



Supplement of

OH-initiated aqueous photooxidation of smoke extracts from maize straw and coal combustion: optical properties 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.

Section S2 Supporting Figures

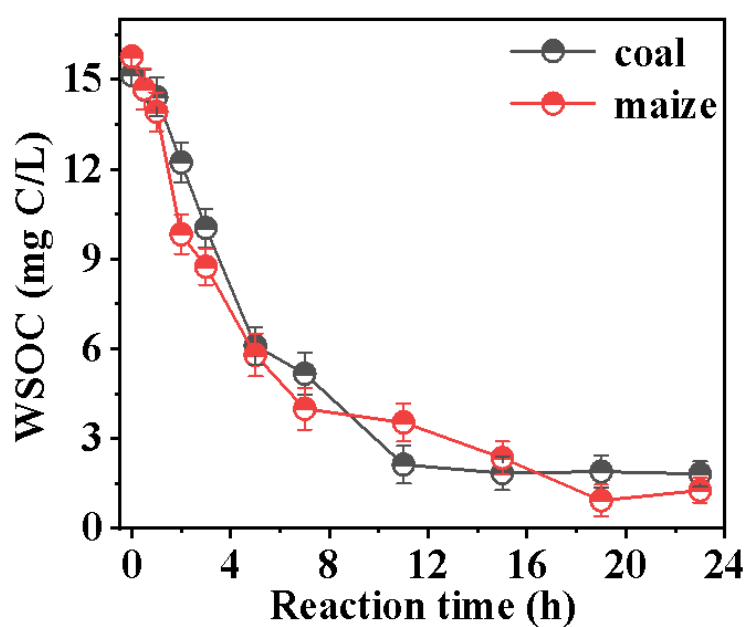


Figure S1 Changes of WSOC of two smoke extracts with reaction time

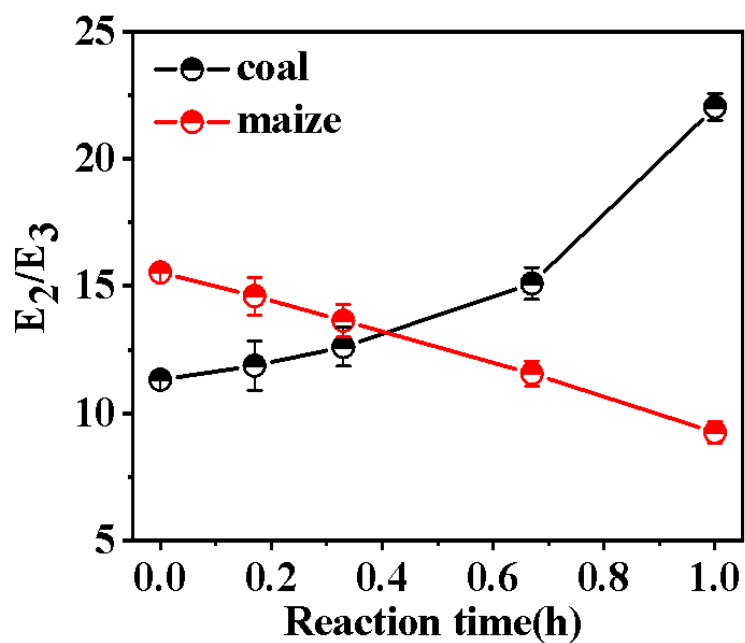


Figure S2 Temporal patterns of E₂/E₃ for two smoke extracts with reaction time

