Study on the Effect of Small Molecule Compounds on the Structure and Properties of Coal

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ABSTRACT: *In this research, small molecular compounds are extracted from Shenfu coal using solvent extraction method, then through analysis and comparison the structure and properties of coal before and after extraction of coal in order to study small molecular compounds affect the structure and properties of coal. The results show that they have been affected to varying degrees and the core of the coal structural unit aromatic ring has not been reduced, the macromolecular structure of coal has not changed after the extraction of coal. And these studies surely help to study the reaction mechanism of coal liquefaction and guide the study of coal macromolecular.*

KEYWORDS: *Small molecule compounds; The structure; The properties; Solvent extraction; Coal.*

INTRODUCTION

The small molecular compounds in coal, small molecular compounds for short, are generally defined as those organic compounds with molecular weight below 500, dissociating, adsorbing or embedding in the main structure of coal macromolecular, which can be interact with the large frame structures of coal in different ways [1-4]. So it is closely bound up to the composition, structure and properties of coal [5-7]. In the coal, small molecular compounds interacted with the main structure of coal in various forms, such as hydrogen bonding, intermolecular forces and so on. Although the proportion of small molecular compounds is not high in the coal, it plays an important role in coking performance and extraction liquification technique [8].

At present, there are few reports on the small molecular compounds in the coal at home and abroad. If small molecular compounds are extracted from coal, the composition, structure and properties of coal could be affected. Usually, the small molecular compounds are extracted from coal using solvent extraction method with benzene, THF, methanol or carbon disulfide, etc as the extraction solvent. Among the extraction solvents, THF has a low boiling point (only 65.8℃), so it will not react with coal and cannot damage the main structure of coal as well. In addition, high solubility of coal in THF is conducive to extracting small molecular compounds from coal [9-12].

In this paper, small molecular compounds are extracted from coal using solvent extraction method. Through comparison the structure and properties of coal before and after extraction of coal, the small molecular compounds affection on the structure and properties of coal is studied.

EXPERIMENTSAL SECTION

Coal samples

Shenfu coal with particle size less than 80 mesh is

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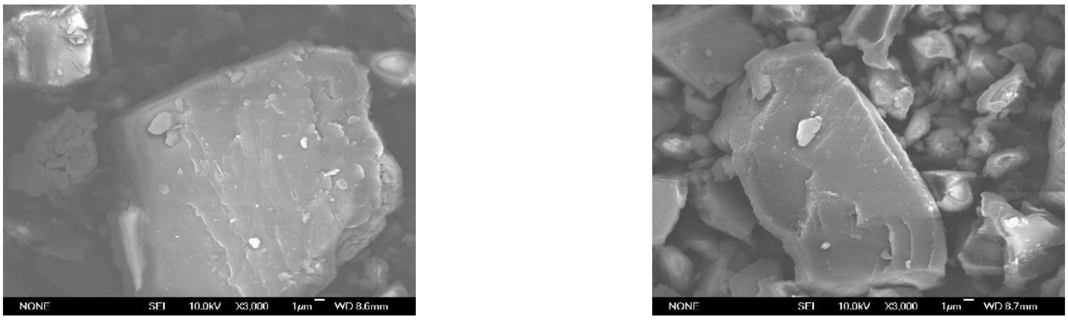
Table 1: Proximate and ultimate analysis data of Shenfu coal.

coal	Proximate analysis w /%				Ultimate analysis daf%				
	M_{ad}	A_d	V_{daf}	FC_{daf}	C	H	N	S	O*
Raw coal	2.80	6.50	39.00	61.00	78.55	4.73	0.92	0.50	15.30
Extracted coal	2.78	6.08	41.09	58.91	77.31	4.51	1.35	2.83	14.0

Obtained by the subtraction, calculated Shenfu's H / C was 0.72, the raffinate coal's H / C was 0.70.
M_{ad}:Air dry basis moisture; A_d: Dry basis ash; V_{daf}: Dry ash free volatile; FC_{daf}: Dry ash free fixed carbon



(a) SEM images of Shenfu (b) SEM images of its THF extracted residue

Fig. 1: SEM images of Shenfu raw coal and its THF extracted residue.

chosen for the study since it is suitable for coal liquefaction process. The coal samples was dryed at 100 °C for 1 hour in vacuum, and then put in the dryer [13]. Table 1 showed the proximate and ultimate analysis of coal.

Characterization

Scanning electron microscopy (SEM) was performed with a LEO-435VP scanning electron microscopy operated at 20 kV and 50 PA.

The average pore size of samples was examined by Micromeritics Tristar 3000. In each case, the sample was actived at 100 ^{O}C for 1 h and outgassed under vacuum at 250 ^{O}C for 4 h before N_2 adsorption, and finally the average pore size of samples was determined.

The coal and extraction products were characterized by Infrared spectrometer (Affinity-1 SHIMADZU).

Extraction experiments

10g Shenfu coal samples were in the Soxhlet extractor with the capacity of 500ml, and then 300ml THF was added into a round bottom flask, which connected to the condensed water. After the extraction, the extraction solution were recovered by a rotary evaporator and the leftover products of round bottom flask were small molecular compounds. Then, the small molecular compounds were placed in a brown grinding-mouth bottle. The leftover coal in the Soxhlet extractor were the THF extracted residue after THF extraction of Shenfu coal [14].

RESULTS AND DISCUSSIONS

SEM

SEM images of Shenfu coal and its THF extracted residue are presented in Fig.1. It is clear that Shenfu coal appears a flat surface, but its THF extracted residue shows porous and uneven morphology. And the average crystal size of Shenfu coal is larger than that of its THF extracted residue. This is possibily due to that the binding force between small molecular compounds and the network structure of coal macromolecular is weak, so it is weakened and destroyed easily during THF extration process. Consequently, in the process of extraction, solvent (THF) dissolved out the small molecular compounds from the network structure of coal macromolecular and it is able to continue to diffuse and permeate, and dissolve small molecular compounds of coal macromolecular further, resulting in the porous and uneven morphology of residue.

