Supporting Information for

Aqueous OH-initiated photooxidation of smoke extracts from maize straw and coal combustion: optical character and molecular composition

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Section S1 Inorganic ions measurement

Extracts solutions (~5 mL) were analyzed using ion chromatography (IC, Aquion, Thermo Fisher Scientific). Five cations (Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) and three anions (Cl^-, NO_3^- and SO_4^{2-}) were measured with a Dionex CS12A and AS11-HC columns (250 mm×4 mm, Thermo Fisher Scientific), respectively. The eluent for anions was 4.5 mM Na_2CO_3+0.8 mM $NaHCO_3$, and 18 mM methanesulfonic acid was used for cations. The flow rate was maintained at 0.8 mL/min. The method detection limits ranged from 5-20 μg/L for anions and 0.05-2.0 μg/L for cations.

Section S2 Supporting Figures

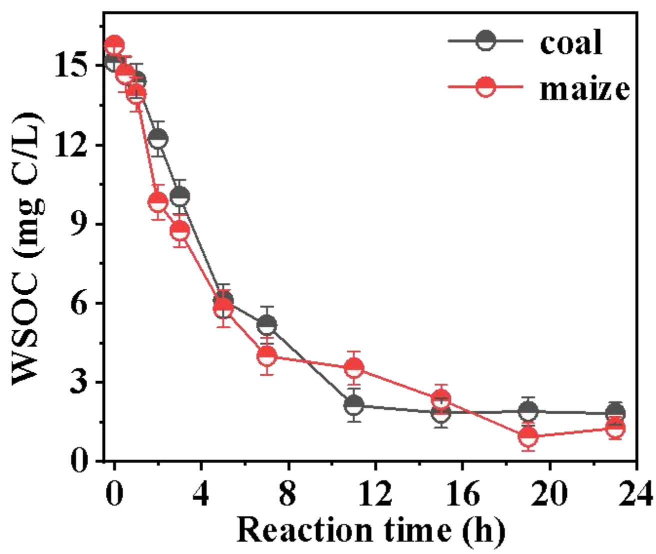

Figure S1 Changes of WSOC of two smoke extracts

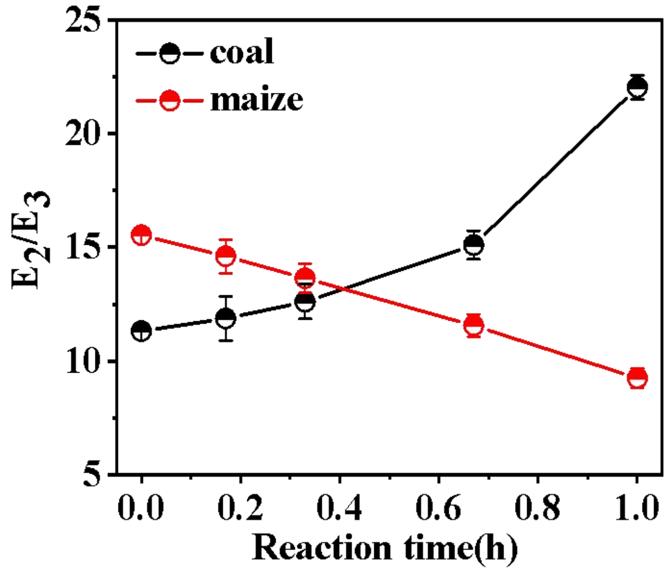

Figure S2 Temporal patterns of E_2/E_3 for two smoke extracts

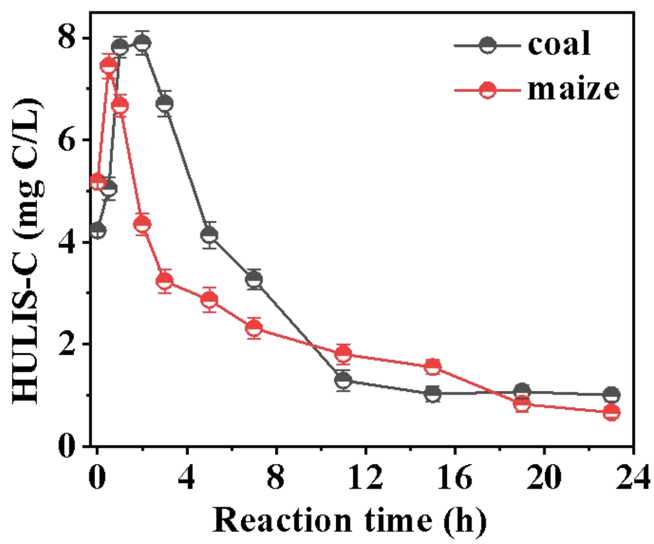

Figure S3 Change in HULIS-C concentration over time for the two smoke extracts

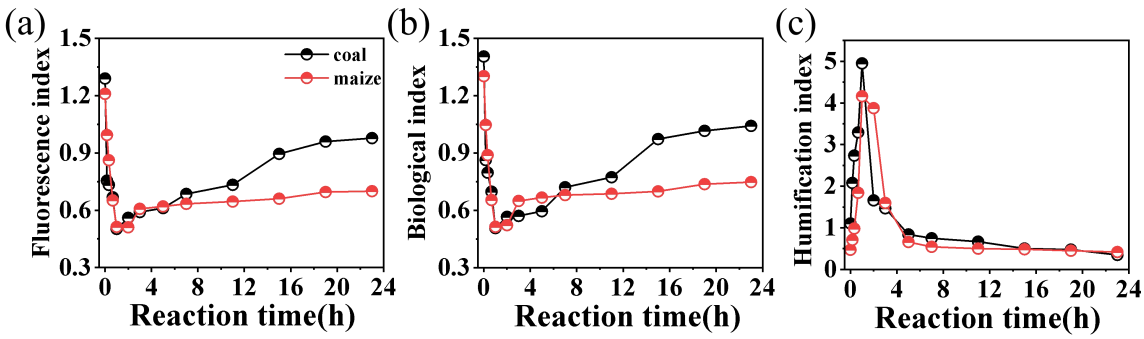

Figure S4 Changes of three fluorescence indices (FI, BIX, and HIX) for two smoke extracts during aqueous-phase OH photooxidation.

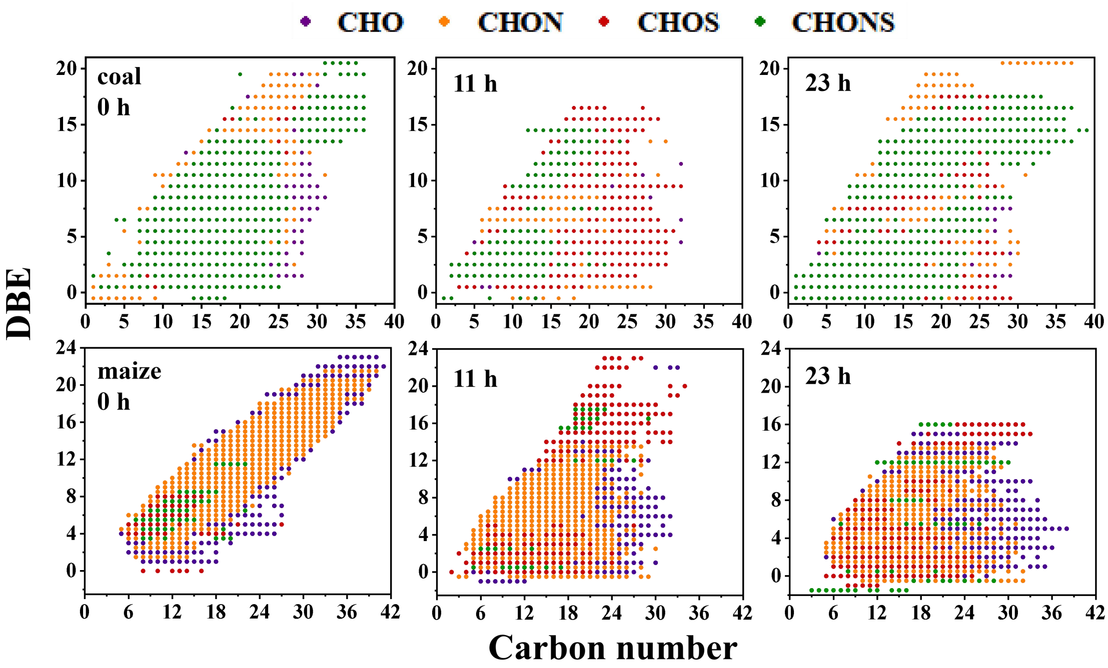

Figure S5 Plot of double bond equivalent (DBE) vs C atomic number in coal and maize smoke extracts before and after 11 h and 23 h of photodegradation.

