



Serious Changing the PAHs Contents in Suncun Coal through Subcritical Isopropyl Ether/Benzene Pretreatment

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ABSTRACT

Suncun coal was pretreated with subcritical isopropyl ether/benzene for observing the changes of the polycyclic aromatic hydrocarbons (PAHs) contents. The raw and pretreated coal samples were extracted by using cyclohexane as the first step then extracted by using benzene as the second step respectively. The extracts were analyzed by gas chromatograph-mass spectrometer (GC/MS), and twelve PAHs in extracts were analyzed quantitatively. The results indicated that all the extracts yields and the contents of these PAHs in extracts were different according to the pretreatments and the extracting solvents; and the PAHs contents in all the extracts from pretreated coals were much higher than them from raw coal. Both isopropyl ether and benzene are common solvents we used in laboratory and in industrial; these results show that we need *new ideas* to study the compositions, the structure and the applications of coal, as well to understand the environmental impact from coal using. And if we want to know what *the genuine coal* is, more researching work should be done.

KEYWORDS: coal; subcritical; isopropyl ether; benzene; extract; PAHs; GC/MS

Introduction

The composition analysis of coal products, especially the quantitative analysis of polycyclic aromatic

hydrocarbons (PAHs) and the related compounds in coal extracts is helpful for coal processing and utilizing. Gas chromatograph/mass spectrometer (GC/MS) is one of the most used instruments for PAHs analysis. Zong et al ^[1], and Wang et al ^[2] had reported a large number of PAHs in coal extracts through one-step extraction of coal by single or mixed solvents, they also found that the PAHs contents are different with coal types. The structure and the composition of coal are very complicated, so, the compounds in coal extracts are very complex and different according to coal samples, extracting solvents or extracting process. Zhao et al ^[3] had quantitatively analyzed PAHs in dichloromethane extract of coal and found the contents of PAHs were varied from 1.2 to 28.3 mg/kg with various coals' rank or type, and Wang et al ^[2] had found the PAHs contents ranged from 3.4-81.1 µg/g. Zhang et al ^[4] studied the extraction of fresh raw coals with three solvents respectively, they found n-C₆H₁₄ has low extraction ability, CS₂ is prefer to extract low-ring PAHs and CH₂Cl₂ to extract high-ring PAHs. Xue et al ^[5] reported that coal properties affect the PAHs distribution in coal; and the extracting time and method affect the PAHs distribution too. As well as Zhang et al ^[4], they found CS₂ is effective in extracting low molecular weight PAHs, CH₂Cl₂ is effective in extracting high molecular weight PAHs. They also found that ultrasonic extraction show a similar PAHs concentration profile with Soxhlet extraction, but the former is less efficient.

Besides extraction under normal pressure, pressurized fluid and supercritical fluid were used too. Assis et al ^[6] found that pressurized fluid extraction (PFE) is superior in the extraction of organic compounds from coal samples than all other techniques investigated, including supercritical fluids extraction (SFE), ultrasonic extraction (USE), and Soxhlet extraction (SLE). And SFE is the worst selective method for extracting some selected classes, such as aromatic hydrocarbons (AHs) and PAHs.

As we know, pretreatments, such as solvent-swelling ^[7] and oxidizing/reducing, can change the extraction yields more or less, and can change other properties of coal. Water-soluble compounds from mild oxidation of Longkou brown coal by H₂O₂ was reported last time ^[8]. Four years ago, we combined the mild pretreatments with step-by-step extraction of Xinwen coal, and by using GC/MS, four PAHs, namely, pyrene, chrysene, benzo[e]pyrene and benzo[a]pyrene were quantitatively analyzed in extracts by petroleum ether as first step and benzene as second step extractions. We found the contents of these PAHs are very different with different pretreatments ^[9]. Just like methanol, ethanol, CS₂, CH₂Cl₂, benzene, etc., isopropyl ether is a common organic solvent in laboratory and in industrial. But up to now, we cannot find reports which used isopropyl ether (Critical point: $t_c = 227.1$ °C, $P_c = 2.83$ MPa) as extraction agent for coal extraction or pressure pretreatments of coal. Recently, by using Suncun coal as sample, we had quantitatively analyzed 12 PAHs in extracts of raw coal and coal samples pretreated under 210 °C with subcritical isopropyl ether/benzene (Critical point:

$t_c = 288.8$ °C, $P_c = 4.90$ MPa), and found subcritical isopropyl ether or subcritical isopropyl ether/benzene mixture, especially the latter, can great increase the PAHs contents in extracts of pretreated coals. These results should be very important to coal utilization and to environmental protection, this article will report the latest results we obtained.

