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# Small molecules from multistep extraction of coal and their effects on coal adsorption of $CH_4$

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ABSTRACT

The influence mechanism of small molecules on methane adsorbed in coal has always been one of the research hotspots in coal mine gas control and coalbed methane extraction. In this paper, three solvents, n-hexane, benzene, and tetrahydrofuran (THF), were used to make multistep extractions from three different metamorphic coals in mining areas, including Buertai (B), Huaibei (H), and Yangquan (Y). The composition of the extracts had been tested by the Gas Chromatography-Mass Spectrometer (GC/MS). The pore structures of residues were characterized by low-temperature $N_2$ and high-pressure isothermal adsorption. According to the research results, it can be shown that the types and contents of small molecules in the extracts decreased with increasing metamorphism. The ability of adsorbing methane, and changes in specific surface area and pore volume are closely related to the degree of coal metamorphism. By adding different solvents, different organic small molecules can be extracted. The multistep solvent extractions of coal will lead to the increase of porosity and the removal of small organic molecules in coal. On the one hand, the increase of porosity by extractions can increase the amount of adsorption methane on coal. On the other hand, less methane was adsorbed on coal when less small organic molecules present. The influences of extractions have the double effects in methane adsorbing on coal.

## 1. Introduction

In China, coal is still the primary energy source [1]. There are some gas outbursts every year. The total proportion of outbursts accounts for 35% in the world [2,3]. It is well known that the interaction of coal and methane may bring about some accidents. Due to the complex chemically heterogeneous structure of coal and the complicated processes occurring in interfaces between the methane and coal [4], a better understanding of the adsorption behaviors associated with coal is useful to reduce disasters. Coal-bed methane is mainly found adsorbed in coal, with a small amount in the free and solid solution states [5]. It is useful to study the coal adsorption of methane, which it can help us reveal the law of coal-bed methane occurrence and prevent serious gas disasters.

Coal is consisted of macromolecular and small organic molecules [6]. Accordingly, it is necessary to have a comprehensive grasp of the small molecular substances in coal, which is good for study the effect of methane adsorption. Small organic molecules are an important part of coal organic matter structure. The proportion of soluble organic compounds is 10%~20%, even up to 30% in highly volatile bituminous coal [7]. It consists of many kinds of organic compounds (i.e. aromatics, aliphatics, functional groups) [8]. It is interacted with macromolecular skeleton structure in different types of force, including strong forces (i.e. ion force, charge-transfer force) and weak forces (i.e. hydrogen bond, van der Waals force, complex bond force and π-π electron interaction) [9]. Zhang et al. [10] proposed that there are π-π stacking interactions or hydrogen bonds in aromatic compounds and the aliphatic compounds have more binding points which were good for forming bonds.

Solvent extraction is a good way to obtain valuable information on coal structure through studying the differences of the extract and residue. Due to all kinds of non-covalent bonds, we need to find several extractions to analyze the interaction. The single solvent cannot weaken the subordinate interactions, so we try to discuss the effect of different valence bonds expect cleaving covalent bonds [11]. By multistep extraction using different solvents, it is possible to obtain aromatics, aliphatics and heteroatom compounds by multistep extraction using different solvents. At present, most of scholars choose some organic

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**Table 1**
Proximate analysis and ultimate analysis of samples.

| Sample | Proximate analysis (w%) | | | | Ultimate analysis (w%) | | | | | $R_{0,max}$/% |
|---|---|---|---|---|---|---|---|---|---|---|
| | $M_{ad}$ | $A_{ad}$ | $V_{daf}$ | $FC_{ad}$ | $C_{daf}$ | $H_{daf}$ | $O_{daf}$[a] | $N_{daf}$ | $S_{t,d}$ | |
| B | 5.68 | 0.42 | 31.49 | 62.41 | 81.91 | 4.10 | 11.55 | 2.26 | 0.17 | 0.63 |
| H | 1.22 | 0.54 | 20.73 | 79.56 | 89.32 | 4.02 | 4.31 | 1.70 | 0.64 | 0.95 |
| Y | 1.83 | 0.17 | 13.39 | 84.61 | 90.09 | 3.69 | 3.88 | 1.77 | 0.57 | 2.82 |

[a] By difference; *M*: moisture; *A*: ash; *V*: volatile matter; *FC*: fixed carbon; $R_{0,max}$: maximum vitrinite reflectance; ad: air dry; daf: dry-and-ash-free basis; t,d: total, dry.