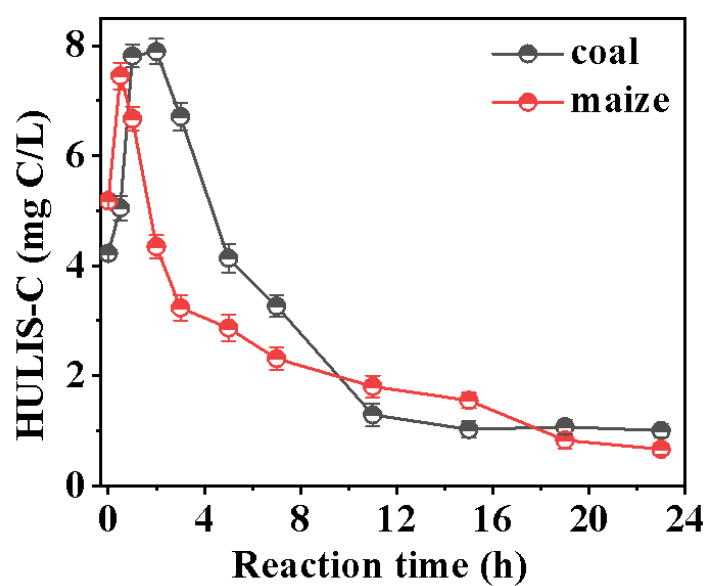


Figure S3 Change in HULIS-C concentration over time for the two smoke extracts

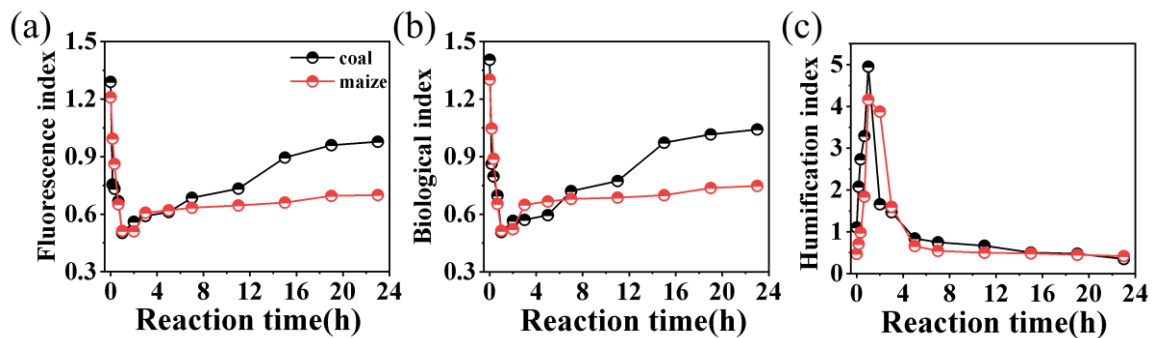


Figure S4 Changes of three fluorescence indices (FI, BIX, and HIX) for two smoke extracts during aqueous-phase photooxidation.

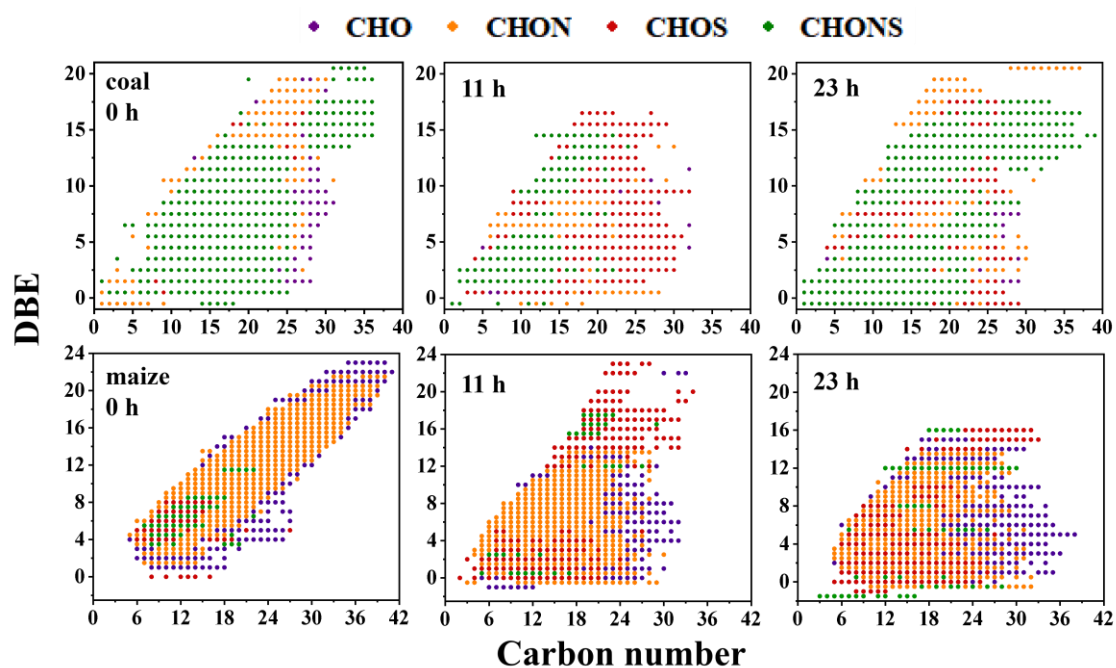


Figure S5 Plot of double bond equivalent (DBE) vs Carbon number in coal and maize smoke extracts before and after 11 h and 23 h of photodegradation.

