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Oxidation of Shenfu Coal with RuO₄ and NaOCl

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Shenfu coal (SFC) oxidation with RuO₄ and NaOCl were studied and compared. Most of organic matter in SFC was converted into soluble species with either of the oxidants. Benzene polycarboxylic acids (BPCAs) and alkanolic acids (AAs) are the main products from the reactions. The products from SFC oxidation with RuO₄ are rich in long-chain AAs, whereas those with NaOCl predominantly consist of chloro-substituted short-chain AAs and BPCAs. The related reaction mechanisms are discussed according to the experimental results.

1. Introduction

Coal oxidation is one of the useful methods for understanding coal structure, especially the composition of organic matter in coals.^{1–4} Many attempts have been made for obtaining organic acids from coals by oxidation in alkali or acid solution.^{5–7} RuO₄, which is well-known as an effective oxidant for selective degradation of macromolecular network in coals, has been widely used for characterizing the aliphatic and aromatic portions in coals.^{8,9} Huang et al.¹⁰ examined the differences in structural features among Shenfu coal (SFC), its liquefaction residue and extraction residue through ruthenium ion-catalyzed oxidation (RICO). A number of alkanolic acids (AAs) and benzene polycarboxylic acids were produced from RICO of SFC and its residues. The resulting carboxylic acids were confirmed to be particularly useful for synthesizing functional material,¹¹ medicines,¹² and aircraft fuel.¹³ Unfortunately, industrial use of RICO is difficult because of its high cost.

SFC is a typical low-rank bituminous coal in China. Because of its very large reserve (223.6 Gt)¹⁴ and very low contents of ash, sulfur, and phosphorus, it is used as one of major power steam coals in China and as a main feedstock for the pilot project of Shenhua coal liquefaction, the largest project for coal hydrolification over the world.¹⁵ Alternative conversions, such as oxidation, of SFC also deserve investigating.

Because of its easy availability, environmental friendliness, and electrolytic renewability,¹⁶ NaOCl is attractive as an industrial oxidant. In addition, it is highly reactive toward coal oxidative degradation.^{17–20} In the present study, we investigated SFC oxidation with RuO₄ and NaOCl, respectively, to understand the difference between the two oxidants for coal oxidation and to find a potential way for obtaining organic acids from coals.

2. Experimental Section

2.1. Coal Sample and Reagents. SFC, collected from Shenmu-Fugu coal field, Shaanxi, China, was pulverized to pass through a 200-mesh screen and dried in a vacuum at 80 °C for 24 h before use. Table 1 shows the proximate and ultimate analyses of the coal sample. RuCl₃, NaIO₄, CH₂N₂, (CH₃CH₂)₂O, CH₃CN, CCl₄, CH₂Cl₂, HCl, NaOCl (6% available chlorine), and anhydrous MgSO₄ used in the experiments are analytical-pure reagents, and all the organic solvents were distilled before use.

2.2. Main Instruments. A Büchi R-134 rotary evaporator was used for distillation of solvents from the reaction mixture. The instruments for quantitative and qualitative analyses of products are a Nicolet Magna IR-560 Fourier transform infrared

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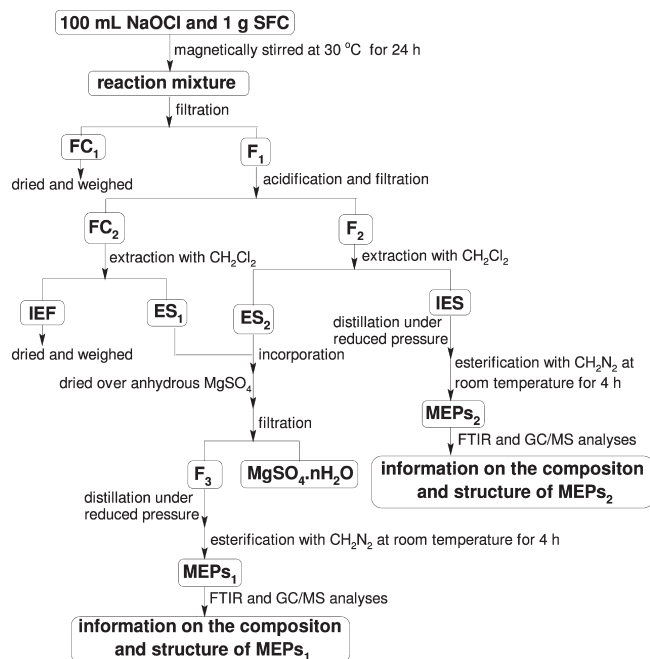
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Table 1. Proximate and Ultimate Analyses (W %) of SFC^a

proximate analysis			ultimate analysis (daf)				
M_{ad}	A_d	V_{daf}	C	H	N	O	S_t
5.33	6.32	30.74	79.82	4.73	1.05	13.90	0.50

^a daf = dry and ash-free base; M_{ad} = moisture (air dried base); A_d = ash (dry base, i.e., moisture-free base); V_{daf} = volatile matter (dry and ash-free base).

