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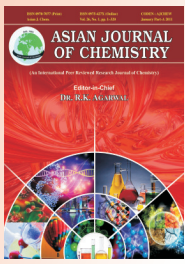

Microwave-Assisted Extraction of Organic Compounds from Yanan Coal at Room Temperature

T. LIU[1,*], Y.L. PENG[2] and J.H. HOU[3]

[1]School of Chemistry & Chemical Engineering, Xuzhou Institute of Technology, Xuzhou 221111, Jiangsu Province, P.R. China
[2]School of Chemical Engineering and Technology, China University of Mining and Technology, Xuzhou 221111, Jiangsu Province, P.R. China
[3]School of Food (Biology) Engineering, Xuzhou Institute of Technology, Xuzhou 221111, Jiangsu Province, P.R. China

*Corresponding author: E-mail: liutongcumt@126.com

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Yanan coal was sequentially extracted with petroleum ether, carbon disulfide, methanol and acetone at room temperature under microwave irradiation condition, affording extracts 1 to 4 (F_1 to F_4). In total, 105 organic compounds were identified from yanan coal by gas chromatography/mass spectrometry analysis, especially, 60 organic compounds were detected in carbon disulfide extracts (F_2). The organic compounds include 17 alcohols, 19 esters, 23 arenes, 9 acids, 8 heteroatom-containing organic compounds, 5 aldehydes, 5 ketones, 2 organic iodines and other organic compounds. The experiment provides an essential and effective approach investigations of coal composition and structure in separable and nondestructive methods.

Keywords: Yanan coal, Microwave irradiation, Organic compounds, GC/MS.

INTRODUCTION

The separation and analysis of organic compounds in coals are quite difficult task because of the complexity in the heteroatom structure and molecular composition of organic species in coals[1-3]. Thus, lots of efforts have been contributed to develop a coal separation method for the effective utilization of coals in the future[4,5]. When using coals as clean energy, effective removal of harmful species such as organic nitrogen, sulfur and halogens in coals must be considered according to understanding of the molecular composition of the organic heteroatomic species[6,7]. In recent years, this interesting work has been extensively studied in extracting of coals with organic solvents[8]. Meanwhile, chromatography coupled with mass spectrometry has been developed for characterizing components in coals and proved a powerful tool for unknown species identification[9].

As a new separation technology, extraction has attracted worldwide attention at present. Compared to the conventional extraction technology, microwave extraction has the following advantages, such as easy automation power control, energy efficiency and operational safety. Moreover, due to the microwave extraction without heating or low heating temperature, the energy consumption greatly reduce and the economic benefit is remarkable[10,11].

In the present work, Yanan coal (YAC) was sequentially extracted with petroleum ether, carbon disulfide, methanol and acetone at room temperature under microwave irradiation condition. This experiment offers an essential and effective approach for investigations of coal composition and structure in separable and nondestructive methods.

EXPERIMENTAL

Yanan coal was collected from the yanan coal mine in Shanxi province and pulverized to 200 mesh sieve (< 75 mm), followed by drying in vacuum at 80 °C for 24 h. Table-1 showed the proximate and ultimate analyses of the coal samples. All the solvents used in the experiment, including petroleum ether (bp. 60-90 °C), carbon disulfide (CS_2), methanol and acetone were commercially-purchased analytical and were purified by distillation with a RE52CS-1 rotary evaporator prior to use.

A CEM Discover microwave reactor was used for the coal extraction. A RE52CS-1 rotary evaporator was applied for distillation of solvents from the reaction mixture. The quantitative and qualitative analysis of extracts were carried out by a Hewlett-Packard 6890/5973C GC/MS equipped with a capillary column coated with HP-5 (cross-link 5 % PH ME siloxane, 60 m × 0.25 mm i.d., 0.25 mm film thickness, mass scanning range of 30-500 amu) and a quadrupole analyzer and operated in electron impact (70 eV) mode.

The compounds were identified by comparing mass spectra, interpretation of MS fragmentation patterns and comparing retention times of their peaks to these of some standard compounds analyzed previously and literature date with NIST08a library data.