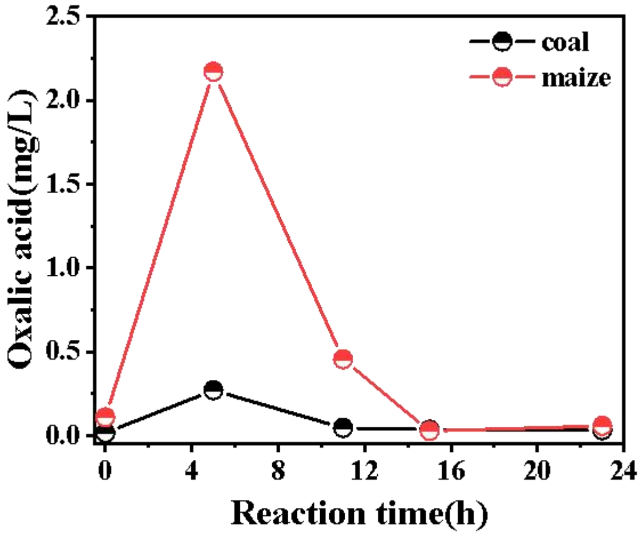

Figure S6 Concentrations of oxalic acids generated under different irradiation time

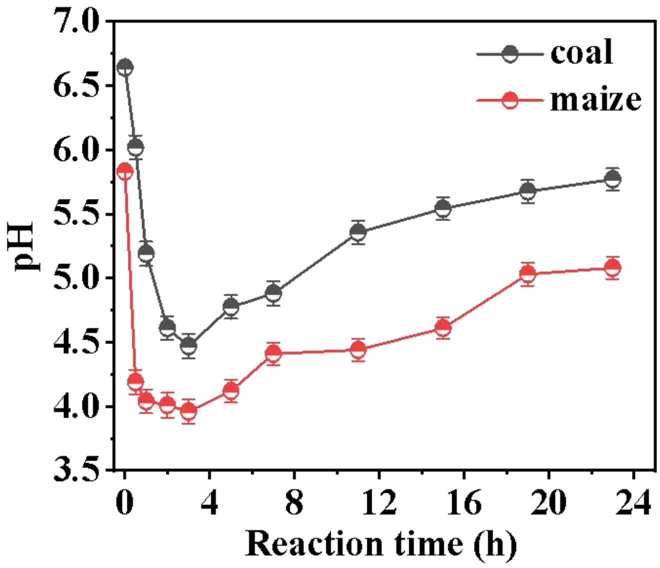

Figure S7 Change of pH value of reaction solution over irradiation time

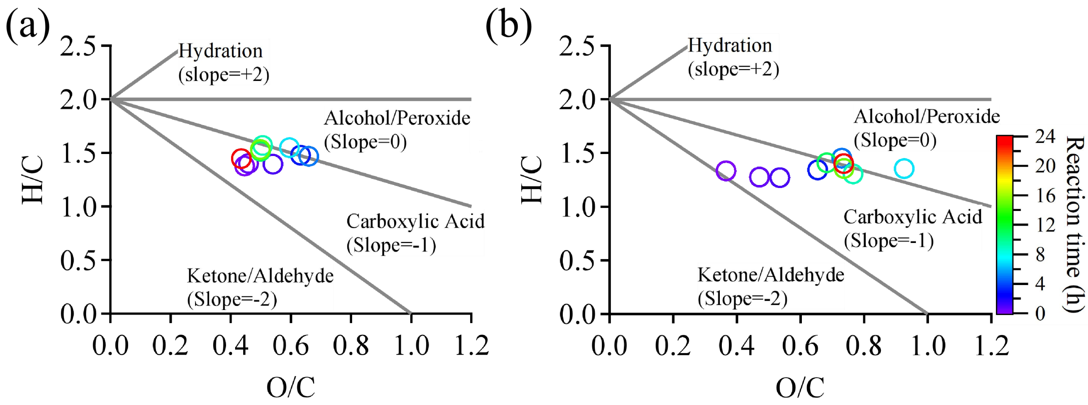

Figure S8 Van Krevelen Diagram of aqSOA products formed in (a) coal and (b) maize OH-initiated photoreaction.