Material and Methods

Coal samples

Suncun coal collected from Suncun coal mine which located at Tai'an city, Shandong province, China, was pulverized to pass through 200 mesh screen and air dried before use. Table 1 shows the proximate and ultimate analyses of the coal sample.

Table 1. Proximate and Ultimate Analyses of Suncun Coal

proximate analysis/wt%			ultimate analysis/wt%, daf			H/C
M_{ad}	A_d	V_{daf}	C	H	N	
1.41	8.25	39.72	78.28	5.37	1.14	0.823

Pretreatment method

About 5.0 g of the coal sample was added to a 100 mL stainless steel pressure pan, added solvent [(a) 10 mL of isopropyl ether or (b) 5 mL of isopropyl ether and 5 mL of benzene mixed solvent], and screwed the lid on tightly. Moved the pressure pan and the coal sample into an oven which preheated to 483.2 K, hold at this temperature for 2 h with shaking 2 min per quarter. After taking out the pressure pan and cooled to room temperature, open the cap, moved the coal sample and solution to a glass beaker carefully; washed the inner wall of the pan with the same solvent for at least three times and the scrubbing solvent was moved together to the same beaker. With a glass dropper, separated the solution from coal sample by sucking the former to another glass beaker carefully, two products, the solutions (SLs) and the subcritical pretreated coals [(a) E01 for isopropyl ether, (b) E02 for isopropyl ether/Benzene mixture] were obtained. Dried the coal sample under 333 K and weighed it, the coal recoveries of E01, E02 can be calculated. After partly removed solvent by volatilization, the SLs were diluted to 5.00 mL for GC/MS detecting respectively; and then, the products in SLs were dried respectively and weighed, the yields of SLs were obtained.

Extracting Process

The E01, E02 were extracted with cyclohexane in Soxhlet extractors for 48 h respectively, evaporating and recovering the solvent, the cyclohexane extracts (CHs) were obtained. The E01, E02 and the extractors were dried in vacuum at 60°C for 12 h, then continued to be extracted with benzene for 48 h respectively, evaporating and recovering the solvent, the benzene extracts (BZs) were obtained as above. Raw coal (RC) was extracted with same process.

GC/MS analysis

All the CHs, BZs and the SLs were analyzed by using an Agilent 6890/5973 GC/MS. The GC was equipped with a 30 m × 0.25 mm × 0.25 μm Agilent HP-5ms column. The carrier gas was helium at a flow rate of 1.0 mL/min. The GC oven temperature program was as follows: 120 °C at the beginning, then heated to 240 °C at 10 °C/min, then heated to 300 °C at 20 °C/min, at which temperature it was kept for 5 min. The MS was set at ionization energy (EI) of 70 eV.

Ten authentic compounds, Acenaphthylene (ANY), Acenaphthene (ANA), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLT), Pyrene (PYR), Benzo[a]anthracene (BaA), Chrysene (CHR), benzo[b]fluoranthene [BbF], benzo[e]pyrene [BeP], and benzo[a]pyrene [BaP] purchased from Aldrich Chemical Company (Co.), Inc., were used for the confirmation and quantification of the compounds identified with GC/MS.

Results and Discussion

Coal recoveries and the extract yields

Table 2 lists the results of coal recoveries (CRs) from subcritical pretreatment and the extraction yields of E01, E02 and RC. For comparing conveniently, all the recoveries and extracts yields were converted to the base of raw coal.

