Effect of Swelling by Organic Solvent on Structure, Pyrolysis, and Methanol Extraction Performance of Hefeng Bituminous Coal

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ABSTRACT: N-methyl-2-pyrrolidone (NMP), pyridine (Py), tetrahydrofuran (THF), and tetralin (THN) were used to swell Hefeng acid-washed bituminous coal (HBCAC). The swelling effect on HBCAC by each solvent is different, among which NMP presented well swelling performance, with a swelling degree of 2.11. FTIR results showed that acid washing and swelling processes presented a marginal effect on HBC, and there was no damage to the macromolecule structure of the coal. TG−DTG profiles of the swollen coals illustrated that the total weight loss of each sample was lower than that of the acid-washing one, while the temperature of the maximum weight loss rate peak was almost unchanged, around 445 °C. Extract yield by methanol followed the order of HBCAC > HBC > HBCAC−NMP (swelled by NMP), showing that acid washing promoted the methanol extraction process, with a higher extract yield of 3.21%, which is twice that of HBC (1.66%).

1. INTRODUCTION

Acid-soluble substances are the main components of minerals in coal. The acid-washing (pickling) process can remove most minerals in coal and may cause the coal structure to collapse and expand. The washing process could bring a marginal effect on crystal structures, functional group distribution, weight loss temperature, and thermochemical performance of coal. Furthermore, removing minerals from coal can promote its solvent extraction performance.1−3 Qiang et al.4 used mixed acid to treat Yongxing lignite and analyzed its structure by13C NMR. Results showed that the mixed acid treatment destroyed more or less the aromatic ring structure in the coal and made the aromatics smaller. Ma et al.5 discussed effect of acid washing on the structure and extraction performance of Hefeng bituminous coal (HBC). Results showed that acid-washing pretreatment removed minerals and inorganic salts from the coal, loosening the structure of the coal sample, with pores larger, extraction resistance reduced, and soluble components dissolved quickly. It is reported that low-rank coal contains many oxygen-containing functional groups, such as hydroxyl and carbonyl groups. These groups might combine with metal ions (Ca2+, Mg2+, etc.) in coal to form stable metal cross-links between coal macromolecules, inhibiting the solvent extraction process. A pickling process could replace the metal cations by providing hydrogen ions, breaking the metal cross-links, and improving the extraction yield.6 Li et al.7 reported the effect of pickling on metal ions in coal. It is found that metal ions could form a hydrogen bond with H+ after pickling and then cross-link with the damaged carboxylic group to form an unstable structure, which is prone to breakage during the solvent extraction process to form small molecular fragments, promoting the extraction efficiency.

Swelling has gradually become one of the main means to study the coal structure and improve its reactivity.8 Polar organic solvent is often used to swell coal samples, where solvent molecule could enter into the macromolecular network, expanding its volume, and the weak bonds in coal might break, with the binding energy between coal macromolecular structures decreasing, and fluidity of small molecular substances in coal could also be enhanced and the small molecules could be easily diffused out easily.9−11 Zhao et al.12 used three solvents, washing oil (WO), 2-methylnaphthalene (MN), and quinoline (QL), to swell Naomaohu coal samples. Results showed that C content and volatile content of the swollen coal samples are reduced to some extent comparing to the raw coal, while H and O contents increased. Shui et al.13 used toluene (TOL), N-methyl-2-pyrrolidone (NMP), and tetralin (THN) to swell coal samples, and solvent extraction and direct liquefaction of the swollen samples were also carried out.

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Table 1. Proximate and Ultimate Results of the Coal Samples

| sample    | $M_{ad}$ | $A_d$ | $V_{ad}$ | FC$_{ad}$ | C    | H    | N    | S    | O$^a$ | H/C |
|-----------|----------|-------|----------|-----------|------|------|------|------|-------|------|
| HBC       | 5.88     | 21.18 | 42.81    | 57.19     | 74.91| 5.65 | 1.50 | 0.37 | 17.57 | 0.91 |
| HBC$_{AC}$| 1.52     | 1.84  | 44.37    | 55.63     | 73.05| 5.33 | 1.50 | 0.38 | 19.74 | 0.88 |

$^a$By difference.

Figure 1. Adsorption–desorption profiles and (b) pore diameter distributions of HBC and HBC$_{AC}$.