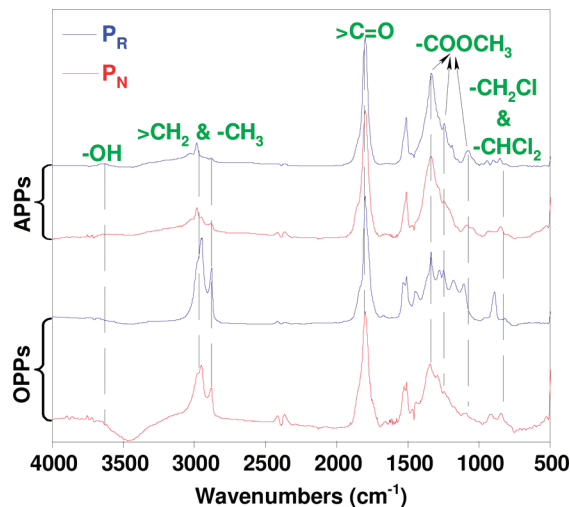
**Figure 1.** Procedure for SFC oxidation with NaOCl, subsequent treatment, and product analyses.

(FTIR) spectrometer and a Hewlett-Packard 6890/5973 gas chromatography/mass spectrometer (GC/MS) equipped with a capillary column coated with HP-5 (cross-link 5% PH ME siloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness) and a quadrupole analyzer and operated in electron impact (70 eV) mode.

2.3. Oxidation, Subsequent Treatment, and Product Analyses.

The oxidation of SFC with RuO_4 was carried out according to a reported procedure.¹⁰ SFC (0.4 g) was added to a mixture of RuCl_3 (20 mg), CH_3CN (20 mL), CCl_4 (20 mL), and distilled water (30 mL). With rapid stirring, NaIO_4 (8 g) was added and the mixture was stirred for 36 h at 35 °C. Then the solid was separated by filtration followed by phase separation of the filtrate to afford the aqueous solution and the organic solution. Both the filter cake and aqueous solution were extracted with CH_2Cl_2 . The extraction solutions and the above organic solution were incorporated and dried over anhydrous MgSO_4 . After removal of the solvents from the dried solution with a rotary evaporator under reduced pressure, the products were esterified with excess CH_2N_2 in $(\text{CH}_3\text{CH}_2)_2\text{O}$ followed by FTIR and GC/MS analyses.

As Figure 1 shows, SFC (1 g) and NaOCl aqueous solution (100 mL) were added to a 250 mL spherical flask and fully mixed by magnetically stirring at 30 °C for 24 h. The reaction mixture was filtrated to afford a filter cake (FC_1) and filtrate (F_1). The FC_1 was dried in a vacuum at 80 °C for 24 h and then weighed. The F_1 was acidified to pH 2–3 to convert $-\text{COONa}$ to $-\text{COOH}$ in the reaction products and filtrated to afford the filter cake (FC_2) and filtrate (F_2). Both FC_2 and F_2 were extracted with CH_2Cl_2 . Then, the extraction solutions (ES_1 and ES_2) were incorporated. The incorporated solution was dried over anhydrous MgSO_4 and filtrated to remove $\text{MgSO}_4 \cdot n\text{H}_2\text{O}$.

**Figure 2.** FTIR spectra of the methyl esterified products from SFC oxidation with RuO_4 and NaOCl.

After removal of CH_2Cl_2 from the filtrate (F_3) with a rotary evaporator under reduced pressure, the reaction products were esterified with excess CH_2N_2 in $(\text{CH}_3\text{CH}_2)_2\text{O}$ to afford methyl esterified products (MEPs_1). The CH_2Cl_2 -inextractable fraction (IEF) from FC_2 , which was defined as black acid,²⁰ was also dried and weighed. Water and a small amount of CH_2Cl_2 in the CH_2Cl_2 -inextractable solution (IES) from F_2 were removed with a rotary evaporator under reduced pressure followed by esterification with CH_2N_2 in $(\text{CH}_3\text{CH}_2)_2\text{O}$ to afford the corresponding methyl esterified products (MEPs_2). Both MEPs_1 and MEPs_2 were analyzed with FTIR and GC/MS.

The mass range scanned was from 30 to 500 amu. Data were acquired and processed using Chemstation software. The compounds were identified by comparing the mass spectra with NIST05a library data. Quantitative analyses were also conducted on the basis of parent SFC mass with GC/MS using a series of authentic compounds as external standards, e.g., methyl caproate for monocarboxylic acids (MCAs), dimethyl adipate for dicarboxylic acids (DCAs) and tricarboxylic acids, and dimethyl phthalate for benzene carboxylic acids (BCAs).

3. Results and Discussion

After oxidation with NaOCl for 24 h, the yields of FC_1 and IEF were only 2% and 12%, respectively, based on organic matter in SFC, indicating that most of organic matter in SFC was converted to water-soluble species. However, quantifying the insoluble fraction from SFC oxidation with RuO_4 is difficult because an uncertain amount of insoluble NaIO_3 was formed during the oxidation.

For convenience in description, the methyl esterified products from SFC oxidation with RuO_4 and with NaOCl are denoted as P_{RuO_4} and P_{NaOCl} , respectively, and total ion chromatograms are denoted as TICs.