solvents as extraction solvents, including $CS_2$, N-methyl-2-pyrrolidone (NMP), Tetrahydrofuran (THF), benzene, n-hexane, $CH_3OH$ and $CH_3CH_2OH$ [12]. Yao et al. [13] investigated the changes of coking coal extracted by THF and found that the hydrophobicity of the coal increased, along with the decrease of the hydrophilic functional groups (hydroxyl, ether oxygen and carbonyl groups, etc.) in the coal structure. Yu et al. [14] studied the changes of coking coal extracted by THF, $CS_2$, acetic acid and showed that the content of aliphatic hydrocarbons and oxygen-containing functional groups reduced compared to raw coal after extraction. Wang et al. [11] believed that it was feasible to use different extractions to obtain the required extractions. Liu et al. [15] reported that the cutinite was sequentially extracted with four solutions and found that the non-covalent interactions played an important role in the extraction stages. So we need to find several extractions to analyze the interaction. The multistep extraction tries to help us to research the different bonds through different extractions [16]. It is necessary to take advantage of different extraction solvents to determine its molecular composition [17]. We selected sequential extraction using solvents of increasing polarity. There were n-hexane, benzene, and THF to obtain three different extracts. In the extraction stages, different substances were obtained. It is easy to extract aliphatic hydrocarbons by N-hexane in coal and the range is from $C_{14}$ to $C_{33}$. The benzene has a better selectivity to aromatic hydrocarbons, aliphatic hydrocarbons and heteroatom-containing compounds, but the range of aliphatic hydrocarbons is from $C_{11}$ to $C_{19}$ and $C_{20}$ to $C_{33}$ [11]. THF is a heteroatom compound with low viscosity and fluidity. It can go deep into the microporous structure of coal, and then dissolve more small molecular organics. Moreover, THF has a good extraction effect on small molecular organics [18].

The different kinds of soluble substances can be dissolved from coal and diffused into solvents in a time sequence, which is related to the nature of coal rank, extraction temperature and extraction method, etc. [19]. So we chose three kinds of coals, Buertai, Huaibei, and Yangquan coals, respectively. The Buertai coal is located in Jurassic coalfields with low-rank coal, which is belong to long flame coal and possesses some special characteristics in Northwest China. It is named as “high quality coal” with the characteristics of low ash, low sulfur content and high calorific value, high volatile matter content and low level of fixed carbon, can been divided into subbituminous coal ($R_{0,max} = 0.63$). The Huaibei sample is remarked as medium-rank and Permian coal, which can stand for the coal in Eastern China. The Huaibei coal is of medium volatile matter content and relatively high fixed carbon, which can be divided into bituminous coals ($R_{0,max} = 0.95$). The Yangquan coal is a typical high-rank coal in North China, which is belong to Carboniferous coal and can be classified as anthracite ($R_{0,max} = 2.82$). These three kinds of coal can reflect the typical coal of different metamorphic coals from different areas in China. They are widely representative.

It is useful to analyze the compounds extracted by these solvents to establish the structure of coal. After removing the soluble organic molecules, the pore structure can be used as a basis for predicting adsorption after extracting of the soluble organic matters. C.R. Clarkson believed that different coal metamorphism and pore structure affected the process of coal adsorption [20]. Ji et al. showed that some soluble organic molecules adsorbed some methane [21]. In this work, we studied differences in the adsorption characteristics between raw and residual coal after extraction. Therefore the effect of small organic molecules during adsorption can be investigated through the comparison. The characteristics of multistep extraction affected the pore structure and adsorption [22], which was a comprehensive study on the extraction of different coals. This research can be used to estimate the number of gas reserves and will make crucial important steps towards controlling and preventing coal steam gas disasters.

## 2. Experimental

### 2.1. Preparation of samples

The experimental coal samples were taken from three different metamorphic coals in mining areas, including Buertai (B), Huaibei (H), and Yangquan (Y). The coal samples were crushed into a powder with a particle size <74 *μm*. The temperature was set at 353 *K, and lasted* for 24 *h* in a vacuum. There is some important information related to these samples listed in Table 1.

### 2.2. Extractions

In accordance with literature, the three kinds of coal samples were deashed separately [23]. The coal sample was extracted by Soxhlet extraction. Approximately 5.0 g of the coal samples were weighed. The extraction experiments were conducted with n-hexane, benzene and tetrahydrofuran (THF), hereafter which is named as B-R, B-N, B-B, B-T, H-R, H-N, H-B, H-T, Y-R, Y-N, Y-B, Y-T (the former is the species of coal; the latter R, N, B, T is raw coal, n-hexane, benzene and THF, respectively.). The samples were first extracted with n-hexane, then benzene, and last with THF. The extraction was carried out at the boiling temperature for 36 hours. The extracts were obtained with a RE-3000 rotary evaporator. Afterwards, funnels were used to separate the solution and residual coal. At 373 *K* the residues were dried lasting for 12 *h* in a vacuum. The compounds in the extracts were subjected to GC-MS analysis using a Shimadzu QP2010 gas chromatography-mass spectrometer (EI, 70 *eV*). Rtx-5 ms capillary column was used to separation by a 30 m × 0.25 mm i. d., 0.25 *μm*. The rate of carrier gas flow was set as 1.0 *ml/min, and the gas was* helium. The injection volume was 0.4 *μL*. The temperature of this test started from 60 *℃ to* 170 *℃, and at* a rate of 5 *℃/min*. The initial temperature of this test is 60 *℃* (hold for 1 min), then increase to 170 *℃* at a rate of 5 *℃/min* and hold for 1 *min*, and finally at a rate of 3 *℃/min* to 300 *℃* (hold for 8 *min*). The temperature of the ion source is maintained at 230 *℃*, and the mass range is 30 *m/z*-500 *m/z*.