Results showed that swelling might destroy some weak bonds between coal macromolecules, such as π–π interaction, hydrogen bond, and Van der Waals force. It is speculated that the swelling process could make the network structure of the coal to be relaxed and improve the extraction and liquefaction processes, and the distribution of extract and the coal to be relaxed and improve the extraction and liquefaction products might thus be changed. Sun et al. investigated the structure and pyrolysis characteristics of ethanol swelled coal (EDSC). Both aliphatic carbon and aromatic carbon of EDSC were reduced, with tar yield increased by 0.42 wt % and semi-coke yield decreased by 1.33 wt %. In addition, effect of solvent electron donation number (EDN), alkalinity ($pK_b$), coal to solvent ratio, and solvent molecular volume on the swelling degree of coal has been studied, and it is found that the larger the solvent EDN and $pK_b$, the higher the swelling degree of the coal.

Many extracts from coal or its derivatives play an important role in scientific research, medicine, industrial conversion, and other fields, such as the production of high-grade aromatic polymers, hydrogenation, and conversion into light oils. Due to the complex interaction between the solvent and coal, it is difficult to understand the specific behavior of solvent extraction. It is generally believed that the solvent extraction of coal is carried out through the process of solvent diffusion and penetration–cross-linking bond breaking–coal network structure opening–organic matter dissolution. Small molecules in coal are usually extracted sequentially, and the composition/structure of the extract and raffinate can be analyzed to build the relationship between extract and coal structure. The number and type of small molecules in the extract can indirectly characterize the reactivity of coal. Hua et al. discussed the dissolution of small molecules in coal during the ultrasonic-assisted extraction process and found that the complex cross-linked state of coal macromolecules was resolved under the ultrasonic field, which effectively accelerated mass transfer efficiency of the solvent, reduced extraction time, and improved extraction yield. Yu et al. compared three methods for extraction of Lihuanggou coal and found that comparing with ultrasonic-assisted extraction, microwave-assisted one is more effective in extracting polycyclic aromatic compounds from coal.

In this paper, HBC, from Xinjiang, China, was selected to reveal the effect of swelling treatment on the coal structure, heating pyrolysis, and methanol extraction performance.

2. RESULTS AND DISCUSSION

2.1. Proximate and Ultimate Analyses. Proximate and ultimate analyses of HBC and HBC$_{AC}$ are shown in Table 1. As presented in Table 1, HBC shows the features of high volatile, high H/C atomic ratio, high ash content, and low sulfur content.

It can also be seen from Table 1 that the content of ash was reduced from 21.18% for HBC to 1.84% for HBC$_{AC}$, indicating that over 90% of the ash species was removed by the acid-washing process. It is reported that the main substances removed by acid washing are crystalline SiO$_2$, Al$_2$O$_3$, and other components soluble in HCl or/and HF, and there are trace metal oxides forming insoluble salts, which are not easy to be removed. As shown in Table 1, moisture content of HBC$_{AC}$ is 1.52%, 74.15% lower than that of HBC, which might be due to the repeated “acid washing–water washing–drying” process, increasing the possibility of water release from the coal. At the same time, the decrease of water content led to the relative increase of volatile matter, which increased by 3.6 from 42.81 to 44.37%. In addition, methylene (–CH$_2$) and methyl (–CH$_3$) on the structure of organic macromolecules in the coal fall off during the acid-washing process, which leads to the decreasing hydrogen content and the ratios of H/C. In order to study the effect of acid washing on pore structures of the sample, N$_2$ adsorption–desorption characterization of HBC and HBC$_{AC}$ was carried out.

2.2. N$_2$ Adsorption–Desorption Characterization. Figure 1a shows the N$_2$ adsorption–desorption isotherms of HBC and HBC$_{AC}$, and both of them present classical IV-type curve and H3 hysteresis loop, meaning that the pickling process did not change the pore structure type of the coal and that both samples are of wedge-shaped mesoporous structure. It can be seen from Figure 1b that the pore size of HBC is
evenly distributed in the range of 30–200 nm, while the size of HBCAC is mainly located in the range of 20–30 and 60–200 nm, showing hierarchical pore structures.