3.1. FTIR Analysis. As Figure 2 displays, almost no absorbance at 3730 cm^{-1} is observed, but those at 1268, 1197, and 1004 cm^{-1} are very strong, suggesting that most of $-\text{COOH}$ in the products was converted to $-\text{COOCH}_3$ by esterification with CH_2N_2 . For both P_{RuO_4} and P_{NaOCl} , the absorbances at 2929 and 2842 cm^{-1} attributed to the aliphatic moiety (AM) in organic phase products (OPPs) are much stronger than those in aqueous phase products (APPs), indicating that most of the AM-rich components were

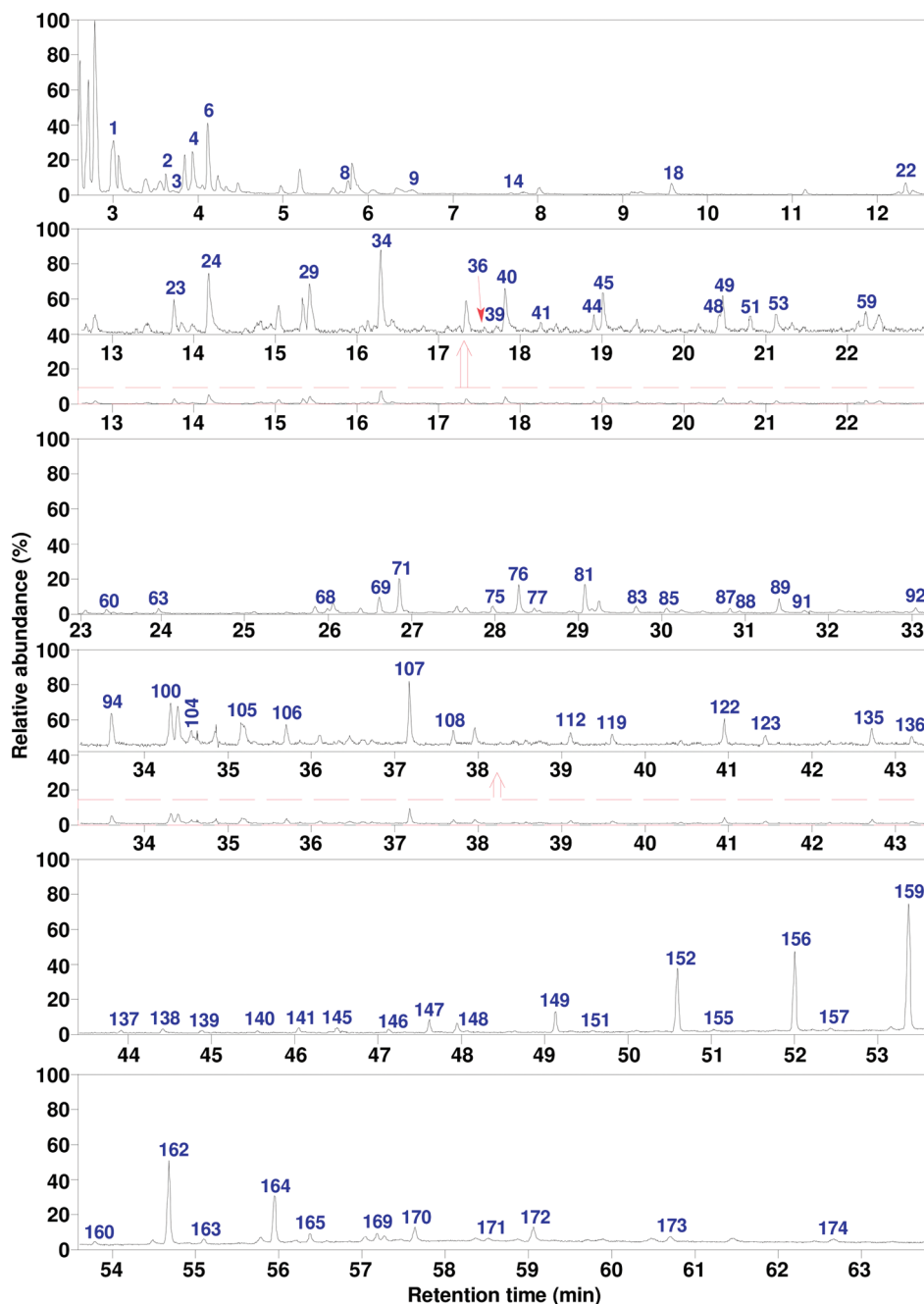


Figure 3. TICs of the methyl esterified products in the organic phase from SFC oxidation with RuO_4 .

extracted by organic solvent. Besides, the absorbances at 2929 and 2842 cm^{-1} in P_{RuO_4} are appreciably stronger than those in P_{NaOCl} , suggesting that more AM-containing products were formed via SFC oxidation with RuO_4 than with NaOCl . The existence of $-\text{CH}_2\text{Cl}$ and $-\text{CHCl}_2$ can be seen from the absorbance at 745 cm^{-1} both in P_{RuO_4} and in P_{NaOCl} , but the absorbance in P_{NaOCl} is significantly stronger than that in P_{RuO_4} , implying that chlorine in the NaOCl aqueous solution was involved in the reaction.

3.2. GC/MS Analysis. As exhibited in Figures 3–6, in total, 174 methyl esterified products were identified by GC/MS analysis and their parent ones can be classified into MCAs, DCAs, BCAs, hydrocarbons (HCs), and others species (OSs). These products can also be divided into organochlorine compounds (OCCs) and nonorganochlorine compounds (NOCCs).

As listed in Tables 2 and 3, 34 AAs and 22 chloro-substituted AAs (CSAAs) were detected in total. In total 32 AAs and only 3 CSAAs (i.e., chloroacetic acid, dichloroacetic acid, and trichloroacetic acid) appeared in P_{RuO_4} . In contrast, all of the 22 CSAAs were detected in P_{NaOCl} , and most of them are α -chloro-substituted MCAs. In addition, long-chain AAs (carbon number > 17) are rich in P_{RuO_4} but were not detected in P_{NaOCl} .

