Supporting Information for

Hydrothermal humification mechanism of typical agricultural waste biomass: A case study of corn straw

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Text S1

Alkali-dissolved barium chloride precipitation potentiometric titration

Alkaline solubilized barium chloride precipitation potentiometric titration is used to determine the total acid functional groups of A-HA, mainly the phenolic hydroxyl and carboxyl groups in their molecules. The standard solutions used included 0.1 mol/L NaOH solution, 0.1 mol/L $BaCl_2$ solution and 0.1 mol/L HCl solution. Specific methods are as follows: 20 mg of A-HA sample was accurately weighed in a 50mL centrifuge tube, 10 mL 0.1mol/L NaOH solution was added to dissolve, then 25 mL 0.1 mol/L $BaCl_2$ solution was added, centrifuged after shaking for several minutes, 25mL supernatant was removed, and 0.1 mol/L HCl solution was used for potential titration. The endpoint of titration was pH 8.4, the blank test performed simultaneously. The total acid group is calculated by Equation 1.

$$C_{ad} = \frac{(V_2 - V_1) \times c(HCl)}{m} \times \frac{35}{25} \quad (1)$$

Where: V_2 is the volume of acid used for blank titration, mL; V_1 is the volume of acid used for sample titration, mL; c(HCl) is the concentration of hydrochloric acid standard solution, mol/L; m is the mass of sample, g.

Physical-chemical analysis

The elemental contents of C, H, N and S in AHAs were measured in an elemental analyzer (FlashSmart, Thermo, USA). The pH was analyzed by a pH meter (PHSJ-5T). The functional groups on the surfaces of the AHAs were analyzed by Fourier transform infrared spectroscopy (FT-IR, Nicolet iS50, Thermo Fisher Scientific, USA) using KBr

pellets over the wavelength range of 400–4000 cm^{-1}. AHA solution of 50 mg/L was prepared with 5 mmol/L NaOH and then 3D EEM analysis was performed in a RF-6000 fluorometer (F-7100FL, Hitachi, Japan). The range of emission wavelength (Em) is 300-650nm, the range of excitation wavelength (Ex) is 250-450nm, the scanning speed is set to 1200 nm/min, both procedures have an interval of 5 nm. The ultraviolet (UV) absorbance of AHA solution (50 mg/L) at 250, 254 and 365 nm was analyzed by UV–vis spectroscopy (UV-1800, Shanghai precision scientific instruments, China). The concentrations of furfural (FF) and 5-hydroxymethylfurfural (5-HMF) produced in each trial during hydrothermal reaction were determined by high pressure liquid chromatography (HPLC; Shimadzu LC20A, Japan) at 254 nm, equipped with an C18 column (250 × 4.6 mm). The mobile phase was consisted of methanol and water (0.3% acetic acid) mixed at a ratio of 1:9 (v/v), and the flow rate was set at 0.6 mL min^{-1}. Glucose, fructose and xylose were also detected by HPLC coupled with 3-methyl-1-phenyl-2-pyrazolin-5-one (PMP) pre-column derivatization [1]. The mobile phase was constituted by 0.02 mol L^{-1} KH_2PO_4 buffer and methanol (9:1 v/v), column oven at 35℃, flow rate at 0.8 mL min^{-1}, the detection wavelength at 250 nm. The graphitization degree of AHA was characterized by Raman spectroscopy (Thermo Fischer DXR, Thermo Scientific, USA), the excitation wavelength was 514 nm, the scanning range was 50-3500 cm^{-1}, and the scanning step was 0.966 cm^{-1}. The analysis of elements on solid surface for AHA was carried out by the X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA) by using Al Kα radiation. The functional groups present in AHA was measured by ^{13}C nuclear magnetic resonance (NMR) analysis

(Bruker AVANCE III HD 600 NMR spectrometer, Germany). Ultrahigh resolution mass spectra were acquired using a Bruker Solari X FT-ICR-MS equipped with a 15.0 T superconducting magnet and a dual-mode ESI/MALDI ion source. The magnitude-averaged molecular characteristics including O/C_w, H/C_w, molecular weight (MW_w), double bond equivalent (DBE_w), and aromaticity index (AI_w) were calculated [2].