### 2.3. Low-temperature nitrogen adsorption

We frequently pay attention to the structure of pore, including pore size distribution, the specific surface area (SSA), total pore volume ($V_{total}$), and average pore diameter (APD). With the help of a low-temperature $N_2$ adsorption experiment, it is possible to determine these and distinguish them before and after solvent extraction. Low-temperature $N_2$ adsorption isotherms at 77 *K* were determined by a Micromeritics ASAP 2020 instrument. With a pressure $p/p_0$ from 0.01 to 0.99, we calculated the specific total pore volumes [24]. It is reasonable to calculate the SSA by the Brunauer-Emmett-Teller (BET) method with a pressure $p/p_0$ from 0.05 - 0.30 [25]. The $V_{total}$ was calculated by the t-plot means [26]. The density function theory (DFT) was population

**Table 2**
Compositions of different coal sample solvents multistep extract by GC/MS analysis.

| Coal sample | n-Hexane | Benzene | THF |
|---|---|---|---|
| B | Methane, oxybis [dichloro- ;<br>② Pentadecane ;<br>③ Pentadecane, 2,6,10,14-tetramethyl- ;<br>④ Naphtho[2,3-b] thiophene ;<br>⑤ Anthracene ;<br>⑥ Phenanthrene ;<br>⑦ Hexadecane, 2,6,10,14-tetramethyl- ;<br>⑧ Naphthalene, 7-butyl-1-hexyl- ;<br>⑨ Octacosane ;<br>⑩ Heneicosane ;<br>⑪ Retene ;<br>⑫ 2-methyloctacosane; | Ethanamine, N-methylene-;<br>② Trichloromethane;<br>③ Pentane, 3,3-dimethyl- ;<br>④ Butane, 2,2,3,3-tetramethyl- ;<br>⑤ Cyclohexane, methyl- ;<br>⑥ Pentane, 2,3,3-trimethyl- ;<br>⑦ Butanol, 2-ethyl- ;<br>⑧ Pentane, 3-ethyl- ;<br>⑨ Heptane, 2-methyl- ;<br>⑩ (S)-(+)-6-Methyl-1-octanol ;<br>⑪ Octyne ;<br>⑫ Cyclohexane, ethyl- ;<br>⑬ Cyclohexane, 1,1,3-trimethyl- ;<br>⑭ o-Xylene ;<br>⑮ Undecane ; | 3-Isopropoxypropylamine ;<br>② Butanoic acid, 4-hydroxy- ;<br>③ Propanoic acid, 2-methyl-, anhydride ;<br>④ Formic acid, hexyl ester ;<br>⑤ Propanoic acid, 2-methyl-, anhydride ;<br>⑥ Butanoic acid, 2-propenyl ester ;<br>⑦ 5-Hexen-1-ol ;<br>⑧ Formic acid, 3-phenylpropyl ester;<br>⑨ 2-Phenylpropyl butyrate ;<br>⑩ Hexanoic acid, 3-oxo-, ethyl ester; |
| H | Methylene chloride ;<br>② 2,2,6,6-Tetramethylheptane;<br>③ Pentane, 3-methyl- ;<br>④ Heptane ;<br>⑤ Benzene,1,1'-(1-methylethylidene) bis- | Ethanimidic acid, ethyl ester ;<br>② Ethanamine, N-methylene- ;<br>③ Pentane, 3,3-dimethyl- ;<br>④ Pentane, 2,2,4-trimethyl-<br>⑤ Cyclohexane, methyl- ;<br>⑥ Pentane, 2,3,3-trimethyl-<br>⑦ 1-Butanol, 2-ethyl- ;<br>⑧ Pyrrolidine ;<br>⑨ Heptane, 2-methyl- ;<br>⑩ (S)-(+)-6-Methyl-1-octanol ;<br>⑪ Cyclohexane, ethyl-;<br>⑫ Cyclohexane, 1,1,3-trimethyl- ;<br>⑬ Ethylbenzene ;<br>⑭ o-Xylene ;<br>⑮ Butanoic acid, 3-butenyl ester ;<br>⑯ Undecane, 4,7-dimethyl-; | 1-Hexanol, 2-ethyl- ;<br>② Propyl propionate;<br>③ Naphthalene, 1-methyl- ;<br>④ Butanoic acid, 2-propenyl ester ;<br>⑤ Butylated Hydroxytoluene;<br>⑥ Butane, 1-bromo-2-methyl-, (S)- ;<br>⑦ 4-(3,5-Di-tert-butyl-4-hydroxyphenyl)butyl acrylate;<br>⑧ Benzene, 1,3,5-tris(1-methylethyl)- ;<br>⑨ n-Hexadecanoic acid ;<br>⑩ 4-(3,5-Di-tert-butyl-4-hydroxyphenyl)butyl acrylate;<br>⑪ Octadecanoic acid ;<br>⑫ 13-Docosenamide, (Z)- ;<br>⑬ 4,4'-Ethylenebis(2,6-di-tert-butylphenol); |
| Y | Ethanamine, N-methylene- | Pentane, 3-methyl- ;<br>② Cyclohexane, methyl- ;<br>③ 1-Pentanol, 2-ethyl-4-methyl- ;<br>④ Naphthalene, 1-methyl-; | 3-Chloropropyl formate;<br>② Propanoic acid, 2-methyl-, 2-propenyl ester ;<br>③ Formic acid, hexyl ester ; |