As illustrated in Figure 7, the yield of MCAs in P_{RuO_4} is much lower than that in P_{NaOCl} . Most of MCAs detected in P_{NaOCl} are OCCs, but OCCs only account for $\sim 36\%$ MCAs detected in P_{RuO_4} . In P_{NaOCl} , trichloroacetic acid (peak 17 in Figure 6) is the most abundant, accounting for $\sim 50\%$ of MCAs, while $\sim 25\%$ of MCAs is dichloroacetic acid (peak 8 in Figure 6). These facts indicate that SFC itself contains OCCs as reported previously,²¹ but chlorine

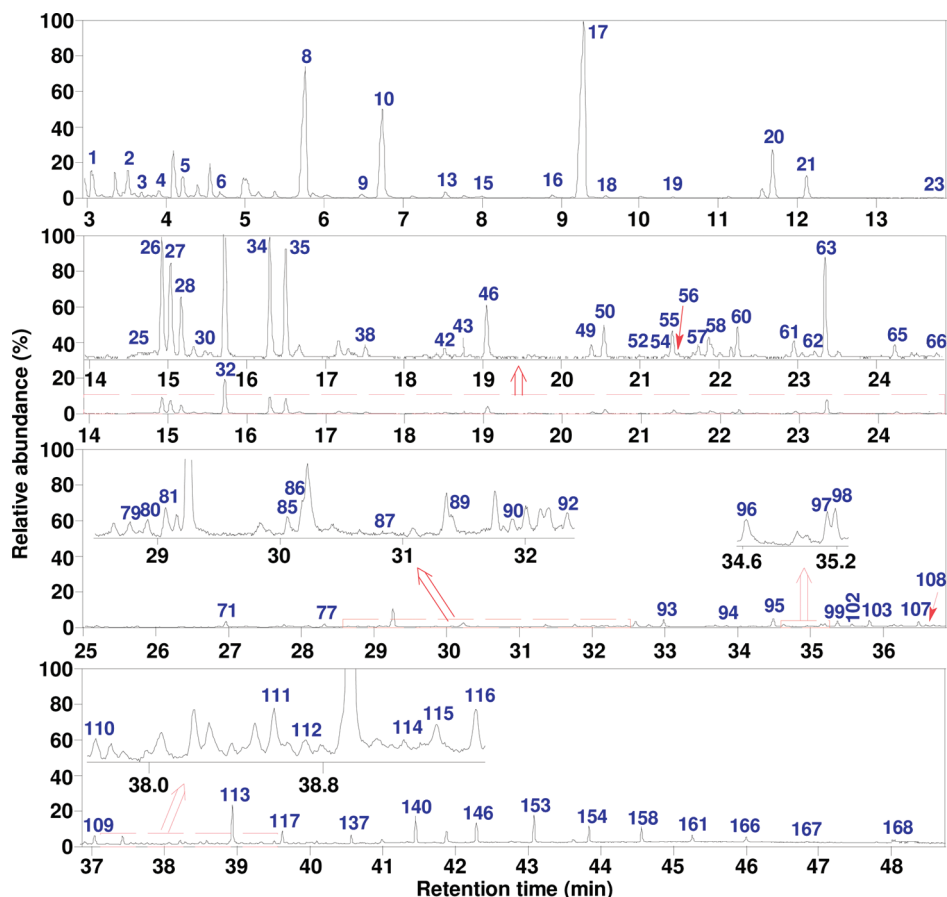


Figure 4. TICs of the methyl esterified products in the organic phase from SFC oxidation with NaOCl.

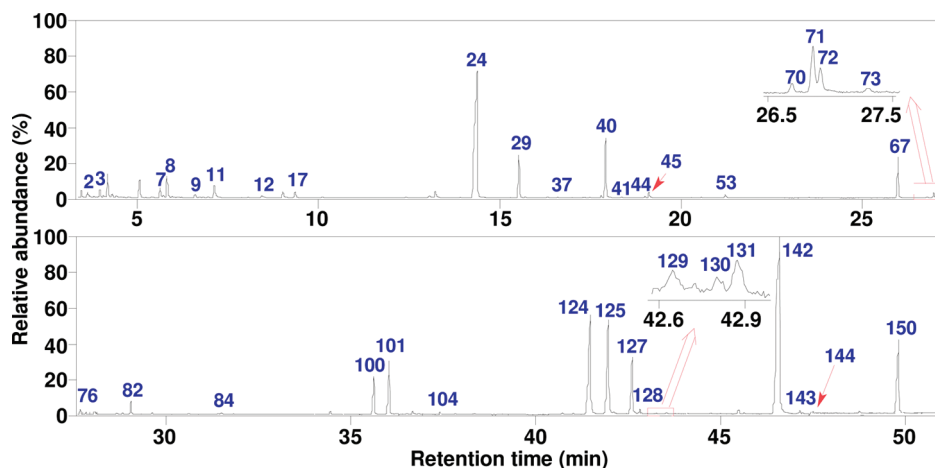


Figure 5. TICs of the methyl esterified products in the aqueous phase from SFC oxidation with RuO₄.

in most of the OCCs from P_{NaOCl} resulted from NaOCl. No OCCs were detected in DCAs, BCAs, and OSs from P_{RuO₄}, whereas ~38% of DCAs, ~21% of BCAs, and almost all the OSs are OCCs. In addition, the yields of MCAs and HCs in P_{NaOCl} are much higher than those in P_{RuO₄}, but the yields of DCAs, BCAs, and OSs in P_{NaOCl} are significantly lower than those in P_{RuO₄}. The above significant differences suggest that the mechanism for SFC

oxidation with RuO₄ is quite different from that with NaOCl.