Pore structure parameters of HBC and HBCAC are listed in Table 2. The specific surface area of HBCAC is increased by 3.21 times compared to HBC, and both the pore volume and pore diameter are increased by more than 2 times, which might probably be derived from the removal of ash from the coal by the acid-washing process.

2.3. Effect of Solvents on Swelling Degree. As can be seen in Figure 2, HBCAC shows different swelling degrees with different solvents. The swelling effect of NMP on HBCAC is more significant, with a swelling degree of 2.11, which is almost 2 times that of THF and THN. The swelling degree of HBCAC follows the order of NMP > Py > THF > THN, which might be related to the EDN and dipole moment (μ) of NMP. Although the solubility parameters (σ) of the four solvents are basically the same, NMP presents larger EDN (27.3) and higher μ (4.09), indicating that NMP has strong polarity and electronic supply capability, which molecules can easily penetrate and enter into the macromolecular network of coal through the diffusion effect, breaking non-covalent bond, such as hydrogen bond and Van der Waals force in coal, occupying coal’s active sites, and replacing its weak bonds, resulting in the expansion of the macromolecular structure. It can be seen from Table 1 that HBC shows higher O content, presenting high content of oxygen-containing functional groups. NMP can strongly interact with these oxygen-containing functional groups, such as hydroxyl groups, to form new hydrogen bonds, and destroy some strong interactions originally existing in coal molecules, resulting in the higher swelling performance.

2.4. FTIR Analysis. Figure 3 shows FTIR spectra of HBC, HBCAC, and the swollen samples. As shown in Figure 3, compared to HBC, hydroxyl absorption peaks (3695 and 3620 cm⁻¹) have no obvious change in HBCAC and the swollen coals, which shows that the peak intensity of free hydroxyl in inorganic minerals is weakened after pickling and swelling treatment. Other peak positions of HBC, HBCAC, and the swollen coals are almost the same, indicating that acid-washing treatment removed most inorganic minerals and showed a weak impact on organic functional groups in coal. Absorption peaks at 2920 and 2850 cm⁻¹ belonging to aliphatic −CH₂ did not change, demonstrating that acid pretreatment had almost no effect on the structure of chain aliphatic hydrocarbons. Peak at 1712 cm⁻¹ is attributed to C=O symmetric stretching vibration of aryl esters, and the peak of HBCAC is stronger than HBC, which might be due to the neutralization of H⁺ with −COOH. While the absorption peak at 1100 cm⁻¹ belonging to aryl ether or/and alkyl ether almost is almost disappeared in HBCAC, meaning that the acid washing process had great influence on the ether bond in coal. The absorption peaks around 1040, 538, and 465 cm⁻¹ are assigned to minerals. It can be seen from Figure 3 that these peaks in HBCAC are vanished, indicating that acid washing can effectively remove minerals from coal. For the bending vibration, absorption peaks out of plane of aromatic rings at 910 and 794 cm⁻¹ are greatly reduced or disappeared by pickling treatment. It is speculated that the alkyl side chains of five substitution of aromatic rings are easier to be removed than the three substitution one via acid washing.

In all samples, the FTIR absorption peaks of HBCAC and the swollen samples appear nearly at the same position, and their peak intensities are barely different, indicating that swelling treatment did not change the main organic network structure of coal. Therefore, it is found that the pretreatment of acid washing influenced the functional group of the coal sample, while swelling presented a much smaller effect on the group.

2.5. Pyrolysis Kinetics Analysis. 2.5.1. TG–DTG Profile. Thermogravimetric profiles (TG–DTG) of the samples were recorded on a SDTQ600 (TA Instruments, U.S.) instrument from room temperature to 1273 K (5 K/min, N₂ atmosphere), as shown in Figure 4.

It can be seen from TG profiles in Figure 4 that HBCAC shows an obvious weight loss trend, with the loss of 48.91%. Weight loss of HBCAC-NMP and HBCAC-Py is around 45.63%, while the loss of HBCAC-THF and HBCAC-THN is 47.06 and 48.52%, respectively. Thus, the weight loss of each sample follows the order of HBC < HBCAC-NMP ≈ HBCAC-Py < HBCAC-THF < HBCAC-THN < HBCAC-AC, which might have resulted from the fact that the weak bonds in coal macromolecules could be broken down by the acid-washing process, and the fluidity of small molecules in coal would be...
enhanced, diffusing out from coal and dissolving into the solvent, resulting in the fact that the weight loss of HBC is less than that of HBC_{AC} and the swollen samples. In addition, the swelling effect of each solvent is different due to their solubility for soluble molecules in the coal. From Figure 2, the swelling degree of HBC_{AC} followed the order of NMP > Py > THF > THN, meaning that the larger the swelling degree, the stronger the solubility for the coal sample, and the lower the weight loss.