Figures

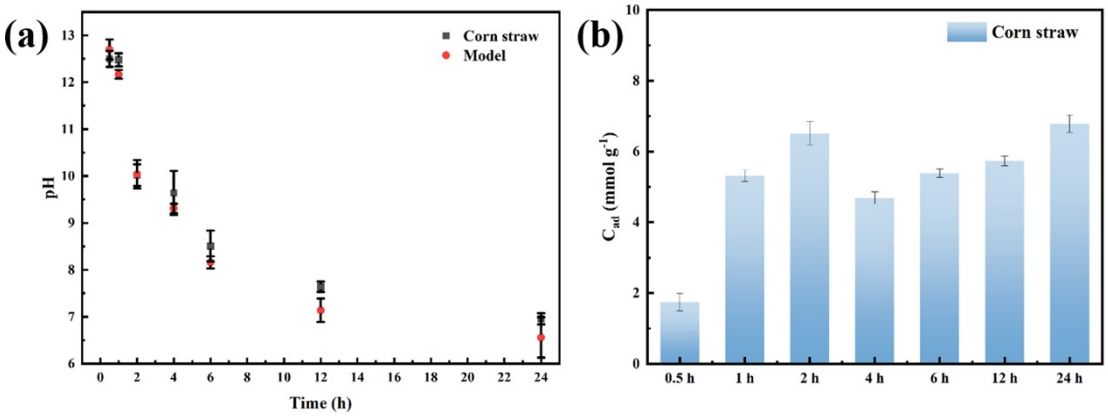

Fig. S1. (a) The pH of reaction system after hydrothermal treatment at different time; (b) Total acid group concentration of A-HA at different times.

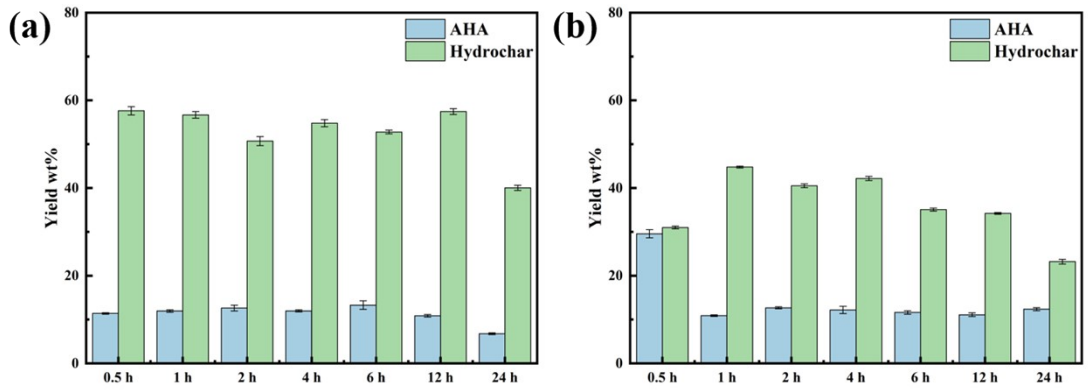

Fig. S2. The yield of A-HA and hydrochar at different times (a) corn straw; (b) the Model.

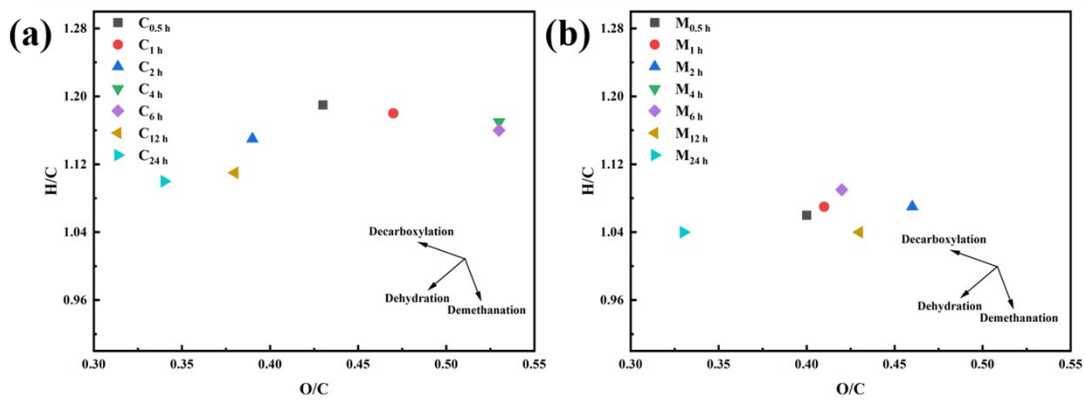

Fig. S3. Van Krevelen diagram of A-HA at different times (a) corn straw; (b) the Model.