Table 2. Coal recoveries and the extraction yields (% , RC)

Samples	CRs	Extraction Yields			
		CH	BZ	SL	Sum
E01	98.60	0.23	0.90	0.02	1.15
E02	94.90	0.73	0.52	2.82	4.07

RC	-	0.37	0.47	-	0.84
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The coal recovery (CR) of E02 is lower than CR of E01. If adds the yield of SLs, the differences of them is only 0.90%, very closely to each other. The total recoveries of E01 and E02 should be CR plus SL, they are 98.62% and 97.72% for E01 and E02 respectively, and only very small amounts were lost. The losses may be due to the water evaporation or the escape of the small molecular compounds when dried, etc.

The extraction yields of the samples are very different between each other. E02 has higher SL yield which leads to much higher Sum extraction yield of E02 than E01 and raw coal (RC). RC has the lowest Sum and the lowest BZ; E01 has the lowest CH and highest BZ.

From the CRs and the extraction yields, we can know that the subcritical pretreatment has changed the structure of coal more or less, although the temperature was not very high. Especially combining isopropyl ether with benzene, the amount of chemicals dissolved in isopropyl ether/benzene mixture, SL, was so high even higher than two times of the sum extraction yield of E01.

PAHs contents in extracts of subcritically pretreated coal and raw coal (RC)

The quantitative analysis results of 12 PAHs in all the extracts and SLs by GC/MS are listed in table 3.

Table 3. PAHs contents in extracts of subcritically pretreated coal and RC ($\mu\text{g/g RC}$)

PAHs	RC		E01			E02			Sum			Ratio
	CH	BZ	CH	BZ	SL	CH	BZ	SL	RC	E01	E02	E02/01
ANY	0.00	0.00	0.00	0.00	1.13	0.00	0.00	0.00	0.00	1.13	0.00	-
ANA	0.00	0.00	0.00	0.00	0.77	0.00	0.00	7.31	0.00	0.77	7.31	9.49
FLU	0.00	0.00	0.48	0.16	2.10	2.68	0.00	5.33	0.00	2.75	8.01	2.91
PHE	0.24	0.37	7.77	1.50	3.23	5.23	3.93	33.65	0.61	12.51	42.80	3.42
ANT	0.01	0.06	0.17	0.11	0.07	0.13	0.31	2.92	0.07	0.34	3.36	9.88
FLT	0.09	0.10	2.26	1.09	4.09	1.88	1.32	22.73	0.19	7.45	25.93	3.48
PYR	0.42	0.22	5.15	2.03	3.95	13.05	1.88	28.54	0.64	11.14	43.46	3.90
BaA*	0.03	0.05	1.56	0.61	0.29	0.36	0.69	4.98	0.08	2.46	6.03	2.45
CHR*	0.07	0.10	4.04	2.09	0.92	0.94	1.51	10.69	0.17	7.06	13.14	1.86
BbF*	0.03	0.02	2.59	1.66	0.44	0.91	0.96	5.19	0.05	4.68	7.05	1.51

BeP	0.05	0.07	2.35	1.59	0.39	0.69	0.75	3.59	0.12	4.32	5.03	1.16
BaP*	0.02	0.02	0.89	0.43	0.17	0.40	0.41	1.65	0.04	1.49	2.46	1.65
Sum	0.96	1.01	27.26	11.27	17.55	26.27	11.76	126.58	1.96	56.1	164.58	
Sum*	0.15	0.19	9.08	4.79	1.82	2.61	3.57	22.51	0.33	15.69	28.68	

* These PAHs considered as carcinogens [2].

The total contents of 12 PAHs are very different between E01, E02 and RC. Comparing to E01 and E02, the PAHs contents of RC is very low, indicates that subcritical pretreatment promotes PAHs contents in extracts significantly. Especially for E02, its PAHs contents are close to three times PAHs contents of E01, shows the great effect of benzene on extraction of PAHs. The only difference between E01 and E02 is benzene was added when subcritical pretreatment of E02. Comparing the PAHs contents, 126.58 and 17.55 $\mu\text{g/g}$ in SL, 38.03 and 38.53 $\mu\text{g/g}$ in (CH + BZ) of E02 and E01 respectively, it's very clearly that PAHs increased mainly through dissolving in SL.