**Table 2** (*continued*)

| Coal sample | n-Hexane | Benzene | THF |
|---|---|---|---|
| | | ⑤ Hexadecane ;<br>⑥ Phenol, 3,5-bis (1,1-dimethylethyl)- ;<br>⑦ Benzene, 1,1'-(1-methylethylidene) bis-;<br>⑧ Dibutyl phthalate; | ④ Propanoic acid, 2-methyl-, 2-propenyl ester;<br>⑤ Butanoic acid, anhydride;<br>⑥ Propanoic acid, 2-methyl-, anhydride;<br>⑦ Propanoic acid, 2-methyl-, 2-propenyl ester ;<br>⑧ Formic acid, 3-phenylpropyl ester;<br>⑨ n-Hexadecanoic acid ;<br>⑩ Octadecanoic acid ; |

with in pore size distribution [27].

### 2.4. High-pressure methane isotherms

$CH_4$ adsorption isotherms were performed with a 3H-2000PH instrument (Beishide Instrument Technology, Beijing Co., Ltd, China), which was shown in the Fig.S2 [28]. We set the temperature at 303 *K* and the pressure was set at 6 *MPa*. First, the coal samples were put in the vacuum oven. The temperature was set at 378 *K* (held for 24 *h*) to eliminate moisture, then to evacuate gases at 378 *K* (held for 10 *h*). Second, the coal samples were filled with methane at a pressure up to 6 *MP*a. After the impurities were completely removed, the sample tube was put in a constant-temperature bath at 303 *K* for over 10 *h* to ensure adsorption equilibrium was achieved at every point. Ten measurement points were done in the experiment, and the adsorption equilibrium time was approximately 12 *h*.

## 3. Results and discussion

### 3.1. Small molecules from multistep extractions

The types detected in the extracts of different coal samples after multistep extraction with different solvents can be seen clearly in Table 2. The total ion chromatogram of extracts from different coal samples was shown in Fig. S1. Some researchers characterized that small molecules are combined with van der Waals forces and hydrogen bonds [29]. There are three states consisted of the free state, and embedded state (micropore and network-embedded) [30]. The main components of the extracts were alkane in the n-hexane extraction. In the benzene extraction, aliphatic hydrocarbons and few heteroatomic compounds were detected. Among the THF extraction, the main components of the extracts were the oxygen-containing compounds. In the first extraction stage, the low molecular compounds are easy to extract, that the weak Van der Waals' forces play a major role in a free state. In the second stage, the solvents are hard to extract, which are influenced by hydrogen bond interaction or in micropore embedded state. In the late stage, these oxygen-containing compounds in the macromolecular structure of coal have stronger hydrogen bond interactions or in a network-embedded state [10].

As seen from Table 2, there were more types of substances in the THF extraction than that in the n-hexane and benzene extractions. The H and Y samples had fewer compounds than B. This is because B is low-rank coal with relatively low aromatic aggregation and many small organic molecules. In contrast, the H and Y samples have a higher degree of metamorphism. The coal was mainly composed of aromatic condensation rings and a few small-molecule compounds.

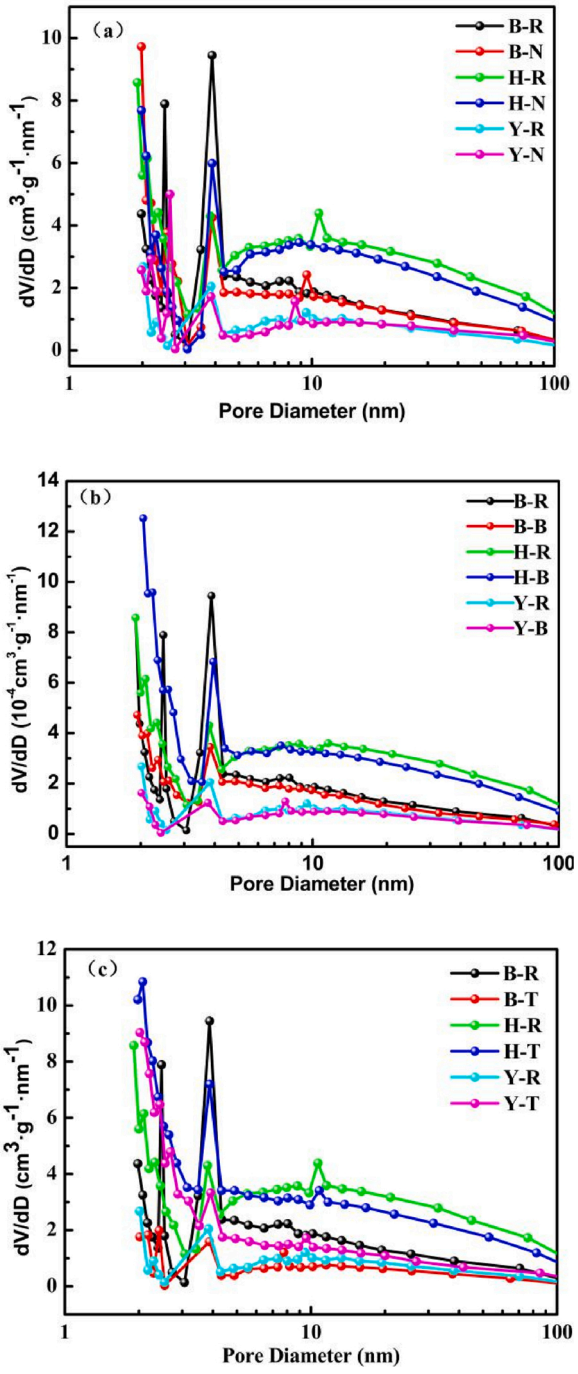



**Fig. 1.** The pore size distribution of different coal samples of (a) n-Hexane extraction of samples; (b) Benzene extraction of samples; (c) THF extraction of samples.

