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Research Paper

Serious changing PAHs contents in Suncun coal through subcritical isopropyl ether/benzene pre-treatment

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ABSTRACT

In order to observe the changes of the polycyclic aromatic hydrocarbons (PAHs) contents Suncun coal was pre-treated with subcritical isopropyl ether/benzene. The raw and pre-treated coal samples were extracted using cyclohexane as the first step and thereafter, extracted using benzene as the second step. The extracts were analyzed by Gas Chromatograph-Mass Spectrometer (GC/MS), and twelve PAHs in extracts were quantitatively analyzed. The results indicated that according to the pre-treatments and the extracting solvents all the extracts yields and the contents of these PAHs in extracts were different, and the PAHs contents in all the extracts from pre-treated coals were much higher than the raw coal. Both isopropyl ether and benzene are common solvents used industrially and in the laboratory. These results indicate that new ideas are required to study the compositions, structure and the applications of coal, as well as, understanding the environmental impact of using coal. Further research is required to ascertain genuine coal.

Key words: 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 utilization and processing. Gas Chromatograph/Mass Spectrometer (GC/MS) is one of the most used instruments for PAHs analysis. Zong et al. (2009) and Wang and Liu (2015) reported a large number of PAHs in coal extracts through one-step extraction of coal by single or mixed solvents; they also observed that the PAHs contents are different from coal types. The structure and the composition of coal are very complicated; according to coal samples, extracting solvents or extracting processes are very complex and different in the compounds of coal extracts. Zhao et al. (2000) quantitatively analyzed PAHs in dichloromethane extract of coal indicating that the contents of PAHs varied from 1.2 to 28.3 mg/kg with various coals' rank or type. Wang and Liu (2015) also reported that the PAHs contents ranged from 3.4 to 81.1 µg/g, respectively.

Additionally, Zhang et al. (2005) studied the extraction of fresh raw coals with three solvents respectively, and observed that n-C_6H_{14} has low extraction ability, while CS_2 is preferred for the extraction of low-ring PAHs and CH_2Cl_2 for the extraction of high-ring PAHs. Xue et al. (2007) reported that coal properties affect PAHs distribution in coal, while the extracting time and method affect PAHs distribution. Zhang et al. (2005) also indicated that CS_2 is effective in extracting low molecular weight PAHs, while CH_2Cl_2 is effective in extracting high molecular weight PAHs. They also reported 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. Assis et al. (2000) established 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). SFE is the worst selective method for extracting some selected classes, such as aromatic hydrocarbons (AHs) and PAHs.

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

Pre-treatments, such as solvent-swelling (Shui et al., 2008) and oxidizing/reducing, can change the extraction yields more or less, and other properties of coal. Liu et al. (2003) reported water-soluble compounds from mild oxidation of Longkou brown coal by H_2O_2. Four years ago, the mild pre-treatments were combined with step-by-step extraction of Xinwen coal, and 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. It was observed that the contents of these PAHs are very different with different pre-treatments (Liu et al., 2014). Just like methanol, ethanol, CS_2, CH_2Cl_2, and benzene, etc, isopropyl ether is a common organic solvent in the laboratory and industries. Till date, there have been no reports on the use of isopropyl ether (Critical point: t_c = 227.1°C, P_c = 2.83 MPa) as extraction agent for coal extraction or pressure pre-treatments of coal. Recently, using Suncun coal as sample, we quantitatively analyzed twelve (12) PAHs in extracts of raw coal and coal samples pre-treated under 210°C with subcritical isopropyl ether/benzene (Critical point: t_c = 288.8°C, P_c = 4.90 MPa), and noticed that subcritical isopropyl ether or subcritical isopropyl ether/benzene mixture, especially the latter, can increase the PAHs contents in extracts of pre-treated coals. These results should be very important for coal utilization and environmental protection. This article reports the latest results obtained.

MATERIALS AND METHODS

Coal samples

Suncun coal collected from Suncun coal mine 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.

Pre-treatment method

About 5.0 g of the coal sample was added to 100 ml stainless steel pressure pan, and 10 ml of isopropyl ether added to solvent a, while 5 ml of isopropyl ether and 5 ml of benzene mixed solvent was added to solvent b and the lid tightly screwed. The pressure pan and the coal sample were placed in an oven and pre-heated to 483.2 K, hold at this temperature for 2 h with 2 min shaking per quarter. After taking out the pressure pan and allowed to cool to room temperature, the cap was opened, while the coal sample and solution were carefully moved to a glass beaker; the inner wall of the pan was washed with the same solvent for at least thrice and the scrubbing solvent moved together to the same beaker. With a glass dropper, the solution was separated from coal sample by sucking the former to another glass beaker carefully, and two products were obtained, the solutions (SLs) and the subcritical pre-treated coals [(a) E01 for isopropyl ether, and (b) E02 for isopropyl ether/Benzene mixture. The coal sample were dried under 333 K and weighed, and the coal recoveries of E01, E02 calculated. After partly removing the solvent by volatilization, the SLs were diluted to 5.00 ml for detection of GC/MS, while the products in SLs were dried and weighed respectively, and the yields of SLs obtained.

Extracting process

The E01 and 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, and continuously extracted with benzene for 48 h, respectively, and evaporating and recovering the solvent, the benzene extracts (BZs) were obtained as earlier mentioned. Raw coal (RC) was extracted using the same process.

GC/MS analysis

All the CHs, BZs and the SLs were analyzed 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, heated to 240°C at 10°C/min, and then heated again to 300°C at 20°C/min, and kept for 5 min at this temperature. The MS was set at ionization energy (EI) of 70 eV. Ten (10) 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

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

Table 3: PAHs contents in extracts of subcritically pre-treated coal and RC (μg/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 (Wang and Liu, 2015).

quantification of the compounds identified with GC/MS.