The average pore size

Fig. 2 and Fig. 3 show the average pore size of Shenfu coal and its THF extracted residue. As shown in Fig.2 and Fig. 3, the average pore size of Shenfu coal is smaller than that of its THF extracted residue, which might be caused by that micropore structures of coal are collapses during the process of extraction, leading to the larger average pore size of THF extracted residue. The larger pore sizes not only affect the mass transfer process of coal reaction, but also affect the heat transfer process of coal reaction. It is especially beneficial to "shuttle" and hydrogen transfer of hydrogen-donating solvent in the coal liquefaction reaction.

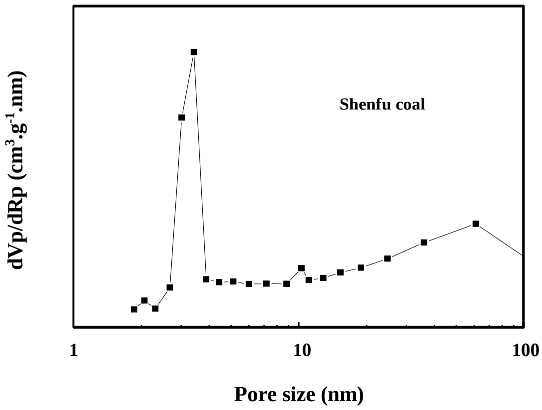


Fig. 2: The average Pore size distribution of Shenfu coal.

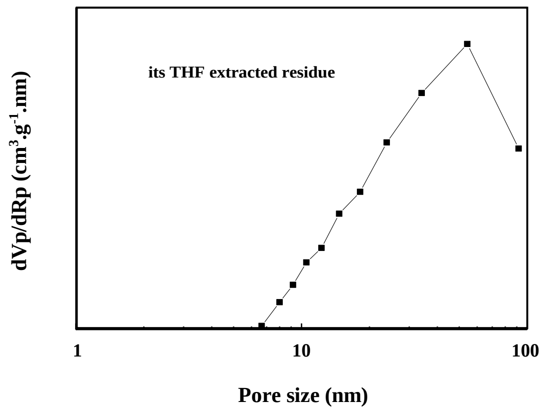


Fig. 3: The average Pore size distribution of its THF extracted residue.

IR spectrum

Fig. 4 shows the IR spectrum of Shenfu coal and its THF extracted residue. The spectrum band from 680 to 880 cm^{-1} represents out-of-plane bending vibration characteristic peak of aromatic hydrocarbon C-H, and the spectrum band from 3000 to 3100 cm^{-1} corresponds to stretching vibration characteristic peak of aromatic hydrocarbon C-H. From skeleton vibration peak change of aromatic hydrocarbon, the THF extracted residue mainly exists in the form of conjugated aromatic ring, and the absorption intensity is stronger than that of Shenfu coal, which indicates that the solvent (THF) extraction does not affect aromatic ring of basic unit in coals. 1380 cm^{-1}, 1450 cm^{-1} and 2925cm^{-1} are due to the hydrogen absorption peak of aliphatic hydrocarbons and cycloalkanes [15-16], as shown in Fig. 4, these peak intensity of Shenfu coal are stronger than those of its THF extracted residue, which illustrates that there is a small part of the small molecule compounds containing alkyl side chains dissolved off from the coal during the solvent extraction process. In addition, Fig. 4 shows that the absorption peak at 2360cm^{-1} of intensity of Shenfu coal is weaker than that of its THF extracted residue, which may be caused by that Shenfu coal is swelling during the process of extraction,, making the structure of coal loosing and thus hydrogen bond is disconnected. Consequently, the out-of-plane bending vibration is more likely to happen and the peak area increases. 1450 cm^{-1}, 1500cm^{-1}, 1580cm^{-1} and 1600cm^{-1} arising from the characteristic peak of aromatic compound [17], as shown in Fig.4, the absorption peak intensity of Shenfu coal is the same as that of its THF extracted residue.

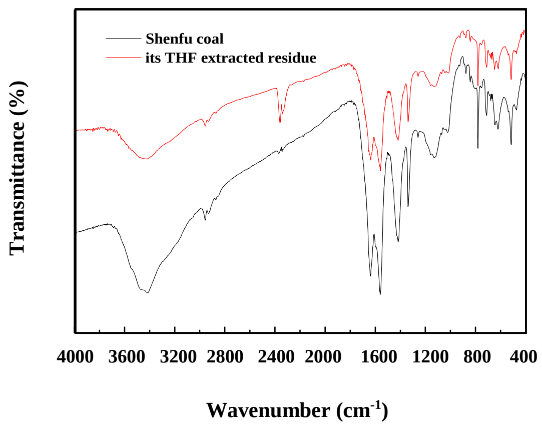


Fig. 4: IR spectrum of Shenfu coal and its THF extracted residue.

CONCLUSIONS

In this paper, the effect of small molecule compounds on the structure and properties of coal was studied through the comparison of the structure and properties of coal before and after THF extraction of coal. The experimental result shows that the surface of Shenfu coal becomes porous and the average pore size of coal increases after THF extration of coal. Also, the functional group of aliphatic hydrocarbon, naphthenic hydrocarbon, alcohol, ether and phenol decreases after small molecular compounds are extracted from coal by THF. Meanwhile, THF extration does not affect aromatic ring of basic unit in coals. These studies is help to learn the reaction mechanism of coal liquefaction and the coal macromolecular.

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