### 3.2. Change of pore structure

Changes in the pores were determined by low-temperature nitrogen isothermal adsorption and, high-pressure methane adsorption was utilized to determine the quantity of methane.

#### 3.2.1. Pore parameters of coal

The BET equation was used to calculate the SSA. The distribution of pore sizes is shown in Fig. 1. The $V_{total}$ and APD were obtained using Barrette-Joyner-Halenda (BJH) theory in Table 3.

The $V_{total}$ of the coal samples hardly changed after the first extraction, and the APD increased. We could infer that the extracts from n-hexane may occupy a large pore, so the APD became greater after they were extracted. This will influence the ability of adsorption $CH_4$. After benzene extraction, the APD decreased compared with the n-hexane extraction. The small molecules are always filled into micropores at first, then into macropores and finally in free state. In the process of solvent extracting, firstly the solvent can seep into some macropores, then some mecropores, and finally some micropores [31]. In the three coals, when n-hexane was used for extraction, the small molecules adsorbed in the large-diameter pores were extracted firstly. This led to increase of the proportion of macropores and the APD. But when the benzene was used for extraction, the substances were mainly extracted from the small-diameter pores. Therefore, the proportion of micropores increased and the APD decreased after benzene extraction. Namely, it formed more micropores which are good for the amount of adsorption $CH_4$. After THF extraction, different rank coals showed different extraction laws. For B coal, there were relatively more small molecular substances. For the H and Y coal, the degree of coal condensation was high, and there were few small molecules.

**Table 3**
Pore parameters of coals.

| Coal sample | APD(*nm*) | $V_{total}$ ( $cm^3 \cdot g^{-1}$) | SSA ( $m^2 \cdot g^{-1}$) |
|---|---|---|---|
| B-R | 18.66 | 0.0111 | 3.8383 |
| B-N | 20.16 | 0.0110 | 3.2320 |
| B-B | 18.68 | 0.0155 | 2.3895 |
| B-T | 23.92 | 0.0053 | 2.2346 |
| H-R | 24.67 | 0.0254 | 5.3820 |
| H-N | 25.58 | 0.0228 | 6.3573 |
| H-B | 21.66 | 0.0220 | 5.8131 |
| H-T | 18.48 | 0.0218 | 7.1912 |
| Y-R | 24.09 | 0.0067 | 2.3727 |
| Y-N | 28.22 | 0.0079 | 2.2840 |
| Y-B | 26.25 | 0.0063 | 2.0883 |
| Y-T | 17.38 | 0.0100 | 2.5203 |

The size of the pore volume was concentrated at 3-4 *nm* (Fig. 1). The detail data of pore size distribution before and after solvent extraction of different coal samples were shown in Table S1. After n-hexane extraction (Fig. 1a), the $V_{total}$ of each coal sample changed little (Table 3). After benzene extraction, the pore volume of B coal with pore diameters less than 10 *nm* increased the most obviously, which agreed with that the solvent enlarged $V_{total}$ of this section. With changing of pore diameter, the $V_{total}$ increased greatly, while the $V_{total}$ of the H and Y coal changed little. After THF extraction, the $V_{total}$ of B coal decreased slightly compared with the raw coal, indicating that the pore of the coal after solvent extraction was destroyed and the average pore size increased, resulting in the SSA and $V_{total}$ decreasing (Table 3). The micropore and mecropore of three coals increased slightly at pore diameters less than 4 *nm*. The $V_{total}$ for Y coal increased, but the change was very small. This outcome suggests that the solvent extraction changed mecropores to macropores and generated new pores with the dissolving of small molecules.

#### 3.2.2. Pore type of coal

The lines of adsorption and desorption of the three kinds of coal are shown in Fig. 2. The detail data of that type of isotherm were shown in Table S2. Based on the IUPAC classification, B should have a type II isotherm. The hysteresis loop is the H3 loop (Fig. 2a–c), which refer to layered structure, producing mesopores or macropores [32]. The results indicate that the quantity of slit-shaped pores in that coal decreased after multiple solvent extraction. For H and Y coal, the adsorption and desorption curves of low-temperature nitrogen coincided before and after solvent extraction, indicating that the pores in coal were mainly cylindrical holes with open-ends (in Fig. 2d–i).