TABLE-1
PROXIMATE AND ULTIMATE ANALYSES (wt. %) OF YANAN COAL (YAC)

Proximate analysis			Ultimate analysis (daf)				$S_{t,d}$
M_{ad}	A_d	V_{daf}	C	H	N	O	
6.43	23.38	23.93	44.39	3.12	0.50	21.76	0.42

Extraction of coal with solvents: The coal sample (Yanan coal, 2 g) and petroleum ether (20 mL) were added into a 50 mL CEM discover microwave reactor with a magnetical stirrer at 30 °C. The reactor was kept for 20 min to offer F_1,. The extraction was concentrated in a RE52CS-1 rotary evaporator at room temperature. Then the residue followed successive extractions sequentially with carbon disulfide (offered F_2), methanol (offered F_3) and acetone (offered F_4) in the same way as described above (Fig. 1). All the concentrated filtrates were analysed by GC/MS. The filter cake (FC) was dried at 80 °C in a vacuum for 12 h. The extract yield Y was calculated according the difference in mass between YAC and FC: $Y = (m_{YAC}-m_{FC})/m_{YAC}$.

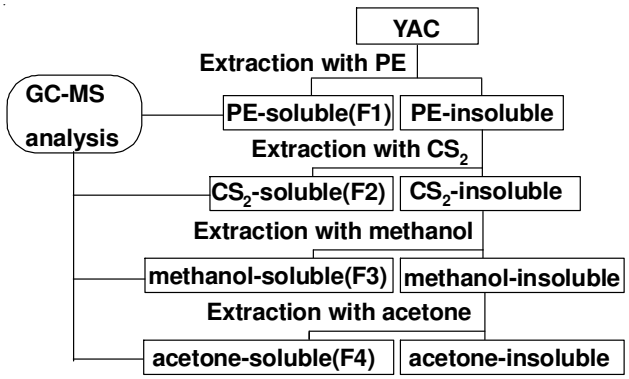

Fig. 1. Process of the sequential extraction

RESULTS AND DISCUSSION

Yield of the extract: Extraction solution of Yanan coal shows colorless in petroleum ether, hazel colour in carbon disulfide and acetone and black in methanol. The extract yields of yanan coal in the solvents used follow the order: petroleum ether < methanol < carbon disulfide < acetone (Fig. 2). The order is largely related to dielectric constant[12,13].

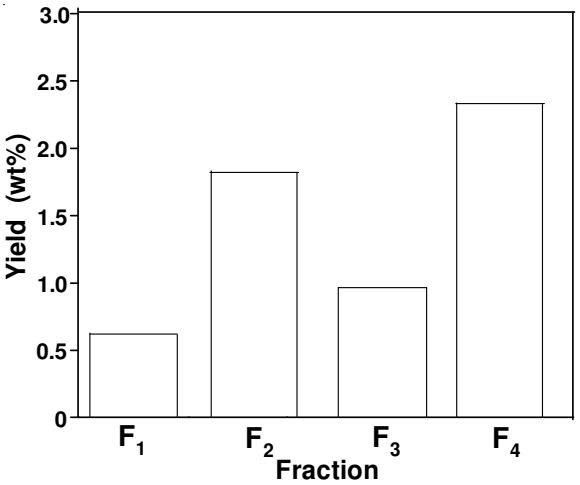

Fig. 2. Yield of F_1-F_4

GC/MS analysis: Figs. 3 and 4 exhibit the total ion chromatograms (TICs) of the extract (F_1 to F_4) from the Yanan coal sample. In total, 105 organic compounds were identified and they can be classified into arenes, esters, alcohols, acids, heteroatom-containing organic compounds (HCOCs) and other organic compounds (OCs) as listed in Tables 2-7.

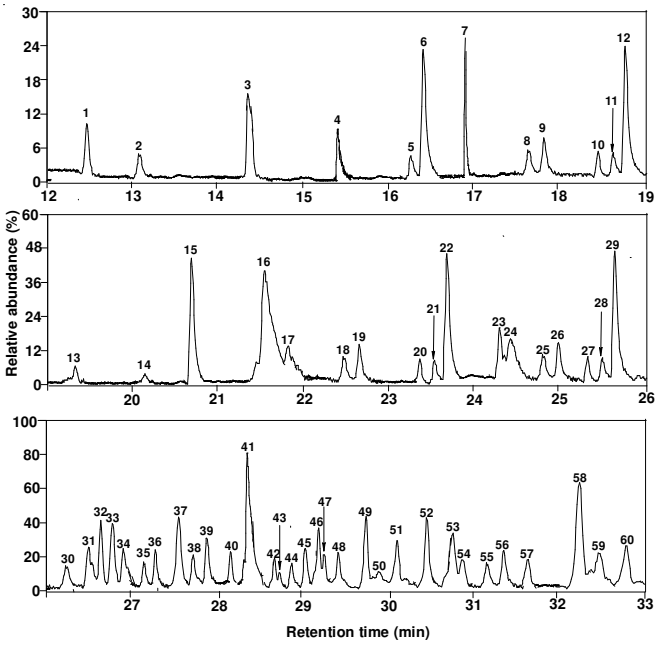

Fig. 3 TIC of F_2 from Yanan coal (YAC)