In total 36 alkane- α,ω -dicarboxylic acids (ADCAs) and 6 chloro-substituted ADCAs (CSADCAs) were detected in the products from SFC oxidation, as listed in Tables 4 and 5, respectively. All the ADCAs appear in P_{RuO₄}, but there are only 8 ADCAs in P_{NaOCl}. In contrast, P_{NaOCl} contains all the CSADCAs, but no CSADCAs are contained in P_{RuO₄}. Similar to the case of MCAs, long-chain ADCAs were only detected in P_{RuO₄}.

As Tables 6 and 7 list, in total 22 BCAs and 30 chloro-substituted BCAs (CSBCAs) were yielded. The BCAs include

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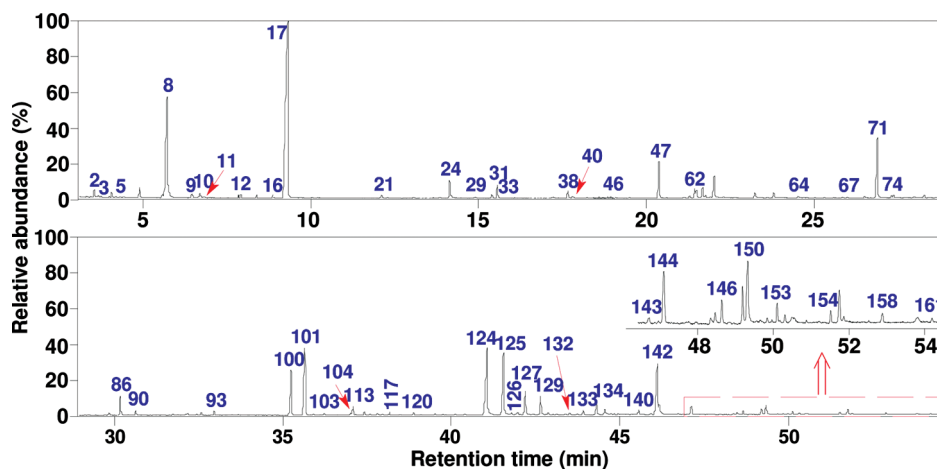


Figure 6. TICs of the methyl esterified products in the aqueous phase from SFC oxidation with NaOCl.

Table 2. AAs Detected in the Products from SFC Oxidation

peak	AAs	with RuO ₄	with NaOCl
1	butanoic acid	×	×
4	3-methylbutanoic acid	×	×
6	pentanoic acid	×	×
14	3-methylpentanoic acid	×	×
15	4-methylpentanoic acid	×	×
18	hexanoic acid	×	×
22	5-methylhexanoic acid	×	×
23	heptanoic acid	×	×
32	3,5-dimethylheptanoic acid	×	×
36	2-methylheptanoic acid	×	×
39	octanoic acid	×	×
49	nonanoic acid	×	×
58	4-methylnonanoic acid	×	×
60	decanoic acid	×	×
68	undecanoic acid	×	×
77	dodecanoic acid	×	×
87	tridecanoic acid	×	×
92	tetradecanoic acid	×	×
105	pentadecanoic acid	×	×
107	palmitic acid	×	×
112	heptadecanoic acid	×	×
122	stearic acid	×	×
135	nonadecanoic acid	×	×
138	icosanoic acid	×	×
141	heneicosanoic acid	×	×
147	docosanoic acid	×	×
149	tricosanoic acid	×	×
152	tetracosanoic acid	×	×
156	pentacosanoic acid	×	×
159	hexacosanoic acid	×	×
162	heptacosanoic acid	×	×
164	octacosanoic acid	×	×
169	nonacosanoic acid	×	×
171	triacontanoic acid	×	×

2 benzoic acids, 6 phthalic acids, 5 benzenetricarboxylic acids, 6 benzenetetracarboxylic acids, 2 benzenepentacarboxylic acids, and benzenhexacarboxylic acid. All the CSBCAs appear in P_{NaOCl} , but there are only 2 CSBCAs in P_{RuO_4} .

Table 8 lists 16 HCs, including 4 arenes and 12 alkanes, detected in the products from SFC oxidation. All the arenes were detected both in P_{RuO_4} and in P_{NaOCl} with almost the same yield. All the alkanes were detected in P_{NaOCl} , but only 3 alkanes with much lower yields were found in P_{RuO_4} .