It can be seen from Figure 4 that two gentle peaks are appeared in all swollen samples before 300 °C. Temperature of the first peak is around 80 °C, which is probably caused by drying or dehydration of coal, releasing gaseous molecules. The second one is located at 230 °C, resulting from the removal of small molecules embedded in coal or low molecular substances with weak bond with coal macro-molecular structure. The weight loss rate of HBC around 230 °C is closer to 0, and the trend of which is smoother than that of swollen coals, indicating that swelling weakened some weak bonds in coal and made coal samples more prone to pyrolysis at low temperature. In addition, temperature of the maximum weight loss rate peak for each swollen coal is located around 445 °C, indicating that swelling did not damage the macromolecular network of the coal. The maximum weight loss rates of the swollen coals are lower than that of HBC_{AC}, which might be derived from the fact that some of the soluble organic components have been dissolved and separated by the used solvent during the swelling process, resulting in the decrease of pyrolytic components.
Table 3. Pyrolysis Kinetic Parameters of the Coal Samples

| T/K   | sample      | regression equation       | R²    | E (kJ·mol⁻¹) | A (min⁻¹) | 2RT/E |
|-------|-------------|---------------------------|-------|--------------|-----------|-------|
| 473–623 | HBCAC-NMP   | y = −9538.4x + 4.4999     | 0.9545| 79.30        | 4.29 × 10⁴| 0.0734|
|       | HBCAC-Py    | y = −9642.1x + 5.0301     | 0.9582| 80.16        | 7.37 × 10⁴| 0.0726|
|       | HBCAC-THF   | y = −9325.7x + 4.3236     | 0.9526| 77.53        | 3.52 × 10⁴| 0.0751|
|       | HBCAC-TMN   | y = −9483.9x + 4.4036     | 0.9545| 78.85        | 3.88 × 10⁴| 0.0738|
|       | HBCAC       | y = −10185x + 5.5541     | 0.9632| 84.70        | 1.32 × 10⁴| 0.0687|
| 623–813 | HBCAC-NMP   | y = −20157x + 15.029      | 0.9882| 167.59       | 3.39 × 10⁵| 0.0536|
|       | HBCAC-Py    | y = −20237x + 15.137      | 0.9882| 167.59       | 3.39 × 10⁵| 0.0534|
|       | HBCAC-THF   | y = −20241x + 15.134      | 0.9885| 168.28       | 3.78 × 10⁵| 0.0534|
|       | HBCAC-TMN   | y = −20483x + 15.479      | 0.9886| 170.30       | 5.41 × 10⁵| 0.0527|
|       | HBCAC       | y = −20505x + 15.546     | 0.9885| 170.48       | 5.79 × 10⁵| 0.0527|
| 813–1173 | HBCAC-NMP   | y = −16720x + 4.076       | 0.9205| 139.01       | 4.92 × 10⁵| 0.108 |
|       | HBCAC-Py    | y = −14794x + 2.3173      | 0.9432| 123.00       | 7.51 × 10⁵| 0.122 |
|       | HBCAC-THF   | y = −15081x + 2.6598      | 0.9474| 125.38       | 1.08 × 10⁶| 0.119 |
|       | HBCAC-TMN   | y = −15099x + 2.6584      | 0.9461| 125.58       | 1.08 × 10⁶| 0.119 |
|       | HBCAC       | y = −14965x + 2.4972      | 0.9498| 124.40       | 9.09 × 10⁵| 0.120 |

2.5.2. Coast-Redfern Fitting. The Coast-Redfern method, based on the single heating rate weight loss profile, was used to fit the kinetics parameters of coal pyrolysis, including activation energy (E), regression degree (R²), and pre-exponential factor (A), which could be seen in our previous work.37,38

To analyze effect of temperature on accumulated pyrolysis conversion, the conversion—temperature relationship was obtained by taking temperature as the horizontal coordinate and accumulated pyrolysis conversion as the vertical ordinate, as shown in Figure 5a. It can be seen from Figure 5a that the points of 2RT/E → 0 and correlation coefficient R² → 1, the method showed better fitting effect as the reaction order n = 2. Thus, kinetics fitting profiles for the swollen coals have been carried out for the three stages, as shown in Figure 5b–d, and the kinetics parameters were calculated accordingly, as shown in Table 3.