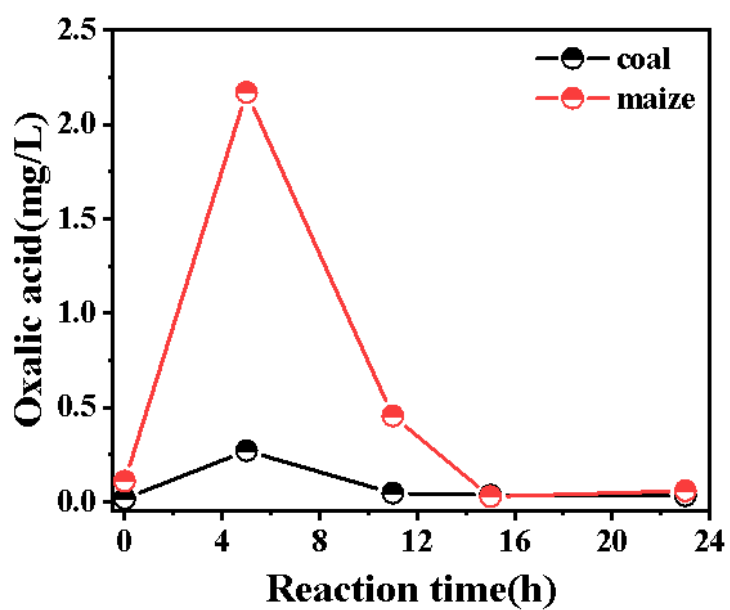


Figure S6 Concentrations of oxalic acids generated under different irradiation time