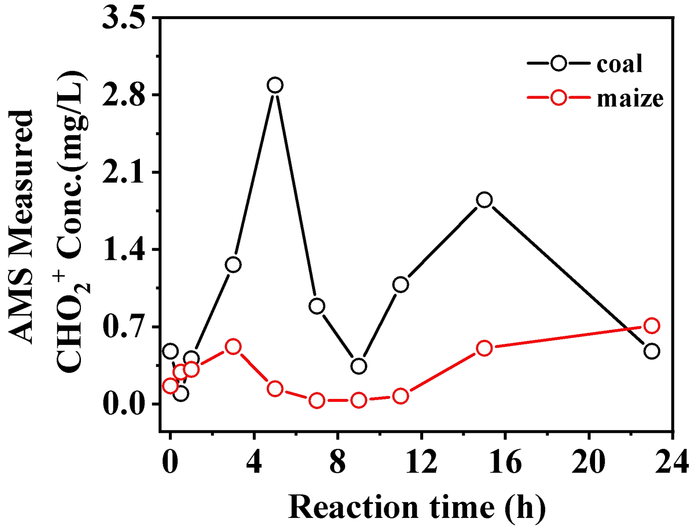

Figure S9 Organic-equivalent concentrations of CHO_2^+ (HR-AMS tracer ion for carboxylic acids).