Comparing the activation energy of each sample in Table 3, it could be concluded that there is no significant difference in the same pyrolysis stage, indicating that swelling did not produce obvious damage to the macromolecular network structure of the coal.

Weak bond in coal plays a key role in coal pyrolysis. Activation energy of each swollen coal was lower than that of HBCAC in the range of 473–813 K, for example, the energy of HBCAC–THF and HBCAC is 77.53 and 84.70 kJ/mol, respectively, illustrating that the used solvent presented a certain effect on coal’s weak bonds, changing the cross-linking state of macromolecules in coal and generally improving pyrolysis activity. Especially, swelling pretreatment could promote decomposition and depolymerization of macromolecular structure of coal in the pyrolysis process in the range of 623–813 K. It can also be seen from Table 4 that from the values of correlation coefficient R² (close to 1) and 2RT/E (close to 0), the fitting effect of the Coast-Redfern model is more appropriate for the second stage in the pyrolysis process. In the stage, which is the main step in coal pyrolysis, distribution of activation energy is more concentrated, and the pre-exponential factors are in the same order of magnitude, indicating that swelling did produce little impact on the mesh structure of coal.

In the region of high pyrolysis temperature (813–1173 K), except HBCAC–Py, the activation energy of each swollen sample is higher than that of HBCAC. It is speculated that we can weaken damage on the coal sample by swelling made the reaction activity of semi-coke production decrease. HBCAC–NMP shows higher activation energy of 139.01 kJ/mol, indicating that the solvent of NMP presented stronger destructive effect on the weak bonds, leaving “hard bonds” in the residue, which would require much activation energy to be pyrolyzed.

In addition, activation energy of each sample follows the order of 623–813 > 813–1173 > 473–623 K, which might have resulted from the fact that some adsorbed small molecules (CO, H₂, CH₄, and CO₂) and the molecules with less interaction with coal network structure are easy to be released during the pyrolysis process in the lower temperature region, such as 473–623 K.35,39 In the range of 623–813 K, with the intense decomposition and depolymerization processes, the cross-linking structure of coal is broken, and free hydrogen radicals might be produced. Thus, a large number of liquid phase components with higher molecular weight, such as tar and hydrocarbon liquid, are formed, and gradually solidified into semi-coke. Therefore, higher activation energy is required in the stage. In the higher temperature region, condensation reactions might be occurred, and the semi-coke could be converted to form coke with the release of some small gaseous molecules, the process of which demands less energy (showing lower activation energy). Additionally, the pre-exponential factor of each swollen coal shows a change order consistent with the activation energy, indicating that there is a compensation relationship between the factor and the activation energy.40

2.6. Extracts. 2.6.1. Yield. Figure 6 shows methanol extract yield of HBC, HBCAC, and HBCAC–NMP. It can be seen from Figure 6 that the yield of HBCAC is 3.21%, 93.4% higher than...
that of HBC, while the yield of HBC\textsubscript{AC−NMP} is lower by 0.81%. Reason for higher extract yield of HBC\textsubscript{AC} might be derived from the fact that the minerals in coal is removed by the acid-washing process, resulting in many pore channels, accelerating the diffusion performance of small soluble molecules from the main network structure of coal. In addition, swelling treatment itself is accompanied with the extraction process, and the small soluble molecules from coal dissolved in the used solvent would be carried out by the solvent removal process, decreasing the amount of soluble molecules in methanol extraction. It can also be seen from Figure 6 that after 20 extract times, the yield plot of HBC\textsubscript{AC} tends to be flat, while HBC and HBC\textsubscript{AC−NMP} get their steady extract yields until 25 extract times, showing lower extraction efficiency.