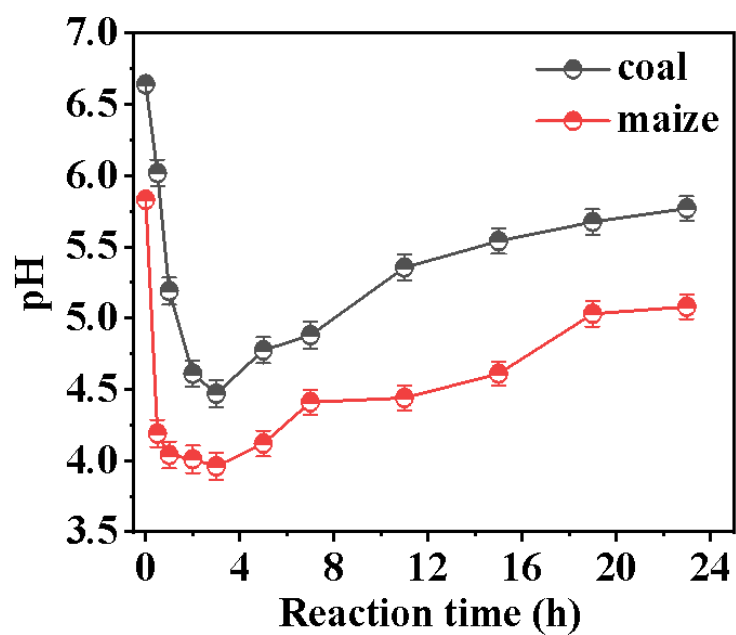


Figure S7 Change of pH value of solution over reaction time

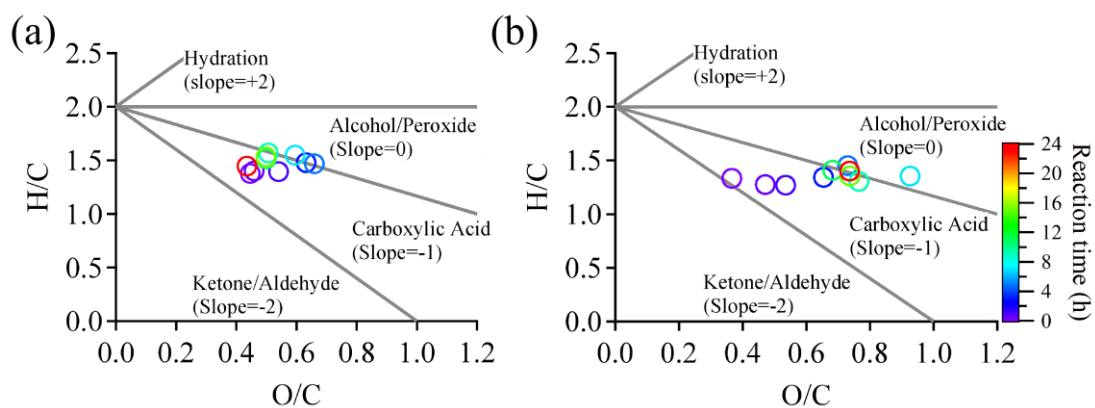


Figure S8 Van Krevelen diagram of aqSOA products formed after (a) coal and (b) maize smoke WSOM photooxidation

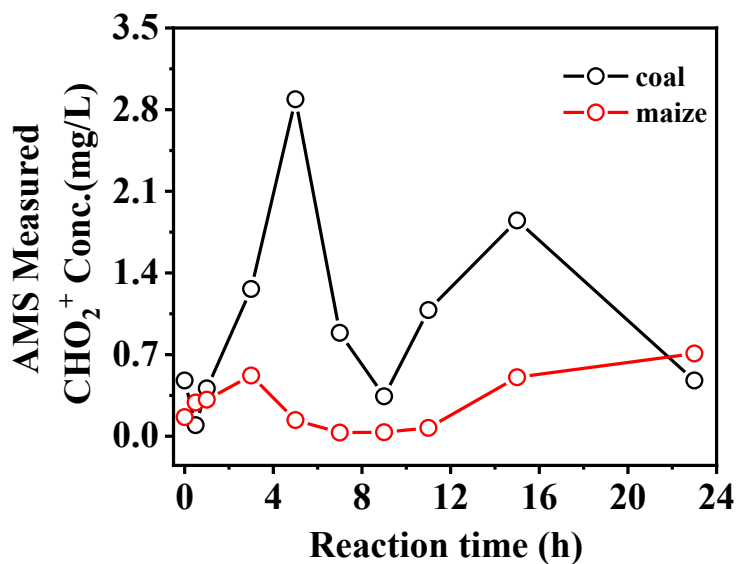


Figure S9 Organic-equivalent concentrations of CHO_2^+ (HR-AMS tracer ion for carboxylic acids).