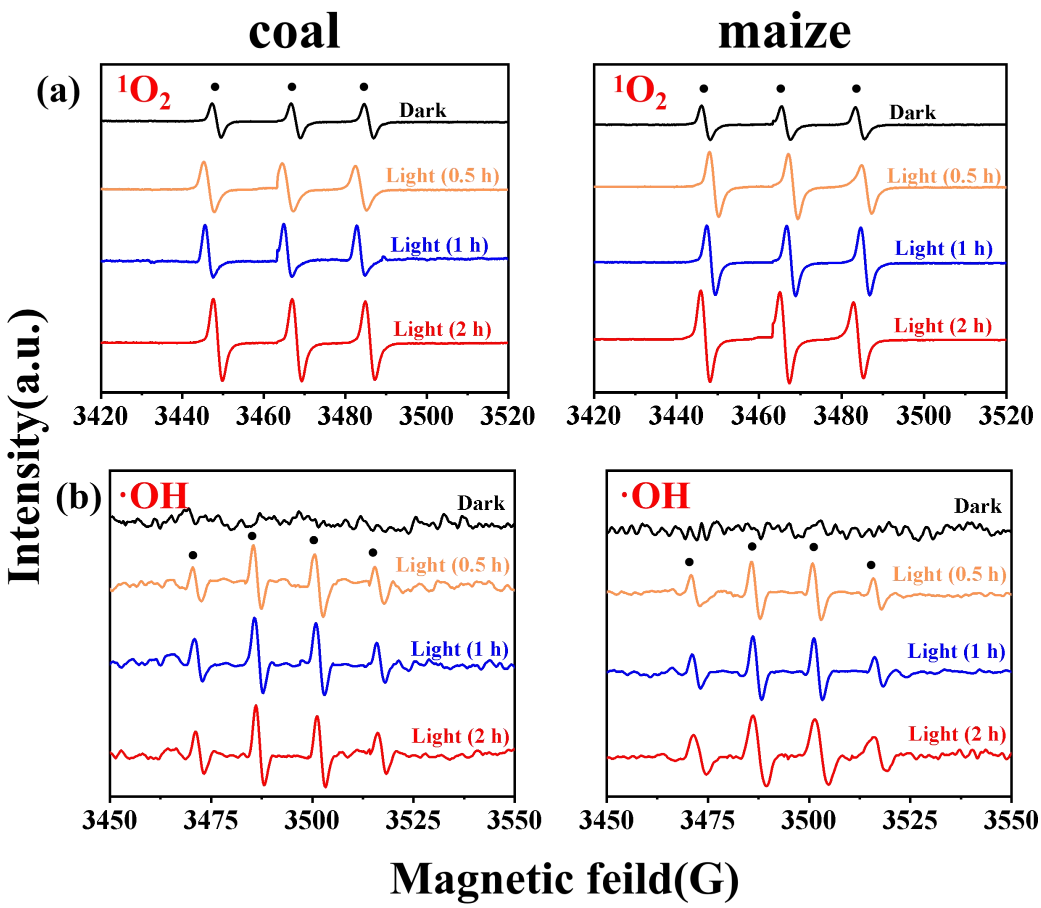

Figure S10 (a) TEMP spin-trapping ESR spectra of $^1O_2$ and (b) DMPO spin-trapping ESR spectra of •OH obtained upon 120 min photodegradation for both smoke extracts (15 mgC/L) with adding of 10 mM H_2O_2.

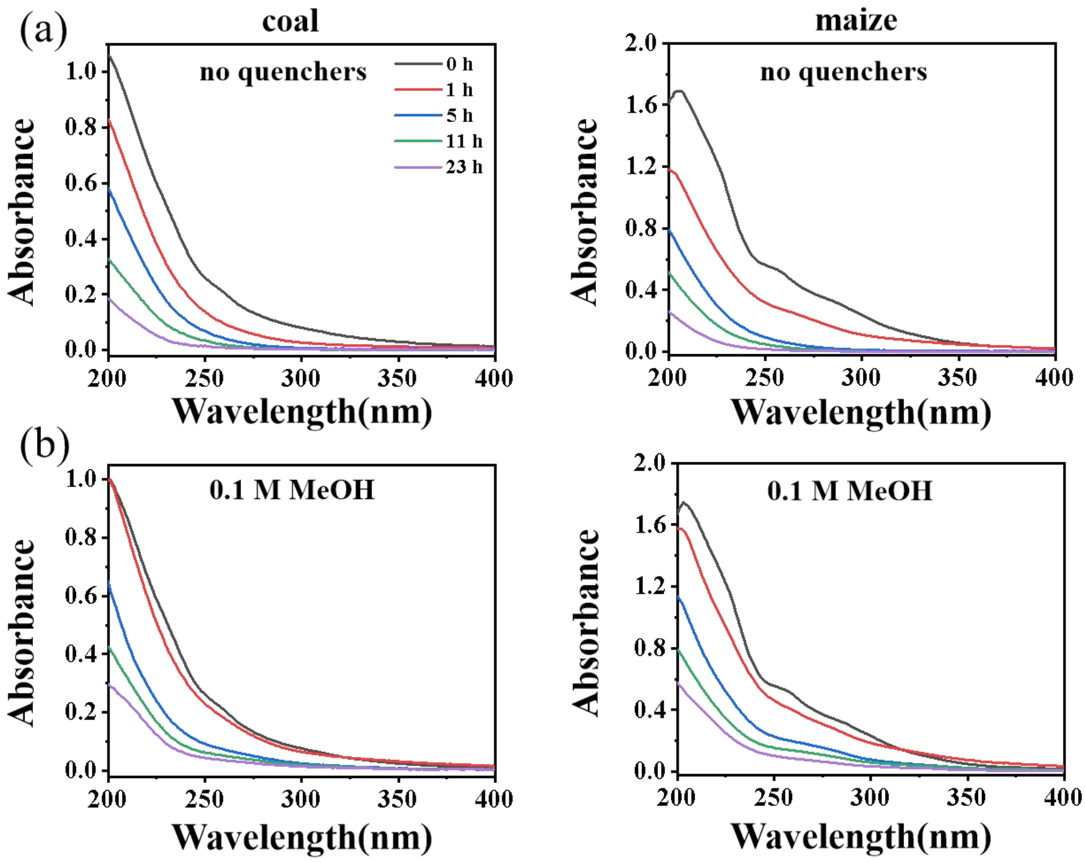

Figure S11 UV-vis absorption spectra of two smoke extracts upon different irradiation time (a) without methanol as quenchers and (b) with 0.1 M methanol