2.6.2. Functional Group. As exhibited in Figure 7, although all FTIR absorption peaks of the three extracts (HBC\textsubscript{−E}, 1620, and 1430 cm\(^{-1}\)) are ascribed to \(-\text{OH}, \text{−CH}_2, \text{−C=O}\), and stretching vibration of aromatic ring (Table 4), and the little change of each peak for the three residues demonstrates that ER\textsubscript{E}, ER\textsubscript{AC} \textsubscript{−E}, and ER\textsubscript{AC−NMP} show well structure similarity, indicating that extraction with methanol did not destroy the main structure of coal. Compared with ER, the absorption peaks at 1040 and 449–634 cm\(^{-1}\) almost disappear in ER\textsubscript{AC} and ER\textsubscript{AC−NMP}, which might be derived from the fact that minerals in HBC\textsubscript{AC} and HBC\textsubscript{AC−NMP} were removed in the acid-washing process. Comparing the main absorption peaks of the three residues, peak intensity of ER\textsubscript{AC−NMP} was higher than that of ER and ER\textsubscript{AC} indicating that the corresponding functional group contents of ER\textsubscript{AC−NMP} were higher, which might have resulted from the fact that more functional groups, such as \(-\text{OH}, \text{−CH}_2, \text{−C=O}\), and aromatic ring were exposed to the surface of coal after the sequential treatment of acid washing, NMP swelling, and methanol extraction.

Figure 6a–d shows FTIR before-and-after profiles of each coal sample. Compared with HBC, the positions of absorption peaks of ER, ranged in 3700–1600 cm\(^{-1}\), belonging to \(-\text{OH}, \text{−CH}_2, \text{−CH}_3, \text{−C=O}\), are almost unchanged, while the peak intensity of which is reduced to some extent. At 1030 cm\(^{-1}\), the intensity of \(=\text{C−O−C}\) peak ascribed to aromatics decreases significantly, indicating that more molecules containing this functional group would be obtained from HBC by methanol extraction. The intensity of peaks at 915–800 cm\(^{-1}\) belonging to three and two substitutions of benzene ring decline obviously, indicating that methanol shows well extraction effect for aromatic compounds.\textsuperscript{32,33} It can be seen from Figure 8c,d that compared with HBC\textsubscript{AC} and HBC\textsubscript{AC−NMP}, the position of each absorption peak in the corresponding FTIR curve is almost unchanged, and the peak intensity is reduced in different degrees, demonstrating that the extraction process does not damage the main functional groups of the coal macromolecular network structure.

2.7.2. TG Characteristics. Figure 9 shows TG–DTG profiles of the extract residues. According to TG diagram, the weight loss of each sample follows the order of HBC < HBC\textsubscript{AC−NMP} < HBC\textsubscript{AC} < ER\textsubscript{AC−NMP} presents higher weight loss, while the weight loss of ER and ER\textsubscript{AC} is about 45.04%, which is 3.1% lower than that of ER\textsubscript{AC−NMP}. Thus, acid washing could not be responsible for the weight loss difference, and the reason would be assigned to swelling treatment, loosening the coal network structure.

It can be seen from DTG profiles that the maximum weight loss rate peak temperature of the three extract residues is around 446 °C, illustrating that the extraction process under ultrasonic field did not damage the macromolecular skeleton structure of coal. In addition, the maximum weight loss rates of ER\textsubscript{AC−NMP} and ER\textsubscript{AC} were 0.305 and 0.297%/min, followed by ER (0.289%/min), which is nearly consistent with the trend of final weight loss obtained by TG profiles. The pyrolysis activation energy of each sample, by rough estimate from the weight loss rate, is nearly the same, demonstrating that extraction with methanol might not produce pyrolysis difference for each residue, and the difference would be derived from acid washing and swelling processes.

3. CONCLUSIONS

HBC treated sequentially by acid washing and swelling was subjected to pyrolysis and methanol extraction. Functional groups of raw coal, acid-washing coal, swollen coal, and their methanol extracts and residues were discussed in detail.
washing could not only reduce minerals in coal but also
decrease its H/C atomic ratio by washing out some small high
H/C ratio molecules and improve the methanol extraction
yield. NMP presented a superior swelling effect on acid-washed
coal, weakened the binding force between coal macro-
molecules, and reduced coal’s pyrolysis activation energy
in the range of 473−813 K. Yield of methanol extraction is as
follows: HBC AC > HBC > HBC AC. Therefore, swelling
treatment is accompanied with the extraction process, and
some small soluble molecules dissolved in the used solvent
from coal would be carried out by the solvent removal process,
decreasing the amount of soluble molecules in methanol
extraction.