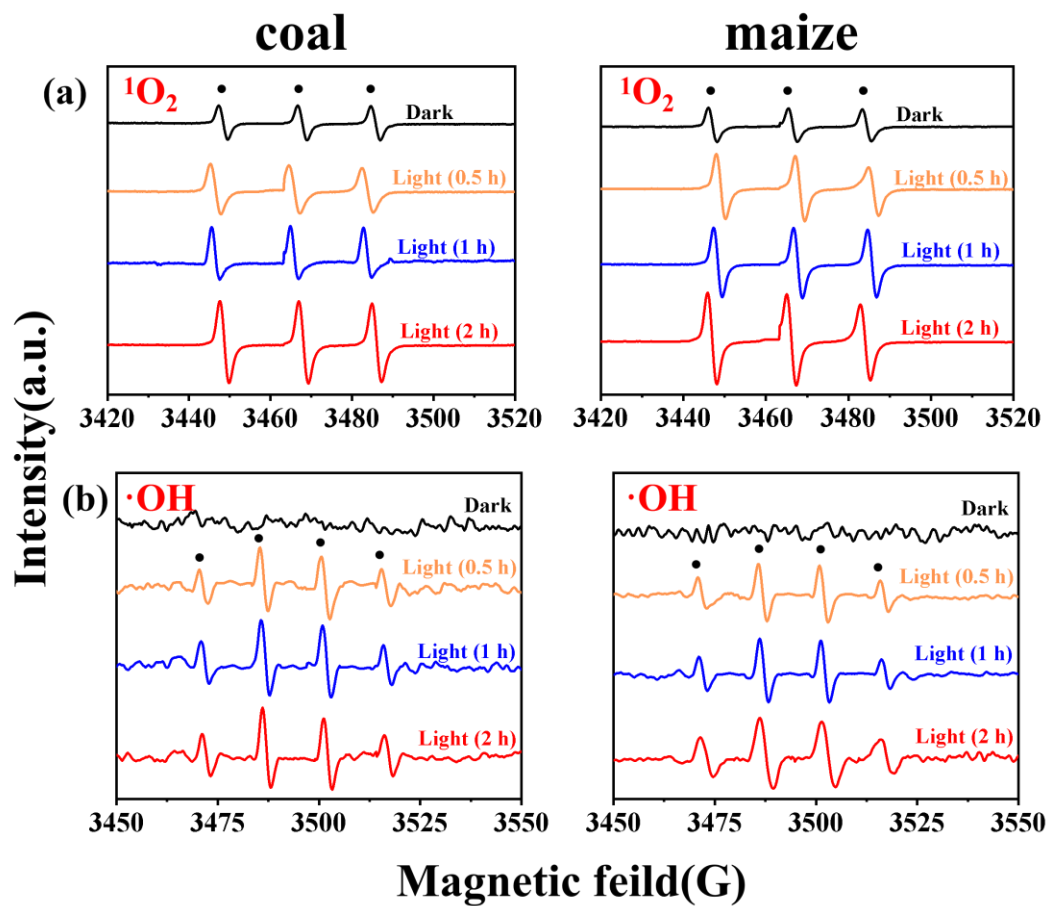


Figure S10 (a) TEMP spin-trapping ESR spectra of $^1\text{O}_2$ and (b) DMPO spin-trapping ESR spectra of $\cdot\text{OH}$ obtained upon 120 min photodegradation for both smoke extracts (15 mgC/L) with adding of 10 mM H_2O_2 .

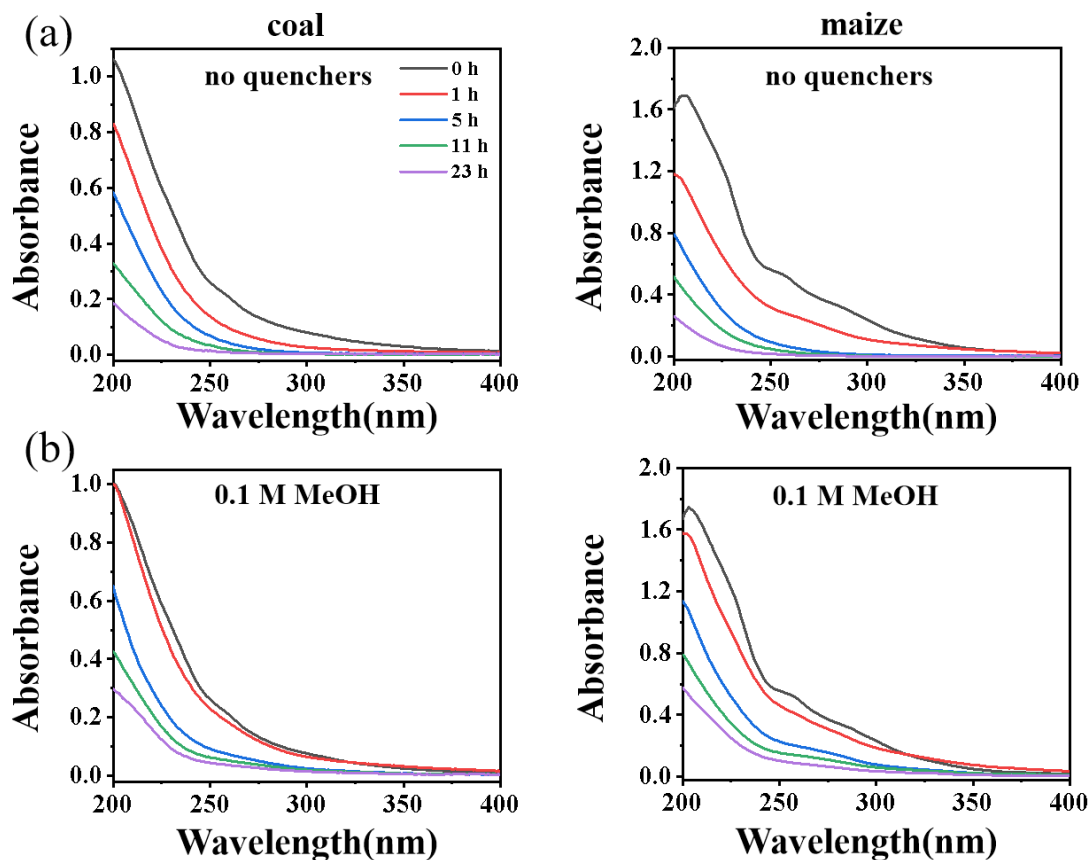


Figure S11 UV-vis absorption spectra of two smoke extracts upon different irradiation time (a) without methanol as quenchers and (b) with 0.1 M methanol