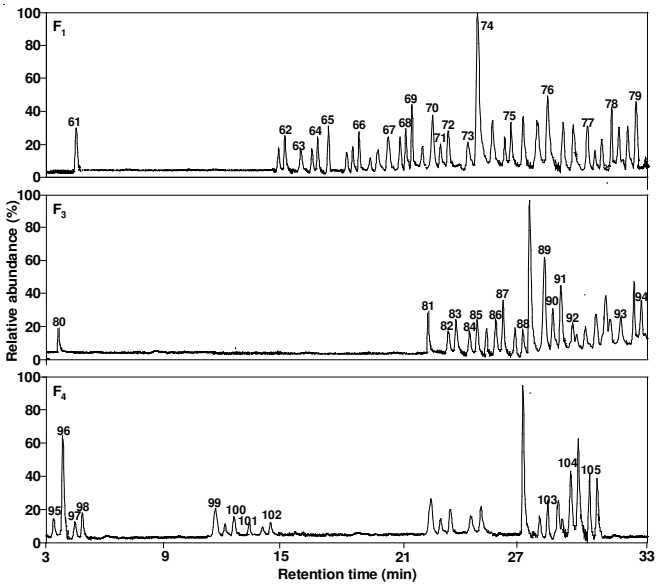

Fig. 4. TIC of F_1, F_3, F_4 from Yanan coal (YAC)

Arenes: As listed in Table-2, in total twenty-three arenes were detected in the extract from Yanan coal (YAC). Almost all arenes detected in F_2, indicated arenes has best solubility

in carbon disulfide than other three solvents under microwave irradiation condition. Most of compounds detected are polycyclic arenes, especially containing-(methyl, dimethyl, trimethyl) derivatives, including a series of alkylnaphthalene (peak 4, 6, 11, 12, 13 and 18) and alkyl phenanthrenes (peak 33, 35, 36, 37, 41, 45 and 54), a methylfluorene (peak 25), a methylanthracene (peak 32), 9-methylene-9*H*-fluorene (peak 68). Only four benzene and phenol derivatives (peak 62, 82, 84 and 87) detected in coal extract, due to larger super delocalizability of polycyclic arenes than that of benzene and phenol. Meanwhile, this results indicate that at least most of alkyl groups are originally attached on aromatic ring in the yanan coal.

Esters: As shown in Table-3, in total nineteen esters were detected in the extract from Yanan coal, most of them are alkanoates and aromatic esters, including phenanthren-9-yl methyl carbonobromidate (peak 34) which appears only in F_2. Alkanoates detected in the extract can further be classified into one alkanoates (peak 80), seven methylalkanoates and four alkenoates. Meanwhile, six aromatic esters were detected in the extract, including two phthalates, *e.g.*, *bis*(6-methylheptyl) phthalate (peak 30) which was only detected in F_2.

Alcohols: As summarized in Table-4, in total seventeen alcohols were detected in the extract from Yanan coal, including five cyclitols (peak 9, 42, 53, 79 and 101), seven alkenols (peak 5, 7, 22, 48, 77, 88 and 95) and five alkanols (peak 2, 8, 19, 59 and 81). The arenols reported were derived from the fungal degradation of wood lignin and natural products such as the tocopherols, whereas alkenols and alkanols from lipid, wax[14]. Cyclitols are considered to be important biomarkers and well detected in the extracts from coals and other fossil[15].