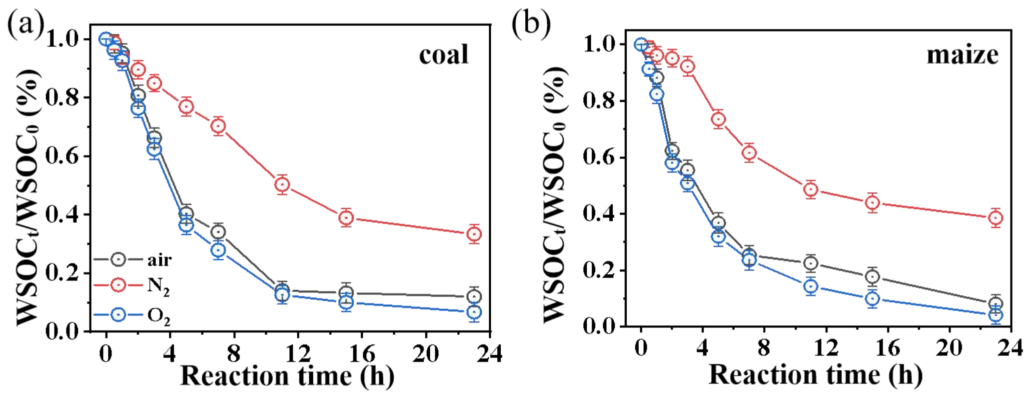

Figure S12 Comparison in residual WSOC proportion between three saturated gases for (a) coal and (b) maize smoke extracts under OH photooxidation. Adding H_2O_2 of 10 mM.

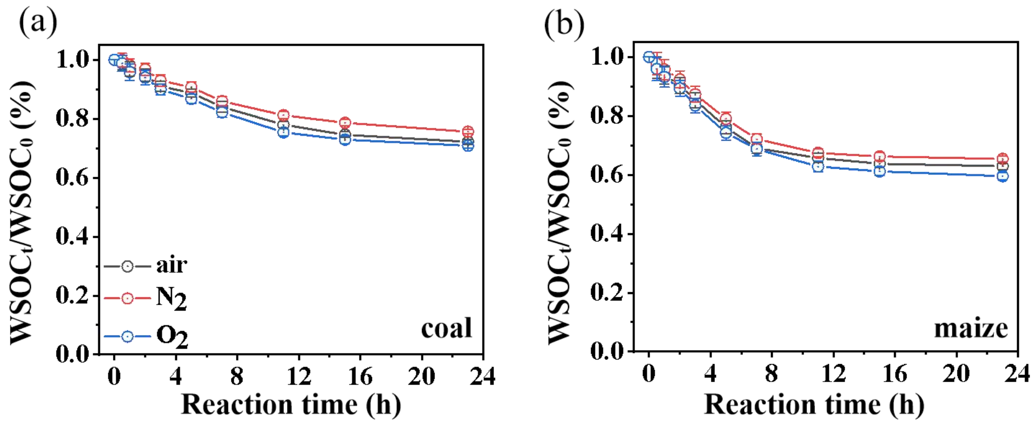

Figure S13 Comparison in residual WSOC proportion between three saturated gases for (a) coal and (b) maize smoke extracts under photolysis

Section S3 Supporting Tables

Table S1 Variation of inorganic ions concentrations over irradiation time (unit: ppm)

Sample	Time	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^+	Cl^-	NO_3^-	SO_4^{2-}
	0 h	0.61	0.06	0.42	0.02	0.27	0.80	0.10	0.54
	5 h	0.58	0.16	0.38	0.02	0.31	0.85	0.18	0.71
coal	11 h	0.52	0.17	0.35	0.02	0.26	0.78	0.11	0.61
	15 h	0.54	0.22	0.37	0.02	0.26	0.79	0.11	0.61
	23 h	0.63	0.31	0.44	0.02	0.32	0.96	0.12	0.73
	0 h	0.38	1.88	0.20	0.04	0.24	6.39	0.37	0.09
	5 h	0.43	2.04	0.24	0.02	0.25	6.58	0.07	0.25
maize	11 h	0.43	2.12	0.25	0.02	0.24	6.63	0.10	0.22
	15 h	0.47	2.29	0.29	0.02	0.36	5.86	0.16	0.18
	23 h	0.43	2.20	0.28	0.01	0.18	6.64	0.05	0.19