Comparing to E01 and E02, both the contents of total PAHs and every single PAH in extracts of RC are very low; and expect ANY, PAHs contents in E02 are times higher than them in RC. For example, PYR, the highest content PAH in total extracts of RC, is 0.64 $\mu\text{g/g}$; and the PYR contents even only in two steps extracts (CH + BZ) from E01 and E02 are 7.18 (5.15 + 2.03) and 14.93 (13.05 + 1.88) $\mu\text{g/g}$ respectively, more than 11 and 23 times of RC. If added PYR in SL, the contents are 11.13 and 43.47 $\mu\text{g/g}$ respectively, more than 17 and 67 times of RC. As for bigger PAHs, BbF and BaP here, the differences are more significant. 0.05 $\mu\text{g/g}$ BbF was detected in CH and BZ of RC, Only one over ninety-four and one over hundred-forty-one of BbF detected in E01 and E02 respectively; and total BaP content detected in CH and BZ of RC was only one over thirty-seven of BaP content from E01, or one over sixty-two from E02. From data in Table 3, we even could find that so much high PAHs contents in pretreated coal as to much higher than PAHs content reported! [2-5, 9-12].

The bottom row of the Table 3 listed the sums of 4 carcinogenic PAHs [2] (CGPs), BaA, CHR, BbF, and BaP, detected in these samples. Their total contents in RC extracts also significantly lower than in E01 and E02, namely, CGPs detected in E01 and E02 are 48 and 87 times higher than in RC, higher than the relative multiples between the sums of total 12 PAHs in these samples; especially for the contents of BbF mentioned above.

The extraction mechanism of PAHs

So great increasing of PAHs contents had been taken place only through the subcritical pretreatment by isopropyl ether or benzene! The reason and the mechanism of these changes were not distinct up to

now, maybe need we spend a lot of time to study. Here, we can give some inferences from the results. First, the solvents used here are common organic reagents, at not a high temperature, 210 °C here, they are stable. Secondly, PAHs discussed here are stable too; all these PAHs cannot be synthesized through simple method in laboratory, so all of them should be from coal itself. Thirdly, if the increased PAHs were produced from chemical synthesis, the yields of them should be very different and ruleless. If comparing the total amount of some PAHs in E01 and E02, it can be found that the ratios of PAHs contents between E02 and E01 are very regular (The rightmost column of Table 3), they are all increase from E01 to E02; if the increase was come from chemical reaction, some PAHs should be decreased. On the other hand, if isopropyl ether had been taken part in chemical reaction, the products should not be PAHs, so the difference of PAHs contents between E01, E02 and RC are not owing to chemical reactions too.

Of course, benzene should have higher PAHs dissolving capacity than isopropyl ether and cyclohexane, but except SLs, the PAHs contents in BZs are not higher than in CHs for both E01 and E02 (Table 3). So, much higher PAHs contents in products (includes SL, CH and BZ) of E02 than E01 could not been explained only by the solubility of benzene, too. Maybe some synergistic effect exists between isopropyl ether and benzene, especially under higher pressure and higher temperature; This synergistic effect helps benzene and isopropyl ether to extract more compounds. On the other hand, π - π interactions between arenes can be destroyed at experiment temperature, lead to release PAHs trapped in the capsule structure of coal [13, 14].

Therefore, the increasing of PAHs contents should be owing to the changes of coal structures by isopropyl ether/benzene under higher pressure and higher temperature. That is, coal structure has been partly changed by subcritical isopropyl ether, and has been greater changed by subcritical isopropyl ether/benzene mixture because of their synergistic effect.

A short Summary

Some small molecular nonpolar or weak-polar organic compounds, such as cyclohexane, benzene, petroleum ether, normal hexane, normal pentane, dichloromethane, trichloromethane, acetone, etc. have been usually used as solvent in coal extracting since decades ago. From the results of this article, we can know the extraction of coal by these solvent are very incomplete. Subcritical pretreatment with isopropyl ether or benzene can increase the extracting yields of PAHs significantly; other processing maybe increases the yields greater. So, if we want to know the authentic contents of PAHs in coal, if we want to know what *the genuine coal* is, more researching work should be done.

In addition, it's regret that only 12 PAHs were quantitatively studied in this communication. We will

study more PAHs henceforward to perfect the researching work.

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