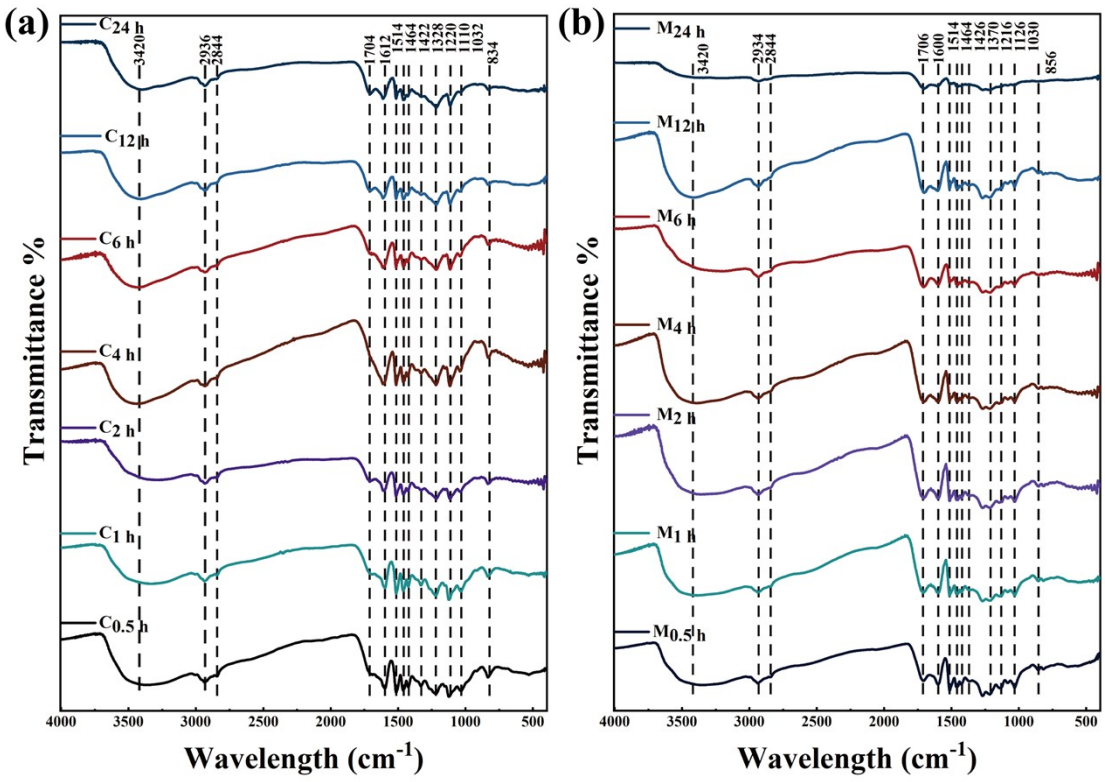

Fig. S4. FT-IR of corn straw A-HA (a) and Model A-HA (b) at different reaction times.

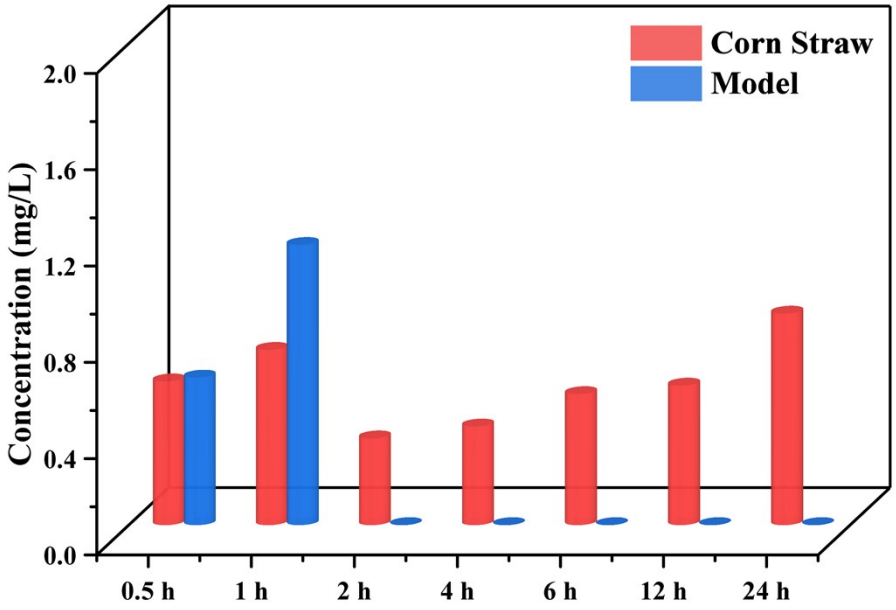

Fig. S5. The concentrations of furfural at different reaction times.