OSs detected in the products from SFC oxidation include 3 OCCs and 5 tricarboxylic acids, as shown in Table 9. All the 3 OCCs were detected in P_{NaOCl} , but no OCCs were found in

Table 3. CSAAs Detected in the Products from SFC Oxidation

peak	CSAAs	with RuO ₄	with NaOCl
2	chloroacetic acid	×	×
5	2-chloropropanoic acid	×	×
8	dichloroacetic acid	×	×
10	2,2-dichloropropanoic acid	×	×
13	2-chlorobutanoic acid	×	×
17	trichloroacetic acid	×	×
19	2-chloro-3-methylbutanoic acid	×	×
20	2,2-dichlorobutanoic acid	×	×
25	2,2,3-trichloropropanoic acid	×	×
26	2,3,3-trichloroacrylic acid	×	×
27	2,2-dichloro-3-methylbutanoic acid	×	×
28	2,2-dichloropentanoic acid	×	×
30	2-chlorohexanoic acid	×	×
35	2,2,3-trichlorobutanoic acid	×	×
42	2,2-dichlorohexanoic acid	×	×
43	2-chloroheptanoic acid	×	×
46	2,2,3,3-tetrachloropropanoic acid	×	×
50	2,2,3-trichloro-3-methylbutanoic acid	×	×
52	2-chlorooctanoic acid	×	×
56	2,2-dichloroheptanoic acid	×	×
61	2,2,3-trichloropentanoic acid	×	×
62	2,2-dichlorooctanoic acid	×	×

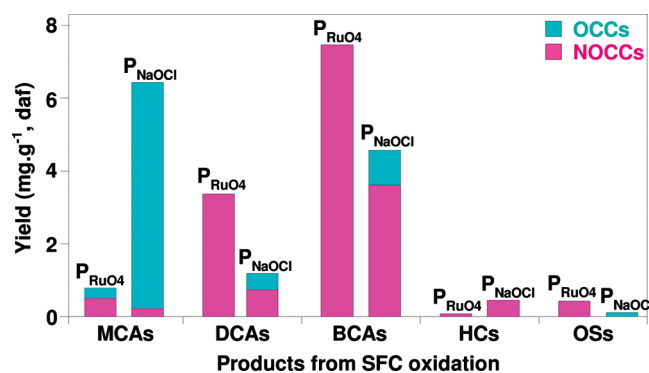


Figure 7. Distribution of P_{RuO_4} and P_{NaOCl} in the products from SFC oxidation.

P_{RuO_4} . In contrast, all the 5 tricarboxylic acids were detected in P_{RuO_4} , but only propane-1,2,3-tricarboxylic acid appears in P_{NaOCl} .

3.3. Examination of Oxidation Mechanism Based on Product Distribution. The mechanisms for the oxidation of coals and their related model compounds with RuO_4 have been extensively investigated.^{22–24} It is usually accepted that

Table 4. ADCAs Detected in the Products from SFC Oxidation

peak	ADCAs	with RuO ₄	with NaOCl
7	oxalic acid	×	
24	succinic acid	×	×
29	2-methylsuccinic acid	×	×
37	2,3-dimethylsuccinic acid	×	
40	glutaric acid	×	×
41	2-ethylsuccinic acid	×	
44	2-methylpentanedioic acid	×	
45	3-methylpentanedioic acid	×	
48	2,2-dimethylpentanedioic acid	×	
51	2,4-dimethylpentanedioic acid	×	
53	adipic acid	×	
59	2-methylhexanedioic acid	×	
63	heptanedioic acid	×	×
69	octanedioic acid	×	
73	3-methylhexanedioic acid	×	
81	nonanedioic acid	×	×
89	decanedioic acid	×	×
94	undecanedioic acid	×	×
106	dodecanedioic acid	×	
108	tridecanedioic acid	×	×
119	tetradecanedioic acid	×	
123	pentadecanedioic acid	×	
136	hexadecanedioic acid	×	
139	heptadecanedioic acid	×	
145	octadecanedioic acid	×	
148	nonadecanedioic acid	×	
151	icosanedioic acid	×	
155	heneicosanedioic acid	×	
157	docosanedioic acid	×	
160	tricosanedioic acid	×	
163	tetracosanedioic acid	×	
165	pentacosanedioic acid	×	
170	hexacosanedioic acid	×	
172	heptacosanedioic acid	×	
173	octacosanedioic acid	×	
174	nonacosanedioic acid	×	

Table 5. CSADCAs Detected in the Products from SFC Oxidation

peak	CSADCAs	with RuO ₄	with NaOCl
31	2-chloro-2-methylmalonic acid		×
38	2-chlorosuccinic acid		×
47	2,3-dichlorosuccinic acid		×
64	2,2-dichloro-3-methylsuccinic acid		×
74	2-chloro-3-(dichloromethyl)fumaric acid		×
96	2,2,4-trichlorohexanedioic acid		×

RuO₄ selectively oxidizes aromatic units to carboxylic acids such as AAs, alkanedioic acids, and BCAs, as demonstrated in Scheme 1. However, only a few researchers paid attention to the mechanism for coal oxidation with NaOCl. Different from RuO₄, NaOCl was reported to oxidize the side chain on the benzene ring rather than the benzene ring itself, as illustrated in Scheme 2.¹⁷ Some polynuclear aromatics can be oxidized with NaOCl to BCAs, especially in the presence of either phenolic or carboxylic functional groups on the polynuclear aromatic rings.¹⁹ For example, naphthalene was reported to be reactive toward oxidation with NaOCl to selectively afford phthalic acid.²⁵ These results and proposals can interpret the formation of MCAs, DCAs, and BCAs to some extent, but there are still some questions that need to be answered. The questions are related to the reasons for a much higher total yield of MCAs in P_{NaOCl} than that in P_{RuO4}, the mechanisms for the formation of short-chain