### 3.3. Multistep extraction effect on the methane adsorption characteristics

To obtain more detailed absolute adsorption data, we set the

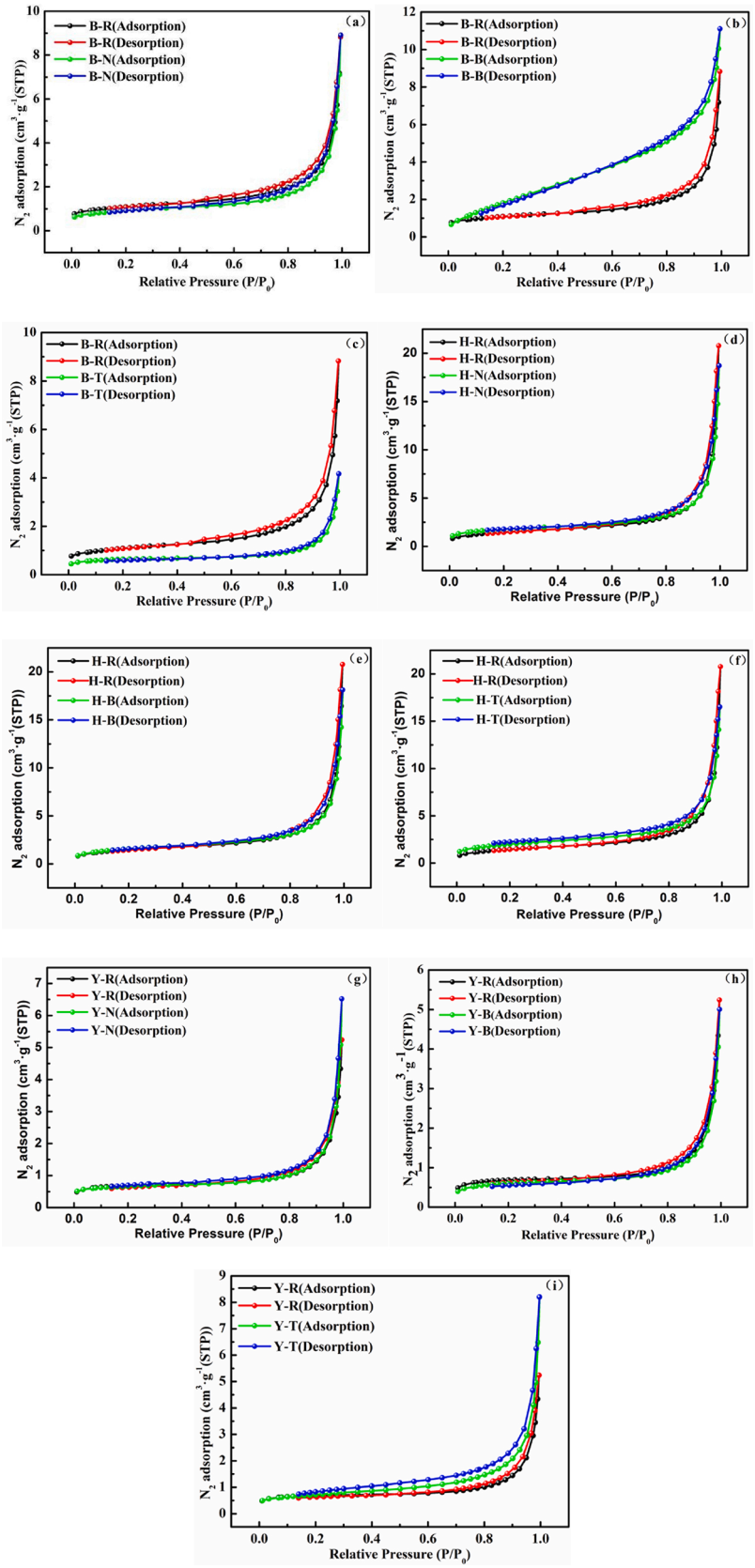



**Fig. 2.** Low-temperature nitrogen adsorption and desorption curves of (a) N-hexane extraction of Buertai; (b) Benzene extraction of Buertai; (c) THF extraction of Buertai; (d) N-hexane extraction of Huaibei; (e) Benzene extraction of Huaibei; (f) THF extraction of Huaibei; (g) N-hexane extraction of Yangquan; (h) Benzene extraction of Yangquan; (i) THF extraction of Yangquan.

**Table 4**
Maximum Methane Adsorption of Samples at 303 *K*, 6 *MPa* ($mmol \cdot g^{-1}$).

| Coal sample | Raw coal | Residue of n-hexane | Residue of benzene | Residue of THF |
|---|---|---|---|---|
| B | 0.52 | 0.32 | 0.51 | 0.45 |
| H | 0.54 | 0.44 | 0.60 | 0.51 |
| Y | 0.85 | 0.31 | 0.77 | 0.40 |

conditions at 303 *K* and 6 *MPa*. The maximum adsorption amounts are shown in Table 4. With increased pressure, the amount of all the coal samples adsorption the gas-methane increased. When the pressure reached a certain value, the adsorption value became constant, and the maximum adsorption capacity corresponded to some pressure in the order Y>H > B. The amount of the three raw coals adsorption the gas-methane was higher than their residue coals. In another words, with the help of solvent extraction the amount of the coal samples adsorption the gas-methane decreased. These outcomes were in line with what was found by previous studies [17,33,34]. In the process of sequential extraction, small molecular substances are removed. At the same time, the swelling leads to the increase of porosity. It is easier for molecules to infiltrate into the coal structure, which played an positive role in adsorption capacity in Fig. 4. The detail data were displayed in Table S3.