Acids: In total, nine acids were detected in the extract from Yanan coal (Table-5). All the compounds can further be

TABLE-2
ARENES DETECTED IN F_1 TO F_4 FROM YANAN COAL (YAC)

No.	Compound	F_1	F_2	F_3	F_4
1	Naphthalene		√		
4	1-Methyl naphthalene		√		√
6	2-Methyl naphthalene	√	√		
11	1,2-Dimethyl naphthalene	√	√		√
12	1,4-Dimethyl naphthalene	√	√		
13	2,3-Dimethyl naphthalene		√		
18	1,6,7-Trimethyl naphthalene		√		
25	1-Methyl-9*H*-fluorene	√	√		
26	*dip*-Tolylmethane		√		
28	Anthracene		√		
32	2-Methyl anthracene		√		
33	1a,9b-Dihydro-1*H*-cyclopropa[l]phenanthrene		√		√
35	1-Methyl phenanthrene		√		
36	2-Methyl phenanthrene	√	√		
37	3-Methyl phenanthrene		√		
41	2,7-Dimethyl phenanthrene		√		
45	2,3,5-Trimethyl phenanthrene		√		
54	7-Isopropyl-1-methyl phenanthrene		√		
62	4-Methylhexa-1,2,5-trienyl benzene		√		
68	9-Methylene-9*H*-fluorene		√	√	
82	4-Isopropyl phenol		√	√	
84	2,5-Di-*tert*-butyl phenol		√	√	
87	2,3-Dimethyl-5-(trifluoromethyl)benzene-1,4-diol	√	√		

TABLE-3
ESTERS DETECTED IN F_1 TO F_4 FROM YANAN COAL (YAC)

No.	Compound	F_1	F_2	F_3	F_4
24	Dodecan-2-yl-2-methoxyacetate		√		
29	Tridecan-2-yl-2-methoxyacetate		√		
30	Butyl octyl phthalate	√	√		
34	Phenanthren-9-ylmethyl carbonobromidate		√		
38	*Bis*(6-methylheptyl) phthalate		√		
49	Ethyl iso-allocholate		√		
52	Methyl-4-hydroxyoctadecanoate		√		
60	2-(Octyloxy)ethyl heptacosanoate		√		
64	(E)-2,5-Dimethylhex-3-enyl acetate		√		
70	(E)-Undec-2-enyl 2,2-dichloroacetate	√			
71	(E)-Methyl hexadec-6-enoate	√		√	
80	Butyl acetate	√		√	√
85	Methyl 3-(4-hydroxyphenyl) propanoate			√	
89	(E)-7-Methyltridec-8-enyl acetate			√	
90	Methyl 14-methylpentadecanoate			√	
91	(E)-(2-Phenyl-1,3-dioxolan-4-yl)methyloctadec-9-enoate			√	
92	(E)-dodecyl nonadec-10-enoate			√	
93	Methyl-9-(3-hexyloxiran-2-yl) nonanoate			√	√
105	1,3-Dihydroxypropan-2-yl stearate				

classified into three alkanoic acids (peak 55, 74, 76), three alkenoic acids (peak 47, 75, 103) and three cyclic acids. In the cyclic acids, 7-methoxy piperonylic acid (peak 27) and erucic acid (peak 50) were only detected in F_2. Meanwhile, in the alkenoic acids, (Z, Z)-9,12-octadecadienoic acid (peak 103) was only detected in F_4.

Heteroatom-containing organic compounds: Six nitrogen-containing organic compounds (NOCs) and two oxygen-containing organic compounds (OOCs) were detected in the extract from Yanan coal (Table-6). In the nitrogen-containing organic compunds, 1-methylpiperidine (peak 3) and *O*-decyl-hydroxylamine (peak 23) were only detected in F_2, N,N-dimethyldodecan-1-amine and 3-(phenethylphenyl)-methanimine were detected in F_3 and F_4, respectively. At present, no detailed information on nitrogen functionality in coal is available because of the low concentration of the heteroatoms and elemental non-specificity of many spectral methods. In other words, concentration and subsequent identification are two important issues for understanding detailed information on nitrogen-containing organic compunds in coals.

Other compounds: Five aldehydes and five ketones were detected in the extract from Yanan coal (Table-7). In the aldehydes, (Z)-7-hexadecenal (peak 31) and (E)-2-hexenal (peak 102) contain double bonds. Meanwhile, two ketones contain cyclic structure, *e.g.*, 9,9-dimethoxybicyclo[3.3.1]-nona-2,4-dione (peak 66) and cyclic 1,2- ethanediylaetal-cholestan-3-one (peak 94).

As Table-7 shows, two novel organic iodines, *e.g.*, 1-iodo-2,3-epoxypropane (peak 97) and diiodo methane (peak 98) were only observed in F_4, to our knowledge, no literature reported them in extracts from yanan coal. Two organic bromides, including 3-bromodecane (peak 10) and 2-bromo-1,4-difluoro benzene (peak 17) were only detected in F_2.