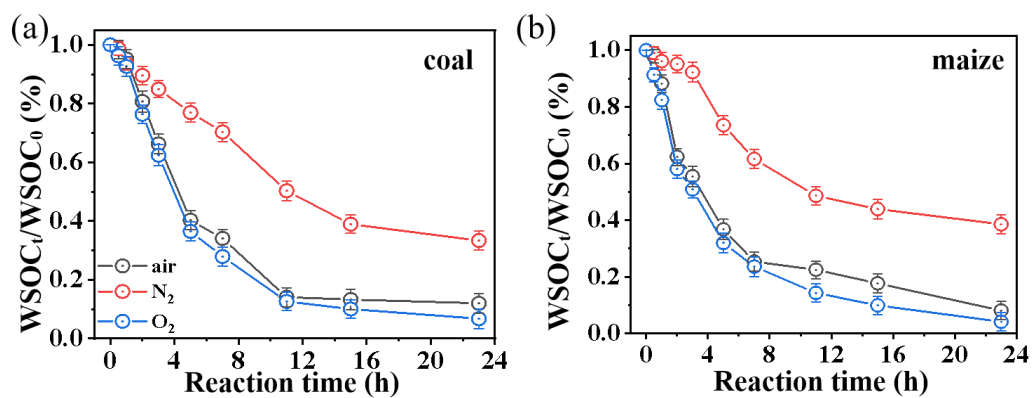


Figure S12 Comparison in residual WSOC proportion between three saturated gases for (a) coal and (b) maize smoke extracts under OH photooxidation. Adding H_2O_2 of 10 mM.

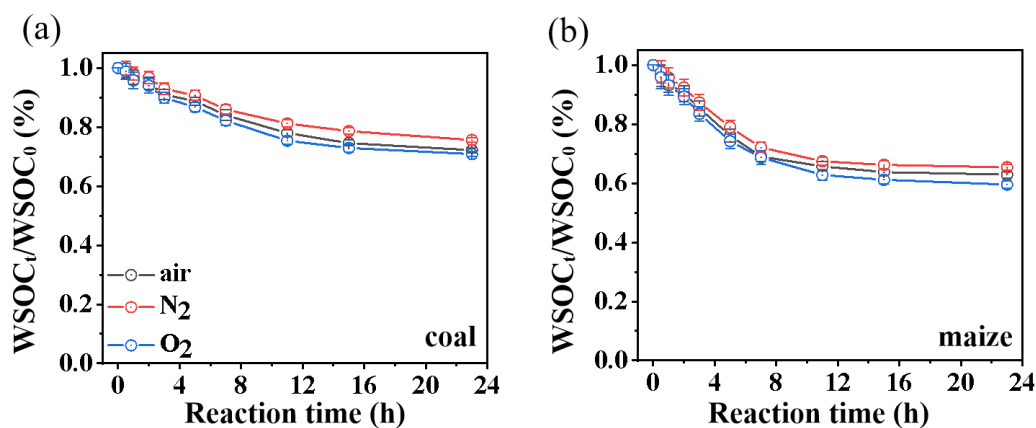


Figure S13 Comparison in residual WSOC proportion between three saturated gases for (a) coal and (b) maize smoke extracts under photolysis without H₂O₂.