With the increase in pressure, the difference in the capacity of adsorption between raw coal and residual coal of Y was the largest after the primary extraction (Fig. 3). After n-hexane extraction, all of the coal samples resulted in a decrease in the methane adsorption capacity. However after benzene extraction, the amount of adsorption of methane increased. It can be concluded that the solvent swelled coal to form some new micropores, so the amount of methane adsorption is higher than that of the n-hexane extraction. After THF extraction, the adsorption capacity decreased. THF has the strongest polarity, so it can extract the largest number of small-molecule substances and species. Under the action of expanding and dredging of pores, the adsorption capacity was changed after extraction.

The APD after benzene extracting was significantly lower than that of the n-hexane extraction, and the amount of the coal samples adsorption the gas-methane was higher than that of the second-stage extraction. Y is high-rank coal with plenty of micropores, so the ability of this kind of raw coal was the highest in the adsorption methane. The content of small molecules and species in coal was less than others, so there was no significant change in pore structure or pore plugging. We can find that after n-hexane extraction, the small molecules compounds were extracted, which occupied a large number of macropores, and then led to a decrease in the ability of adsorption. When the benzene was used as the second extractant, the swelling played a leading role and formed a large number of new micropores that is beneficial for the adsorption. Therefore the swelling and molecules have the double effects on coal adsorption of methane.

In general, the ability of samples adsorption gas was related to coal rank. The amount of adsorption of raw coal was larger than the residual coals. With increasing solvent polarity, the kinds and quantities of small molecules extracted by the solvent increased. By adding different solvents, different organic small molecules can be extracted. The multistep solvent extractions of coal will lead to the increase of porosity and the removal of small organic molecules in coal. On the one hand, the increase of porosity by extractions can increase the amount of adsorption methane on coal. On the other hand, less methane was adsorbed on coal when less small organic molecules present. The influences of extractions have the double effects in methane adsorbing on coal.

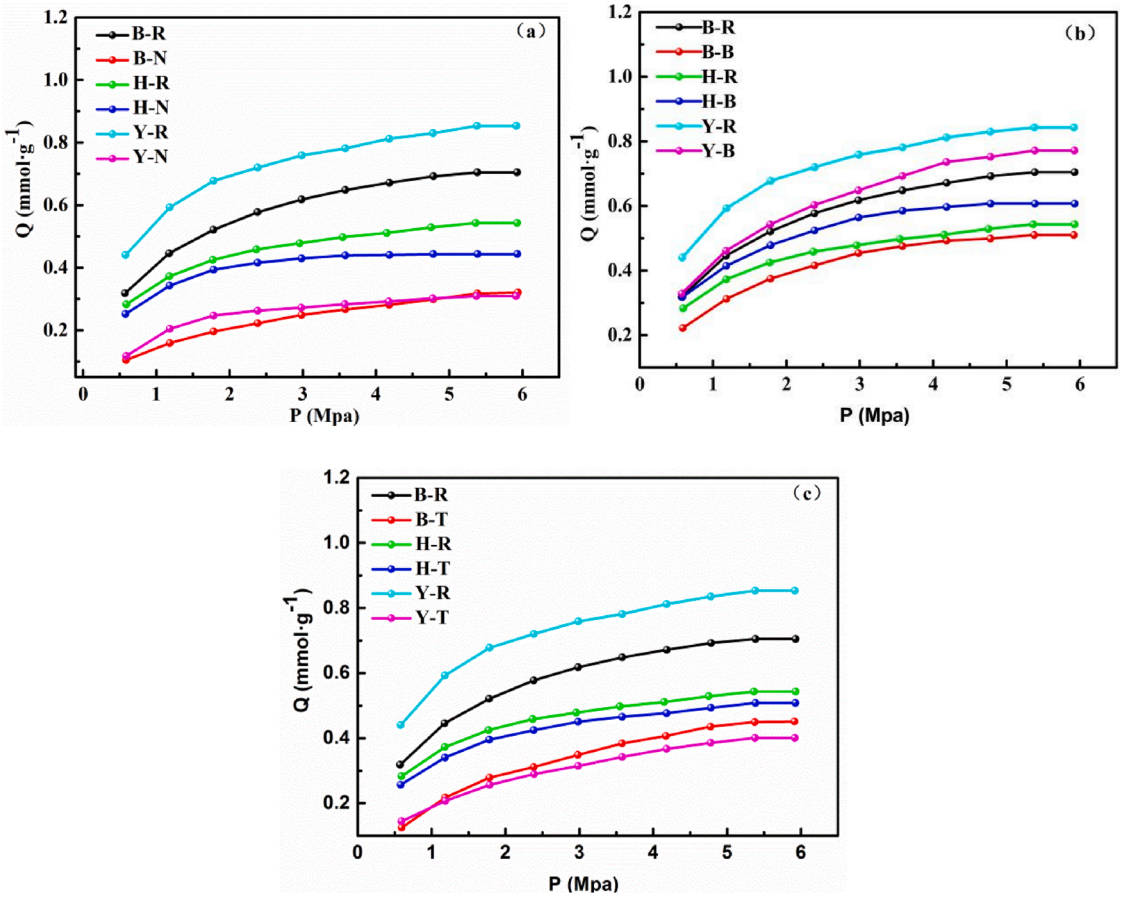



**Fig. 3.** Isothermal adsorption curves of coal samples on methane at 303 *K* of (a) N-hexane extraction of samples; (b) Benzene extraction of samples; (c) THF extraction of samples.

