Effect of Small Molecule Compounds on the Pyrolysis Behavior of Coal

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ABSTRACT: *The effect of small molecule compounds on the pyrolysis behavior of coal is discussed by comparing TG and DTG curves of Yanzhou coal and its tetrahydrofuran (THF) extracted residual in this paper. Based on the thermal gravimetric analysis of Yanzhou coal and its THF-extracted residual, it is revealed that part of the chemical bonds are weakened after the small molecular compound is extracted from coal, which promotes the pyrolysis of its THF-extracted residual. The optimum reaction temperature is 490 °C for the high-temperature fast liquefaction of the THF-extracted residual. The maximum temperature of weight-loss rate for Yanzhou Coal and its THF extracted residual is 439 °C and 437 °C, respectively. The liquefaction reaction temperature of them is 389-490 °C and 380-525 °C, respectively. The results we studied could give some help to the further perfection of the theory of the pyrolysis behavior of coal, and its application. And it is further helpful to study the mechanism of the theory of the pyrolysis behavior of coal.*

KEYWORDS: *Coal; Small molecule compounds; Coal pyrolysis; TG; DTG.*

INTRODUCTION

Coal pyrolysis, also termed "coal carbonization", refers to that coal being heated under the condition of air isolation or inert gas atmosphere, and then occurs a series of complicated physical and chemical reactions in different scope temperatures [1-8]. And coal pyrolysis is the the initial step in coal liquefaction, accounting for up to 70% of the weight loss of the coal. It is also the process that is most dependent on the organic properties of the coal, and it is important because of its influence on the subsequent coal liquefaction [9-12]. *Gao. et al* studied the pyrolysis

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characteristics of long-flame coal and determined the product and output law of pyrolysis gas in the coal pyrolysis process, the results showed that the research results were of great significance for understanding the pyrolysis characteristics of test coal samples and the recovery and utilization of tar products [13]. *Xu. et al* researched the pyrolysis characteristics of Indonesia lignite by means of thermogravimetric analysis. The results indicated that the heating rate affects the pyrolysis characteristics of Indonesia lignite [14]. *Hu. et al* analyzed coal pyrolysis characteristics of coal samples from the Renlou coalmine, and Huaibei coalfield under different heating rates, and different grain size extent conditions from temperature 30-1000 ^{o}C process. The study thought that different heating rates had a large impact on coal pyrolysis, while the impact from grain size was on the small side. Slow heating rate and fine grain size could make coal sample pyrolysis more sufficient, and the reaction more complete, but the coking effect was inferior [15] . *Chang. et al* investigated the influence of the heating rate and particle size on the pyrolysis process in the coal pyrolysis of Hulunbeier lignite. The findings showed the heating rate and the particle size of the lignite effect the pyrolysis curve, the final weight loss did not indicate a definite rule and the maximum rate temperature increased with the heating rate increasing [16].

The small molecular compounds in coal

Small molecular compounds for short, are generally defined as those organic compounds with a molecular weight below 500 dissociating, adsorbing, and embedding in the main structure of coal macromolecular, which can interact with the large frame structures of coal in different ways [17-21]. A survey of the literature available shows that these small molecular compounds come mainly from some components of coal-forming plants (such as tree wax, resin, terpenes, and Mykola) and the compounds that are not involved in the polycondensation reaction in the process of coal-forming [22-28]. So small molecular compounds have a relation with the structure and properties of coal. When small molecular compounds are extracted from the coal, and inevitably leads to a change in the structure of coal, so some properties of coal also changed. So, it's essential to study the effect of small molecule compounds on coal pyrolysis behavior for the research of coal liquefaction.

In this paper, by comparing TG and DTG curves of Yanzhou coal and the residue of the extracted Yanzhou coal, the effect of small molecule compounds on the pyrolysis behavior of coal was discussed for the first time. And characteristic parameters of them were also discussed.

EXPERIMENTAL SECTION

Coal samples preparation

Yanzhou coal with a particle size of less than 80 mesh was chosen for the study because they were suitable for coal liquefaction. The coal samples were dried at 100 ^{o}C for 1 hour in a vacuum, and then put it in the dryer.

The THF-extracted residue of Yanzhou coal was the residue of the extracted Yanzhou coal.

Experimental testing

The extraction process of Yanzhou coal is as follows: 10g Yanzhou coal samples were in the Soxhlet extractor with a capacity of 500mL, and then add 300mL THF (AR 99.9%) was into a round bottom flask, which was connected to the condensed water. After the extraction, the extraction solution was recovered by a rotary evaporator, and the leftover products of the round bottom flask were small molecular compounds. The residue of Yanzhou coal was the THF extracted residue of Yanzhou coal.