Section S3 Supporting Tables

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

Samples	Time	Na ⁺	NH ₄ ⁺	K ⁺	Mg ²⁺	Ca ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻
coal	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
	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
maize	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
	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 aqueous photooxidation

Samples	Time	Tannin	Lignin	Aromatic	Lipid	Aliphatic	Carboh ydrate	Unsatur ated	Others
coal	0 h	1.8	58.2	3.59	15.9	17.9	1.2	0.01	1.4
	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	0 h	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
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Unstaturated: Unsaturated hydrocarbon

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

Samples	Time	Molecules	Total number	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 yield for both smoke extracts

Samples	Time	O/C	H/C	O _{Sc}	<i>f</i> ₄₃	<i>f</i> ₄₄	SOA mass conc. (mg/L)	SOA mass yield (%)
coal	0	0.446	1.377	-0.485	0.049	0.148	50.77	-
	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	-
	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

Table S5 Concentration and contribution to WSOM photodegradation of each ROS under different H₂O₂ concentration

Samples	[H ₂ O ₂] (mM)	[ROS] (M)			Contribution ratio (%)		
		[•OH] _{ss} (×10 ⁻¹⁴)	[¹ O ₂] _{ss} (×10 ⁻¹³)	[³ C*] _{ss} (×10 ⁻¹³)	•OH	¹ O ₂	³ C*
coal	0.5	0.7	4.0	1.0	25.8	0.5	73.7
	1	1.6	3.4	1.0	46.6	0.3	53.1

	3	5.7	3.5	2.1	58.8	0.1	41.1
	5	8.7	4.1	2.6	63.5	0.1	36.4
	10	9.1	3.5	9.0	86.4	0.8	12.8
	0.5	1.3	9.4	1.2	37.2	0.8	62.0
	1	2.2	8.7	1.8	39.3	0.5	60.2
maize	3	3.8	2.5	1.3	60.9	0.1	39.0
	5	7.3	7.2	2.3	62.2	0.2	37.6
	10	8.6	0.2	7.1	80.9	3.1	16.0

Table S6 The top 10 most abundant compounds identified in coal smoke WSOM by FT-ICR MS

Samples	DBE	Formula	Percentage (%)	Functional groups	FTIRC-MS category
	0.5	C ₁₂ H ₂₆ O ₄ S	3.44	organosulfate	lipid -like
	4.5	C ₁₇ H ₂₈ O ₃ S	2.97	organosulfate	lipid-like
	7.5	C ₁₂ H ₁₂ O ₅	1.94	aromatic compound	lignin-like
	4.5	C ₁₈ H ₃₀ O ₃ S	1.82	organosulfate	lipid -like
coal	4.5	C ₁₆ H ₂₆ O ₃ S	1.32	organosulfate	lipid -like
0 h	1.5	C ₁₆ H ₃₂ O ₂	1.20	fatty acid	lipid -like
	0.5	C ₁₄ H ₃₀ O ₅ S	1.03	hydroxy-organosulfate	lipid -like
	1.5	C ₁₈ H ₃₆ O ₃	0.99	hydroxy fatty acid	lipid-like
	7.5	C ₁₃ H ₁₄ O ₅	0.85	trimethoxybenzoic acid	lignin-like
	9.5	C ₁₄ H ₁₂ O ₆	0.84	lignin-like dimer	lignin-like
	1.5	C ₁₆ H ₃₂ O ₂	4.21	palmitic acid	lipid-like
	0.5	C ₁₈ H ₃₉ NO ₅	2.09	hydroxy fatty acid amide	lipid-like
	1.5	C ₁₈ H ₃₆ O ₂	1.91	octadecanoic acid	lipid-like
	4.5	C ₁₈ H ₃₀ O ₃ S	1.33	unsaturated organosulfate	lipid-like
coal	0.5	C ₁₉ H ₄₀ O ₆	1.13	polyhydroxy nonadecane	lipid-like
11 h	3.5	C ₁₂ H ₂₀ O ₃	1.02	dodecadienoic acid	lipid-like
	4.5	C ₁₇ H ₂₈ O ₃ S	0.96	unsaturated organosulfate	lipid-like
	2.5	C ₁₈ H ₃₄ O ₃	0.96	unsaturated fatty acid	lipid-like
	4.5	C ₁₉ H ₃₂ O ₃ S	0.85	unsaturated organosulfate	lipid-like
	1.5	C ₁₈ H ₃₆ O ₃	0.81	hydroxyl octadecanoic acid	lipid-like
	0.5	C ₁₆ H ₃₅ NO ₂	6.21	fatty amide	lipid-like
	4.5	C ₁₄ H ₂₂ O	5.80	alkyl acetophenone	lipid -like
	1.5	C ₁₆ H ₃₂ O ₂	3.41	hexadecanoic acid	lipid -like
coal	0.5	C ₁₈ H ₃₉ NO ₃	3.24	hydroxy fatty acid amide	lipid -like
23 h	1.5	C ₁₂ H ₂₄ O ₂	2.86	saturated fatty acid	lipid -like
	0.5	C ₁₈ H ₃₉ NO ₄	2.73	organic nitrate	lipid -like
	0.5	C ₁₂ H ₂₆ O ₄ S	2.52	organosulfate	lipid -like
	0.5	C ₂₀ H ₄₃ NO ₅	1.99	hydroxy organic nitrate	lipid-like
	5.5	C ₁₇ H ₂₆ O ₄	1.91	dicarboxylic acids	lipid-like