RESULTS AND DISCUSSION

Coal recoveries and the extract yields

Table 2 shows the results of coal recoveries (CRs) from subcritical pre-treatment and the extraction yields of E01, E02 and RC. For convenient comparison, all the recoveries and extracts yields were converted to the base of raw coal.

The coal recovery (CR) of E02 is lower than CR of E01. If the yield of SLs is added, the difference becomes only 0.90%, and close to each other. The total recoveries of E01 and E02 should be CR plus SL, that is, 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 water evaporation or the escape of small molecular compounds when dried, etc.

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

From the CRs and the extraction yields, it was observed that the subcritical pre-treatment changed the structure of coal more or less, although the temperature was not very high. Principally, the amount of chemicals dissolved in isopropyl ether/benzene mixture, SL, was high and higher than twice the sum extraction yield of E01 when isopropyl ether was combined with benzene.

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

Table 3 shows the quantitative analysis results of twelve (12) PAHs in all the extracts and SLs by GC/MS. The total contents of 12 PAHs between E01, E02 and RC are very different. Comparing E01 to E02, the PAHs contents of RC is very low, indicating that subcritical pre-treatment significantly promotes PAHs contents in the extracts. Especially for E02, its PAHs contents are close to thrice the PAHs contents of E01, indicating the great effect of benzene on extraction of PAHs. The only difference between E01 and E02 is the addition of benzene in subcritical pre-treatment of E02. Comparing the PAHs contents, 126.58 and 17.55 μg/g in SL, 38.03 and 38.53 μg/g in (CH + BZ) of E02 and E01 respectively, it is obvious that PAHs increased mainly by dissolving in SL.

Comparing E01 and E02, both the contents of total PAHs and every single PAH in extracts of RC are very low; Acenaphthylene (ANY), and PAHs contents in E02 are higher than RC. For example, PYR, the highest content of PAH in total extracts of RC, is 0.64 μg/g, while the PYR contents in only two steps extracts (CH + BZ) from E01 and E02 are 7.18 (5.15 + 2.03) and 14.93 (13.05 + 1.88) μg/g, respectively, more than 11 and 23 times of RC. If PYR added in SL, the contents are 11.13 and 43.47 μg/g, respectively, more than 17 and 67 times of RC. As for bigger PAHs, BbF and BaP, the differences are more significant. 0.05 μg/g BbF was detected in CH and BZ of RC. Only one over ninety-four and one over one hundred and forty-one of BbF were 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, very high PAHs contents in pre-treated coal to higher PAHs content was observed (Wang and Liu, 2015; Zhao et al., 2000; Zhang et al., 2005; Xue et al., 2007; Liu et al., 2014; Stout and Emsbo-Mattingly, 2008; Wang et al., 2010; Zubkova and Czaplicka, 2012). The bottom row of Table 3 listed the sums of four carcinogenic PAHs (CGPs), BaA, CHR, BbF, and BaP, detected in these samples (Wang and Liu, 2015). Their total contents in RC extracts was also significantly lower than in E01 and E02, namely, CGPs detected in E01 and E02 are 48 and 87 times higher than in RC, and higher than the relative multiples between the sums of total 12 PAHs in these samples, especially for the contents of BbF earlier mentioned.

The extraction mechanism of PAHs

Increasing of PAHs contents occur only through the subcritical pre-treatment by isopropyl ether or benzene. The reason and the mechanism of these changes were not distinct till date; maybe there is also need to spend time studying. Here, we can give some inferences from the results. First, the solvents used here are common organic reagents, and not kept at high temperature, 210°C, hence, they are stable. Secondly, PAHs discussed here are also stable; all these PAHs cannot be synthesized by applying a simple method in the laboratory, this shows that all of them should be from coal itself. Thirdly, if the increased PAHs were produced from chemical synthesis, the yields should be very different and ruleless. Comparing the total amount of some PAHs in E01 and E02, indicated that the ratios of PAHs contents between E02 and E01 are very regular (The rightmost column of Table 3), and they all increase from E01 to E02; if the increase comes from chemical reaction, some PAHs will decrease. On the other hand, if isopropyl ether had been taking part in chemical reaction, the products should not be PAHs, hence, the difference of PAHs contents between E01, E02 and RC are not due to chemical reactions.

Obviously, benzene should have higher PAHs dissolving capacity than isopropyl ether and cyclohexane with exception of SLs; the PAHs contents in BZs are not higher than in CHs for both E01 and E02 (Table 3). Therefore, much higher PAHs contents in products (includes SL, CH and BZ) of E02 than E01 could not be explained only by the solubility of benzene. 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, thereby leading to the release of PAHs trapped in the capsule structure of coal (Liu et al., 2008; Wang et al., 2015).

Therefore, the increase of PAHs contents is due to changes of coal structures by isopropyl ether/benzene under higher pressure and temperature. That is, coal structure has been partly changed by subcritical isopropyl ether, and greatly changed by subcritical isopropyl ether/benzene mixture as a result of their synergistic effect.

Conclusion

Some small molecular non-polar or weak-polar organic compounds, such as cyclohexane, benzene, petroleum ether, normal hexane, normal pentane, dichloromethane, trichloromethane, and acetone, etc have been used as solvent in coal extraction since decades ago. The results obtained revealed that the extractions of coal by these solvents are incomplete. Subcritical pre-treatment with isopropyl ether or benzene can increase the extracting yields of PAHs significantly; other processing may also lead to more increase in the yield. Hence, further research is required in order to ascertain the authentic contents of PAHs in coal, and to identify the genuine coal. In addition, only 12 PAHs were quantitatively studied in this research and there is need to further carry out more study on PAHs.

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