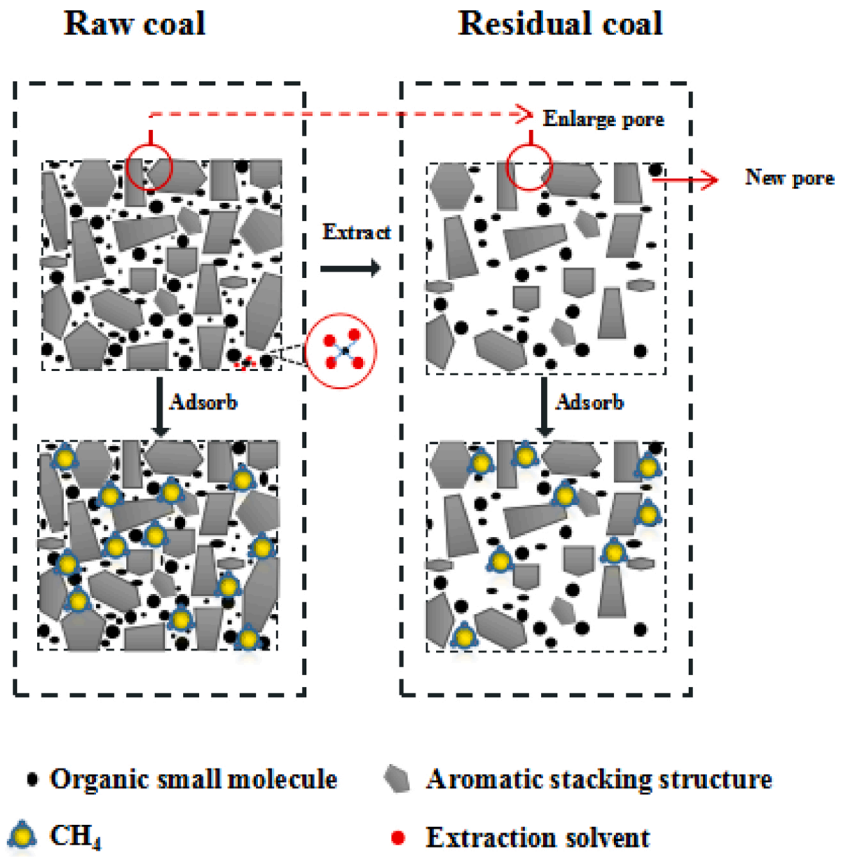



**Fig. 4.** The double effects in methane adsorbing on coal adsorption of methane.

## 4. Conclusions

Based on the GC-MS of the extracts from different ranks of coal after multistep extraction of n-hexane, benzene, and THF, combined with the results of low-temperature $N_2$ adsorption and high-pressure methane adsorption, the conclusions are as follows:

(1) The results show that the multistep extraction of coal mainly includes aromatic compounds, aliphatic substances and some heteroatom matter; as the metamorphic degree of coal rose, the types and contents of compounds in the extracts decreased.
(2) The size of the pore volume was concentrated at 3-4 *nm*. The change in the pore structure of the coal samples was related to the coal rank after extraction, which leads to an increase or decrease of the pore volume and SSA. The results of the low-temperature $N_2$ adsorption showed that solvent extraction had effects on the amount of the gas adsorption.
(3) In the n-hexane extraction stage, the low molecular compounds are easy to be extracted, because there is a free state or the forces of Van der Waals' are playing an important role. In the benzene stage, the solvents are hard to extract, which are influenced by hydrogen bond interaction or in micropore embedded state. In the THF stage, these oxygen-containing matters are provided with some hydrogen bonds which are of strong interactions with the structure of coal or in the network-embedded state.
(4) The adsorption capacity of B coal was the lowest, H coal was the second, and Y coal was the largest. The methane adsorption capacity of the raw coals was higher than their residue coals. After extraction, a decrease in small molecular organic matter leads to a decrease in methane adsorption. By adding different solvents, different organic small molecules can be extracted. The multistep solvent extractions of coal will lead to the increase of porosity and the removal of small organic molecules in coal. On the one hand, the increase of porosity by extractions can increase the amount of adsorption methane on coal. On the other hand, less methane was adsorbed on coal when less small organic molecules present. The influences of extractions have the double effects in methane adsorbing on coal.

### Associated content

Supplementary data related to this article can be found at Supporting Information.

The authors declare no competing financial interest.

### CRediT authorship contribution statement

**Zhiyuan Yang:** Methodology, Writing - original draft. **Yinyan Li:** Formal analysis, Writing - review & editing. **Wenying Xue:** Experiment, Writing - review & editing. **Zhiqiang Yin:** Investigation, Data curation. **Zhuoyue Meng:** Investigation, Data curation. **Anning Zhou:** Validation.

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## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cattod.2020.09.009.

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