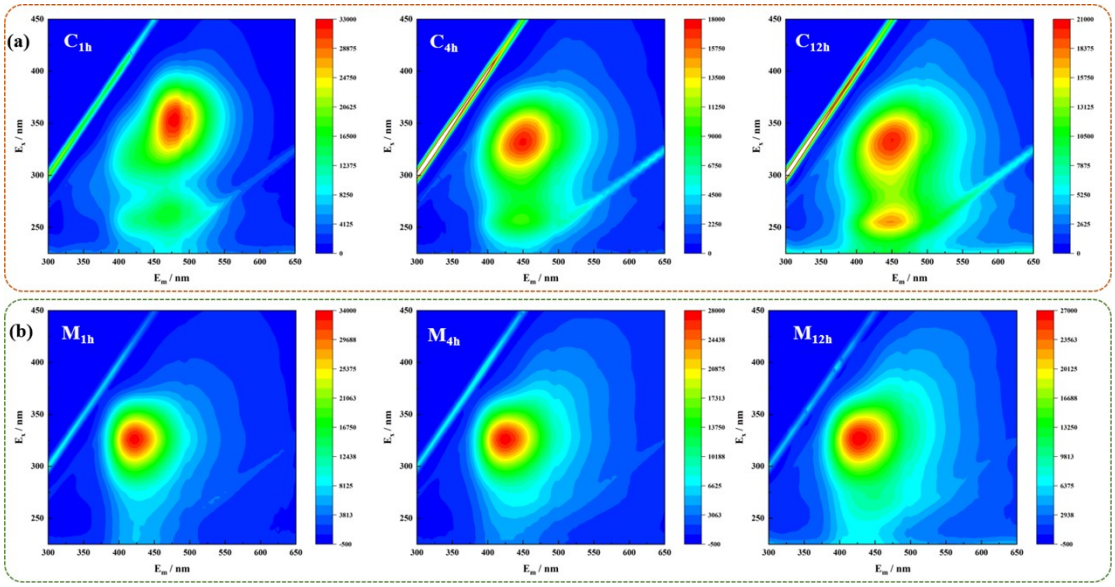

Fig. S6. The 3D EEM spectra of A-HA at different reaction times for corn straw (a), for Model (b).

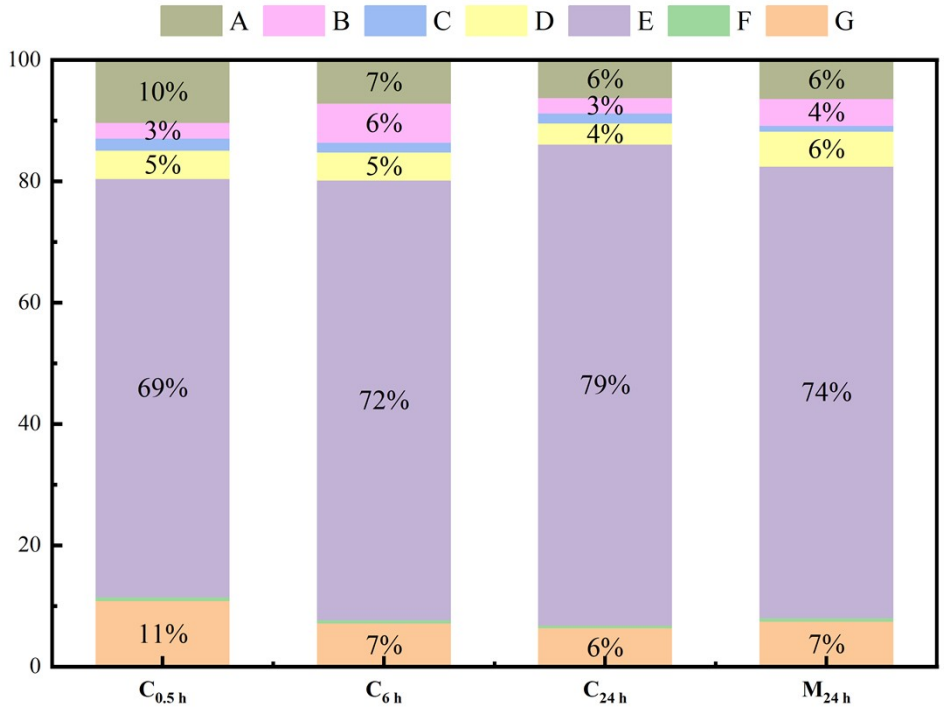

Fig. S7. Proportion of the seven components of the FT-ICR-MS (A-G are condensed aromatics, tannins, lignin, unsaturated hydrocarbons, carbohydrates, proteins and lipids separately.)