1.5 C₁₈H₃₆O₂ 1.74 octadecanoic acid lipid-like

Table S7 The top 10 most abundant compounds identified in maize smoke WSOM by FT-ICR MS

Samples	DBE	Formula	Percentage (%)	Functional groups	FTIRC-MS category
maize 0 h	5.5	C ₉ H ₁₀ O ₄	9.56	vanillic acid	lignin-like
	6.5	C ₈ H ₆ O ₄	4.63	Phthalic acid	lignin-like
	5.5	C ₁₀ H ₁₂ O ₄	1.62	veratric acid	lignin-like
	5.5	C ₇ H ₇ NO ₄	1.36	nitrobenzoic acid	lignin-like
	6.5	C ₉ H ₈ O ₃	1.18	hydroxycinnamic acid	lignin-like
	5.5	C ₉ H ₁₀ O ₃	1.16	vanillin	lignin-like
	10.5	C ₁₈ H ₁₈ O ₇	0.81	guaiacyl dimer	lignin-like
	8.5	C ₁₁ H ₈ O ₃	0.74	hydroxyanthraquinone	condensed aromatic
	6.5	C ₁₀ H ₁₀ O ₄	0.71	ferulic acid	lignin-like
	6.5	C ₉ H ₈ O ₄	0.66	polyphenols	lignin-like
maize 11 h	4.5	C ₁₄ H ₂₂ O	2.63	aromatic ketone	aromatic
	1.5	C ₁₆ H ₃₂ O ₂	2.58	saturated fatty acids	lipid-like
	1.5	C ₁₈ H ₃₆ O ₂	2.15	saturated fatty acids	lipid-like
	2.5	C ₁₃ H ₂₅ NO ₃	2.04	n-hydroxytridecanamide	lipid-like
	0.5	C ₁₂ H ₂₆ O ₄ S	1.67	alkyl organosulfate	aliphatic
	1.5	C ₁₂ H ₂₄ O ₂	1.50	lauric acid	aliphatic
	1.5	C ₉ H ₁₈ O ₆	1.18	polyhydroxy nonanoic acid	carbohydrate
	5.5	C ₉ H ₁₀ O ₇	0.96	hydroxyphthalic acid	tannin-like
	2.5	C ₁₈ H ₃₄ O ₃	0.75	hydroxy unsaturated fatty acid	lipid-like
3.5	C ₁₇ H ₃₀ O ₅	0.74	polyhydroxy unsaturated fatty acids	lipid-like	
maize 23 h	4.5	C ₁₄ H ₂₂ O	13.18	aromatic ketone	aromatic
	1.5	C ₁₆ H ₃₂ O ₂	7.03	saturated fatty acids	lipid-like
	1.5	C ₁₂ H ₂₄ O ₂	5.83	lauric acid	aliphatic
	1.5	C ₁₈ H ₃₆ O ₂	5.26	saturated fatty acids	lipid-like
	0.5	C ₁₂ H ₂₆ O ₄ S	3.37	alkyl organosulfate	aliphatic
	2.5	C ₁₈ H ₃₄ O ₃	2.99	unsaturated fatty acid	lipid-like
	0.5	C ₁₆ H ₃₅ NO ₂	2.15	fatty acid amide	lipid-like
	7.5	C ₂₈ H ₄₄ O ₂	1.81	ergosterol peroxide	lipid-like
	4.5	C ₁₅ H ₂₄ O ₃	1.48	sesquiterpenic acid	lipid-like
	0.5	C ₁₄ H ₃₀ O ₅ S	1.32	hydroxyl organosulfate	lipid-like