Table 6. BCAs Detected in the Products from SFC Oxidation

peak	BCAs	with RuO ₄	with NaOCl
34	benzoic acid	×	×
71	phthalic acid	×	×
75	isophthalic acid	×	×
76	terephthalic acid	×	
83	4-methylphthalic acid	×	
85	3,4,5-trimethylbenzoic acid	×	×
88	5-methylisophthalic acid	×	
91	4,5-dimethylphthalic acid	×	
100	benzene-1,2,3-tricarboxylic acid	×	×
101	benzene-1,2,4-tricarboxylic acid	×	×
104	benzene-1,3,5-tricarboxylic acid	×	
115	3-methylbenzene-1,2,4-tricarboxylic acid		×
116	5-methylbenzene-1,2,4-tricarboxylic acid		×
124	benzene-1,2,3,4-tetracarboxylic acid	×	×
125	benzene-1,2,3,5-tetracarboxylic acid	×	×
127	benzene-1,2,4,5-tetracarboxylic acid	×	×
128	5-methylbenzene-1,2,3,4-tetracarboxylic acid	×	
130	4-methylbenzene-1,2,3,5-tetracarboxylic acid	×	
131	3-methylbenzene-1,2,4,5-tetracarboxylic acid	×	
142	benzene-1,2,3,4,5-pentacarboxylic acid	×	×
143	6-methylbenzene-1,2,3,4,5-pentacarboxylic acid	×	×
150	benzene-1,2,3,4,5,6-hexacarboxylic acid	×	×

Table 7. CSBCAs Detected in the Products from SFC Oxidation

peak	CSBCAs	with RuO ₄	with NaOCl
54	2-chlorobenzoic acid		×
55	3-chlorobenzoic acid		×
57	4-chlorobenzoic acid		×
65	2-chloro-4-methylbenzoic acid		×
66	3-chloro-4-methylbenzoic acid		×
78	3,5-dichloro-4-methylbenzoic acid		×
79	2,5-dichloro-4-methylbenzoic acid		×
80	2,6-dichloro-4-methylbenzoic acid		×
86	3-chlorophthalic acid		×
90	4-chlorophthalic acid		×
93	4-chloro-5-methylphthalic acid		×
95	4-chloro-5-ethylphthalic acid		×
97	4-chloro-5-isopropylphthalic acid		×
98	3,4,5-trichloro-2,6-dimethylbenzoic acid		×
99	2,3,4-trichloro-5,6-dimethylbenzoic acid		×
102	3,6-dichloro-4-methylphthalic acid		×
103	3,5-dichloro-4-methylphthalic acid		×
110	3,4-dichloro-5,6-dimethylphthalic acid		×
113	4-chlorobenzene-1,2,3-tricarboxylic acid		×
114	5-chlorobenzene-1,2,3-tricarboxylic acid		×
117	6-chlorobenzene-1,2,4-tricarboxylic acid		×
118	2-chlorobenzene-1,3,5-tricarboxylic acid		×
120	6-chloro-5-methylbenzene-1,2,4-tricarboxylic acid		×
121	6-chloro-3-methylbenzene-1,2,4-tricarboxylic acid		×
126	3,6-dichloro-5-methylbenzene-1,2,4-tricarboxylic acid		×
129	5-chlorobenzene-1,2,3,4-tetracarboxylic acid	×	×
132	4-chlorobenzene-1,2,3,5-tetracarboxylic acid		×
133	3-chlorobenzene-1,2,4,5-tetracarboxylic acid		×
134	5-chloro-6-methylbenzene-1,2,3,4-tetracarboxylic acid		×
144	6-chlorobenzene-1,2,3,4,5-pentacarboxylic acid	×	×

CSAAs as the most abundant components in P_{NaOCl} and for the formation of a much larger amount of alkanes in P_{NaOCl} than that in P_{RuO4}.

Rook²⁶ investigated the oxidation of fulvic acid, one of main components of humic substances, with NaOCl. He

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(23) Raymond, J.; Guy, S.; Geoffrey, E. *Fuel* **1991**, *70* (6), 695–702.

(24) Mallia, N.; Zingaro, R. A. *Fuel* **1984**, *63* (3), 423–425.

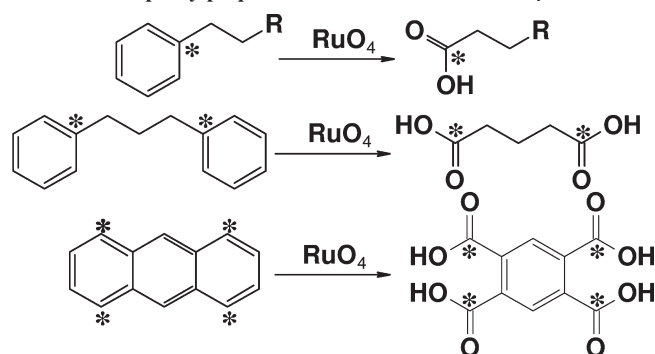
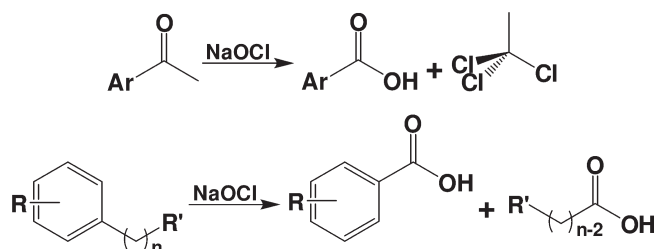
(25) Landolt, R. G. *Fuel* **1977**, *56* (2), 224–225.