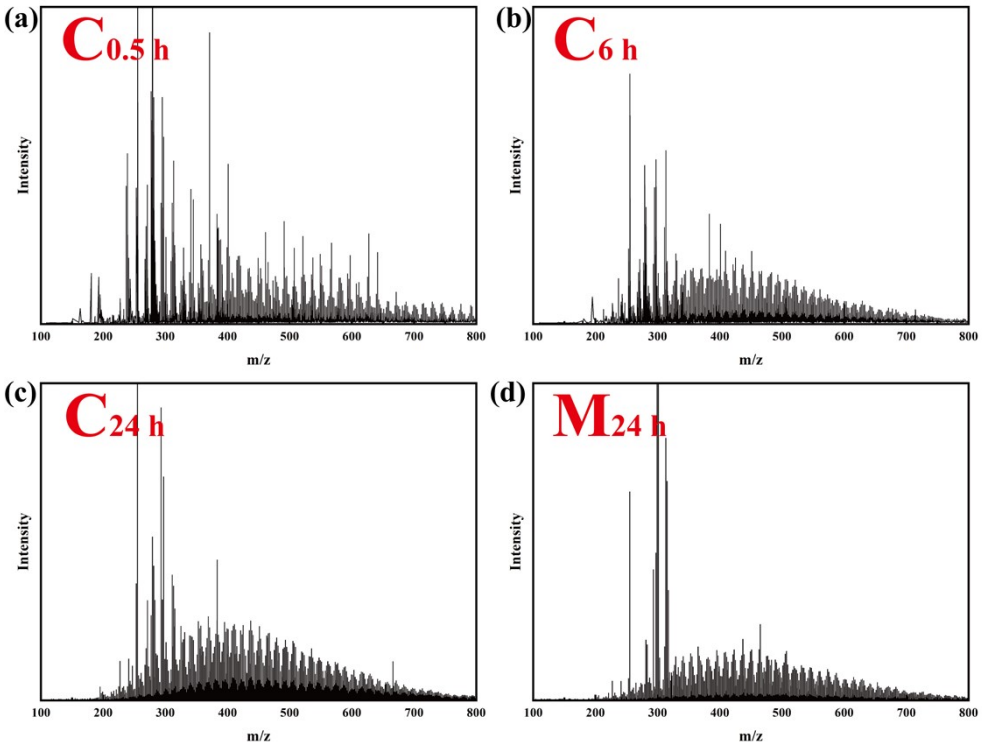

Fig. S8. The broadband ESI-FT-ICR-MS spectra of A-HA at different reaction times, corn straw: (a) 0.5 h, (b) 6 h, (c) 24 h; (d) Model: 24h.

Tables

Table S1. The element analysis of A-HA at different time.

	N (wt%)	C (wt%)	H (wt%)	S (wt%)	O (wt%)	H/C	O/C
Corn straw	1.20	38.00	5.10	1.02	54.68	1.61	1.08
$C_{0.5\ h}$	0.94	58.24	5.79	1.46	33.58	1.19	0.43
$C_{1\ h}$	0.88	57.46	5.67	0.00	35.99	1.18	0.47
$C_{2\ h}$	0.79	61.13	5.88	0.53	31.67	1.15	0.39
$C_{4\ h}$	0.71	55.19	5.40	0.00	38.70	1.17	0.53
$C_{6\ h}$	0.96	54.56	5.27	0.56	38.65	1.16	0.53
$C_{12\ h}$	0.87	61.78	5.74	0.00	31.61	1.11	0.38
$C_{24\ h}$	1.21	63.73	5.85	0.63	28.59	1.10	0.34
$M_{0.5\ h}$	0.43	61.23	5.43	0.00	32.91	1.06	0.40
$M_{1\ h}$	0.44	60.95	5.42	0.00	33.19	1.07	0.41
$M_{2\ h}$	0.39	58.61	5.21	0.00	35.79	1.07	0.46
$M_{4\ h}$	0.39	54.27	4.95	0.00	40.40	1.09	0.56
$M_{6\ h}$	0.43	60.37	5.46	0.00	33.74	1.09	0.42
$M_{12\ h}$	0.42	60.09	5.20	0.00	34.30	1.04	0.43
$M_{24\ h}$	0.49	64.45	5.57	0.00	29.50	1.04	0.33

Note: O (%) = 100 − N (wt %) − C (wt %) − H (wt %) − S (wt %).