Table S2 Percentages (%) of seven categories components before and after OH photooxidation

	time	Tannin	Lignin	Aromatic	Lipid	Aliphatic	Carbohydrate-	U	Others
	0 h	1.8	58.2	3.59	15.9	17.9	1.2	0.01	1.4
Coal	11 h	11.2	31.6	1.3	22.7	21.2	4.3	0.5	7.2
	23 h	1.1	16.8	1.4	35	16.2	1.5	2.6	25.4
Maize	0h	1.3	93.1	2.8	0.7	1.7	0.3	0	0.1
	11 h	31.8	26.4	1.6	17.6	16.3	3.6	0.2	2.5

23 h	2.1	16.8	1.9	54.6	15.3	1.4	0.3	7.6

U: Unsaturated hydrocarbon

Table S3 The number and percentage of resistant, degraded and produced molecules for two extracts samples

Samples	Aging processes	Molecules	Total	CHO	CHON	CHOS	CHONS
coal	11 h	Resistant(n)	2514	1277	988	187	62
		Degraded(n)	3082	451	707	515	1409
		Produced(n)	2643	798	1041	629	184
		Percentage of degraded (%)	55.1	8.1	12.6	9.2	25.2
		Percentage of produced (%)	51.3	15.3	20.2	12.2	3.6
	23 h	Resistant(n)	1847	821	686	186	154
		Degraded(n)	3749	907	1009	516	1317
		Produced(n)	3223	526	1284	536	877
		Percentage of degraded (%)	67.0	16.2	18.0	9.2	23.5
		Percentage of produced (%)	63.5	10.4	25.3	10.6	17.3
maize	11 h	Resistant (n)	2146	1137	995	14	0
		Degraded (n)	2972	1016	1778	93	85
		Produced (n)	3890	1514	1960	381	35
		Percentage of degraded (%)	58.2	19.9	34.9	1.8	1.7
		Percentage of produced (%)	64.6	25.1	32.5	6.3	0.6
	23 h	Resistant(n)	2248	1214	1004	30	0
		Degraded(n)	2853	924	1767	77	85
		Produced(n)	2897	1432	991	369	105
		Percentage of degraded (%)	55.9	18.1	34.6	1.5	1.7
		Percentage of produced (%)	56.3	27.8	19.3	7.7	2.0

Note: n denotes number, percentage of degraded represents its percentage in fresh sample, while percentage of produced represents its percentage in aging sample.

Table S4 Chemical properties and SOA mass yieldof both coal-/maize- aqSOA

Sample	Time	O/C	H/C	OSc	*f*43	*f*44	SOA mass conc.（mg/L）	SOA mass yield(%)
coal	0	0.446	1.377	-0.485	0.049	0.148	50.77	0
	1	0.54	1.395	-0.315	0.057	0.167	71.05	148.44
	3	0.632	1.479	-0.215	0.048	0.201	82.48	64.01
	5	0.659	1.468	-0.15	0.058	0.203	102.97	20.92
	7	0.595	1.548	-0.358	0.056	0.203	82.10	16.65
	9	0.506	1.569	-0.557	0.067	0.195	91.41	1.87
	11	0.499	1.515	-0.517	0.068	0.182	58.83	24.35
	15	0.498	1.531	-0.535	0.061	0.144	132.51	23.04
	23	0.435	1.446	-0.576	0.060	0.141	126.95	33.91
maize	0	0.366	1.334	-0.602	0.039	0.072	162.82	0
	1	0.535	1.270	-0.2	0.042	0.123	70.11	5.51
	3	0.654	1.343	-0.035	0.040	0.151	61.72	2.46
	5	0.73	1.451	0.009	0.052	0.199	71.63	3.89
	7	0.926	1.354	0.498	0.054	0.202	72.69	6.36
	9	0.765	1.305	0.225	0.024	0.101	75.71	2.72
	11	0.683	1.358	-0.042	0.053	0.198	84.44	4.24
	15	0.737	1.355	0.119	0.056	0.255	76.90	2.68
	23	0.736	1.401	0.071	0.051	0.250	81.66	2.86