Conclusion

In order to acquire a better knowledge of Yanan coal, a sequential extraction with petroleum ether, carbon disulfide,

TABLE-4
ALCOHOLS DETECTED IN F_1 TO F_4 FROM YANAN COAL (YAC)

No.	Compound	F_1	F_2	F_3	F_4
2	3-Methyl cyclopentanol		√		
5	(E)-2-Methyl buta-1,3-dien-1-ol		√		
7	4-Methyl-2-propyl pentanol		√		
8	2-Ethyl-2-propyl hexanol		√		
9	2-Chlorocyclohexanol		√		
19	2-Butyl octanol		√		
22	2-Dodecenol	√			√
42	Estra-1,3,5(10)-trien-17- ol		√		
48	Heptatriacotanol		√		
53	Olean-12-ene-3,28-diol		√		
59	Hexatriacontan-1-ol		√		
77	(2 E,14 E)-13-Methylheptadeca-2,14-dien-1-ol		√	√	√
79	Estra-1,3,5(10)-trien-17-ol	√			√
81	2-Butyl octan-1-ol	√	√		
88	1,4a-Dimethyl-7-(prop-1-en-2-yl)-2,3,4,4a,5,6,7,8-octahydronaphthalene-2,3-diol		√	√	
95	(E)-Hex-3-ene-2,5-diol				√
101	2,5-Cyclooctadien-1-ol				√

TABLE-5
ACIDS DETECTED IN F_1 TO F_4 FROM YANAN COAL (YAC)

No.	Compound	F_1	F_2	F_3	F_4
27	7-Methoxy piperonylic acid		√		
47	Oleic acid	√	√	√	√
50	Erucic acid		√		
55	22-Tricosenoic acid	√	√		
67	2-(2-Oxocyclooctyl)acetic acid	√			√
74	Hexadecanoic acid	√			√
75	(E)-7-Methyltridec-9-enoic acid	√			√
76	6-Octadecenoic acid	√			
103	(Z,Z)-9,12-Octadecadienoic acid				√

TABLE-6
HETEROATOM-CONTAINING ORGANIC COMPOUNDS DETECTED IN F_1 TO F_4 FROM YANAN COAL (YAC)

No.	Compound	F_1	F_2	F_3	F_4
3	1-Methyl piperidine		√		
14	2,2-Diphenyl-N-(3,3,5-trimethylcyclohexyl)acetamide	√			
20	9H-Xanthene		√		
21	4-Methyl-dibenzofuran		√		
23	O-Decyl-hydroxylamine		√		
63	1-(4-Bromobutyl)piperidine		√		
83	N,N-Dimethyldodecan-1-amine	√			
100	3-(Phenethylphenyl)methanimine		√	√	√

TABLE-7
OTHER COMPOUNDS DETECTED IN F_1 TO F_4 FROM YANAN COAL (YAC)

No.	Compound	F_1	F_2	F_3	F_4
10	3-Bromodecane		√		
16	Hexathiane		√		
17	2-Bromo-1,4-difluoro benzene		√		
31	(Z)-7-Hexadecenal		√		√
40	Octathiocane		√		
46	5-Methyl-6-heneicosen-11-one		√		
57	12-Hydroxy-1-propoxyoctadecan-2-one	√	√		
61	1,1,3-Trimethyl cyclohexane	√	√		
65	4-Tridecene				
66	9,9-Dimethoxybicyclo[3.3.1]nona-2,4-dione	√			√
69	13-Octadecenal	√			
78	2-Brom octadecanal				
87	2,3-Dimethyl-5-(trifluoromethyl)benzene-1,4-diol	√		√	
94	Cyclic 1,2-ethanediyl aetal-cholestan-3-one			√	√
96	5-Hydroxy-5-methylhexan-2-one				√
97	1-Iodo-2,3-epoxypropane				√
98	Diiodo methane				√
99	Octanal				√
102	(E)-2-Hexenal				√

methanol and acetone was conducted in Yanan coal. One hundred and five organic compounds were identified in the extracts from Yanan coal. They can be classified as arenes, esters, alcohols, acids, heteroatom-containing organic compounds and other compounds. Among them, novel compounds were found such as 1-iodo-2,3-epoxypropane and diiodo methane. Compared to traditional heating extraction, the microwave irradiation provides an essential and effective approach investigations of coal composition and structure in separable and nondestructive methods.

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