Table S2. Surface element composition and surface functional group distribution of A-HA

	C (%)	C-C (%)	C-O (%)	C=O (%)	COO (%)	O (%)	N (%)	Si (%)	S (%)	P (%)
$C_{0.5\ h}$	55.96	61.68	32.97	2.72	2.62	18.09	1.38	0.92	0.31	0.78
$C_{6\ h}$	61.40	70.21	21.80	7.50	0.50	18.14	1.64	0.64	0.35	0.57
$C_{24\ h}$	75.07	77.25	21.32	0.66	0.77	13.78	1.60	1.60	0.30	0.57

Table S3. 3D EEM interval and their associated characteristics

Region	Wavelength range	The material properties
C1	E_x = 200-250 nm E_m = 280-380 nm	Amino acids and proteins
C2	E_x = 200-250 nm E_m = 380-600 nm	Fulvic acid-like substances
C3	E_x = 250-400 nm	Dissolved microbial metabolites

C4	E_m = 280-380 nm E_x = 250-400 nm E_m = 380-600 nm		Humic acids-like substances

Table S4. Weighted average of A-HA molecular related parameters

Sample	Number of assigned formulas	(Molecular formula)$_w$	MW_w	$(O/C)_w$	$(H/C)_w$	AI_w	DBE_w
C0.5h	3321	$C_{27.95}H_{29.57}O_{6.84}N_{0.62}S_{0.13}$	487.80	0.29	1.11	0.44	14.17
C6h	3515	$C_{26.37}H_{29.68}O_{7.38}N_{0.95}S_{0.23}$	485.40	0.30	1.16	0.39	12.35
C24h	4817	$C_{27.34}H_{29.19}O_{7.25}N_{0.72}S_{0.07}$	486.13	0.27	1.03	0.43	13.75
M24h	3465	$C_{27.33}H_{29.90}O_{6.84}N_{0.66}S_{0.22}$	484.13	0.24	1.05	0.42	13.38

Table S5. The functional group distribution in the ^{13}C NMR of A-HA

Sample	Alkyl (%) 0-45ppm	Methoxyl (%) 45-63ppm	Carbohydrate (%) 63-108ppm	Aryl (%) 108-148ppm	O-Aryl (%) 148-165ppm	Carboxyl (%) 165-190ppm	Carbonyl (%) 190-220ppm	Aliphatic C (%)	Aromatic C (%)	Aromaticity (%)	Aliphaticity (%)
$C_{0.5\ h}$	5.49	48.37	1.95	34.79	7.12	1.75	0.54	55.81	41.91	42.89	57.11
$C_{6\ h}$	5.69	38.36	3.13	41.23	2.60	2.18	6.82	47.18	43.83	48.16	51.84
$C_{24\ h}$	4.82	31.84	1.76	45.39	6.86	3.60	5.70	38.42	52.25	57.63	42.37
$M_{24\ h}$	6.21	32.90	4.37	49.40	3.07	3.03	2.56	43.48	52.47	54.68	45.12

Aromaticity = 100 * Aromatic C (93-165 ppm) / (Aromatic C (93-165 ppm) + Aliphatic C (0-93 ppm)); Aliphaticity= 100 x Aliphatic C (0-93 ppm) / (Aromatic C (93-165 ppm) + Aliphatic C (0-93 ppm)).

References

[1] M. Wen, Y. Cui, C. Dong, L. Zhang, Quantitative changes in monosaccharides of Keemun black tea and qualitative analysis of theaflavins-glucose adducts during processing. Food Res. Int., 2021, 148, 110588.

[2] K. Sun, L. Han, W. Y. Yang, X. Xia, Z. Yang, Wu, F. Li, F. Yan, B. Xing, Application of Hydrochar Altered Soil Microbial Community Composition and the Molecular Structure of Native Soil Organic Carbon in a Paddy Soil. Environ. Sci. Technol. 2020, 54, 2715−2725.