Table 8. HCs Detected in the Products from SFC Oxidation

peak	HCS	with RuO ₄	with NaOCl
3	toluene	×	×
9	ethylbenzene	×	×
11	<i>p</i> -xylene	×	×
12	<i>o</i> -xylene	×	×
109	icosane		×
111	heneicosane		×
137	tricosane	×	×
140	tetracosane	×	×
146	pentacosane	×	×
153	hexacosane		×
154	heptacosane		×
158	octacosane		×
161	nonacosane		×
166	triacontane		×
167	hentriacontane		×
168	dotriacontane		×

Table 9. OSs Detected in the Products from SFC Oxidation

peak	OSs	with RuO ₄	with NaOCl
16	ethyl 2,2-dichloroacetate		×
21	ethyl 2,2,2-trichloroacetate		×
33	1,1,1,3,3-pentachloropropan-2-one		×
67	propane-1,2,3-tricarboxylic acid	×	×
70	butane-1,2,3-tricarboxylic acid	×	
72	butane-1,2,4-tricarboxylic acid	×	
82	butane-1,1,4-tricarboxylic acid	×	
84	3-(carboxymethyl)hexanedioic acid	×	

Scheme 1. Mechanisms for the Oxidation of Alkylbenzene, 1,3-Diphenylpropane and Anthracene with RuO₄**Scheme 2. Mechanism for the Oxidation of Arylethanones and Alkylbenzenes with NaOCl Proposed by Chakrabartty^a**

^a R denotes an electron withdrawing group.

concluded that the resorcinol-type moiety of fulvic acids yields dichloroacetic acid, trichloroacetic acid, and other α -chloro-substituted MCAs during the oxidation. The resorcinol-type moiety contained in coals may not be as rich as in fulvic acids. We found that phenol oxidation with NaOCl yielded methyl 2,2,3,3-tetrachloropropanoate and

ethyl 2,2,2-trichloroacetate as the main products along with a much smaller amount of methyl 2-chloroacetate, methyl 2,2-dichloroacetate, ethyl 2,2-dichloroacetate, methyl 2,2,2-trichloroacetate, and methyl 2,3,3-trichloroacrylate as byproducts (Figure SI-1 in the Supporting Information). These compounds are also relatively abundant in P_{NaOCl}. Hence, we suppose that most of the short-chain CSAAs detected in P_{NaOCl} were produced from the phenolic moiety of SFC during its oxidation. We also examined 1,3-diphenylpropane oxidation with NaOCl and found that a series of long-chain alkanes were formed during the oxidation (Figure SI-2 in the Supporting Information), although the related mechanism remains unclear. This fact corroborates that most of the alkanes were produced from the oxidation of α,ω -diarylalkanes in SFC with NaOCl.

4. Conclusions

Most of organic matter in Shenfu coal was converted into soluble species through oxidation with either RuO₄ or NaOCl. The products from the oxidation of Shenfu coal with NaOCl are more complex and contain much more chloro-substituted species than those with RuO₄, while the soluble species obtained with RuO₄ are rich in long-chain alkanic acids and alkane- α,ω -dicarboxylic acids, but those with NaOCl consist of considerable amounts of short-chain chloro-substituted alkanic acids and alkanes. Most of the short-chain chloro-substituted alkanic acids were confirmed to be derived from the phenolic moiety of Shenfu coal, while α,ω -diarylalkanes could be precursors of some alkanes.

NaOCl is expected to be an industrial oxidant for obtaining organic acids from coals due to its easy availability, environmental friendliness, and electrolytic renewability, but optimization of reaction conditions, such as molar ratio of NaOCl to coal, reaction temperature and time, and pH value, is needed for inhibiting side-reactions, especially chlorination.

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Supporting Information Available: Methyl esterified products from the oxidation of phenol and 1,3-diphenylpropane with NaOCl. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Nomenclature

SFC = Shenfu coal

BPCAs = benzene polycarboxylic acids

AAs = alkanic acids

RICO = ruthenium ion-catalyzed oxidation

FC₁ = filter cake from the reaction mixture of SFC with NaOCl aqueous solution

F₁ = filtrate from the reaction mixture of SFC with NaOCl aqueous solution

FC₂ = filter cake from acidified F₁

F₂ = filtrate from acidified F₁

ES₁ = extraction solution from FC₂ with CH₂Cl₂

ES₂ = extraction solution from F₂ with CH₂Cl₂

IEF = CH₂Cl₂-inextractable fraction from FC₂

F₃ = filtrate from dried ES₁ and ES₂ over anhydrous MgSO₄
MEPs₁ = methyl esterified products from distilled F₃
IES = CH₂Cl₂-inextractable solution from F₂
MEPs₂ = methyl esterified products from distilled IES
MCAs = monocarboxylic acids
DCAs = dicarboxylic acids
BCAs = benzene carboxylic acids
P_{RuO₄} = methyl esterified products of SFC oxidation with RuO₄
P_{NaOCl} = methyl esterified products of SFC oxidation with NaOCl
TICs = total ion chromatograms

AM = aliphatic moiety
OPPs = organic phase products
APPs = aqueous phase products
HCs = hydrocarbons
OSs = other species
OCCs = organochlorine compounds
NOCCs = nonorganochlorine compounds
CSAAs = chloro-substituted alkanoic acids
ADCAs = alkane- α,ω -dicarboxylic acids
CSADCAs = chloro-substituted alkane- α,ω -dicarboxylic acids
CSBCAs = chloro-substituted benzene carboxylic acids