4. EXPERIMENTAL SECTION

4.1. Samples and Reagents. Coal sample used in this
work was collected from Hefeng, Xinjiang, China and was
pulverized to pass through a 200-mesh sieve (<0.74 μm) and
dried at 105 °C for 2 h before the experiment.

Hydrochloric acid (35 wt %) and hydrofluoric acid (20 wt
%) were purchased from Zhiyuan Chemical Reagent Co., Ltd,
Tianjin, China. NMP (purity ≥ 99.0%), pyridine (Py, purity ≥ 99.0%),
tetrahydrofuran (THF, purity ≥ 99.0%), and tetralin (THN, purity ≥ 99.0%) were purchased from Yongsheng Fine
Chemical Co., Ltd, Tianjin, China. Methanol (purity ≥ 99.5%)
was purchased from Xin Bo Chemical Co., Ltd, Tianjin, China.
The above solvents were analytical-grade chemical reagents
and used without further purification.

4.2. Acid Washing. 30 g of HBC and 50 mL of
concentrated hydrochloric acid were placed in a 200 mL
beaker and stirred sufficiently for 4 h. Standing for 2 h, the upper liquid was removed, and the solid portion was washed several times with distilled water to neutralize. Then, same as the above procedure, 80 mL of hydrofluoric acid (20 wt %) was used to wash the solid part, after which the part was dried at 105 °C for 2 h to obtain the acid-washing coal (HBCAC).

4.3. Swelling Treatment. A scale test tube with 1 g HBCAC was placed in centrifuge and centrifuged at 4000 r/min for 15 min, and the height of the sample was recorded as \( h_1 \). 10 mL of NMP was added to the tube, swelling naturally for 48 h, and the tube was also centrifuged in the same way as above, and the height of the swollen coal was set as \( h_2 \). The mixture was washed repeatedly with acetone and dried in a vacuum drying oven at 110 °C for 8 h to obtain the swollen coal sample (HBCAC-NMP). With the same procedure, HBCAC was respectively swelled with pyridine (Py), tetrahydrofuran (THF), and THN to get the corresponding swollen coal samples, which was labeled as HBCAC-Py, HBCAC-THF, and HBCAC-THN respectively. The swelling degree of each sample was calculated as follows

\[
Q = \frac{h_2}{h_1}
\]

4.4. Ultrasonic-Assisted Extraction. Each swollen sample was treated by ultrasonic-assisted extraction with methanol at room temperature, \( F = 100 \) kHz, \( P = 210 \) W, for 2 h. The filtrate was collected and dried naturally after evaporation and concentration to obtain the extract (E). The raffinate was dried at 110 °C for 8 h to get the extract residue (ER).

Yield of extract from each sample was calculated as follows

\[
Y = \frac{G_i}{G} \times 100\%
\]

where \( Y \), \( G \), and \( G_i \) are yield of extract (wt %), mass of coal sample (daf, g), and mass of extract (g), respectively.

4.5. Characterization. The proximate analyses of samples were carried out according to the National Standard of China (GB/T 212-2008). The ultimate analyses of samples were analyzed by using a Vario EL III elemental analyzer, which was in accordance with the National Standard of China (GB/T 476-2008). The Brunauer–Emmett–Teller specific surface area, total pore volume, and average pore diameter were obtained via the \( N_2 \) adsorption and desorption isotherm method by a Builder ASAP2020 absorber (Micromeritics Builder Tech., Ltd.). The functional groups of coal samples, extracts, and residues were measured by a Fourier transform infrared spectrometer (FTIR, EQUINOX-55, Bruker, Germany) using the KBr pellet technique, where the sample (particle less than 0.075 mm) was fully mixed with KBr dried for 24 h in a drying oven at 110 °C with a mass ratio of 1:160. The spectra were recorded from 400 to 4000 cm\(^{-1}\) at a resolution of 4 cm\(^{-1}\). TG–DTG experiments were carried out on a thermogravimetric analyzer SDT-Q600. The temperature range was from room temperature to 1000 °C with a heating rate of 5 °C/min in a \( N_2 \) (99.999%) atmosphere.

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