Characterization

The ThermoGravimetric (TG)analysis was recorded on a ZRY-2P thermal analyzer (NETZSCH, Germany) at a heating rate of 10 ^{o}C/min in nitrogen (99.999%) with a flow rate of 30mL/min.

RESULTS AND DISCUSSIONS

The TG curves of Yanzhou coal and its THF-extracted residue

The TG curves of Yanzhou coal and its THF extracted residual was shown in Fig.1. As shown in Fig.1, it was found that from room temperature to 350 ^{o}C, the weight loss of Yanzhou coal was very small, only about 3%, while the weight loss of its THF-extracted residue reached about 7%. Within this temperature range, the weight loss of Yanzhou coal was attributed to the removal of water from the coal and the overflow of gas molecules (such as N_2, CH_4, etc.) adsorbed in the network structure of coal. Due to the amount of water and gas molecules being little, the weight loss of Yanzhou coal was not high and there were only physical

changes in this temperature range. While the weight loss of its THF-extracted residue was higher than that of Yanzhou coal because the THF extraction penetrated into macromolecular structures of Yanzhou coal in the process of THF extraction, and thus some small molecular compounds were dissolved in the THF and a portion of weakly bonds was further weakened. During the TG analysis of the sample, these weakly bonds broke at a lower temperature, and then some volatile compounds overflowed, resulting in the weight loss of its THF-extracted residue. And there were not only physical changes (such as dehydration, degassing, etc.) but also chemical changes in this temperature range, thus coal pyrolysis of its THF-extracted residue was more sufficient.

Part of the volatile components in the residue has been decomposed and overflowed from room temperature to 350 °C. And the THF extraction caused that weight to lose from 350 °C to 550 °C shown in Fig.1 was attributed to the active pyrolysis zone. The weight loss rate of Yanzhou coal and its THF-extracted residue reached its maximum in this temperature range. However, the weight loss rate of Yanzhou coal was higher than that of its THF-extracted residue at 420 °C. For Yanzhou coal, a large amount of volatile gas is released, and the weight loss rate is very high. For its THF-extracted residue, the portion of the small molecules, which should have decomposed and released at this zone, was dissolved in THF solvent and removed. Therefore the weight loss for its THF-extracted residue was somewhat lower than that of the primitive coal, resulting in the first decrease at 420 °C. The previous study showed that the optimum reaction temperature of high-temperature rapid liquefaction for Yanzhou coal was 490 °C. Therefore, 490 °C was used in our following study.

From Fig.1, it can be seen that the weight loss of Yanzhou coal at 490 °C was about 82.8%, which is around 8.07% above the weight loss of its THF-extracted residue. And the extraction rate for Yanzhou coal extracted by THF was about 8.30%. So, it was equal to the weight of Yanzhou primitive coal if the TG weight loss of Yanzhou primitive coal were added to the THF-treated coal. This indicated that there were major differences between the thermal decomposition of Yanzhou coal and that of its THF-extracted residue before 490 °C, Also the weight loss of Yanzhou coal and that of its THF-extracted residue were almost the same from room temperature to 490 °C. So if 490 °C was chosen as the endpoint of the pyrolysis process, there was substantially no difference in the degree of thermal decomposition of the coal body structure. Therefore, the reaction temperature of the high-temperature fast liquefaction of coal can be used as a reference for the reaction temperature of the solvent-extracted coal.

Fig. 1 showed that the weight loss of Yanzhou coal was about 77.7%, around 5% above the weight loss of its THF-extracted residue at 550 °C. And the weight loss of Yanzhou coal and that of its THF-extracted residue were not large after 550 °C, the weight loss of its THF-extracted residue gradually approached that of Yanzhou coal. This phenomenon indicated that the partial chemical bond of the coal was weakened after the extraction of the small molecule compounds, which could promote the pyrolysis of coal to a certain extent.

It was thus concluded that the partial chemical bonds of Yanzhou coal have been weakened after the small molecule compounds were extracted, which promoted the pyrolysis of the THF-extracted coal and changed its pyrolysis behavior to some extent. This was also one of the reasons why the THF-extracted coal exhibited particular characteristics or features in high-temperature rapid liquefaction.

The DTG curve of Yanzhou coal and its THF-extracted residue

Fig. 2 showed the DTG curves of Yanzhou coal and its THF-extracted residue, which were obtained by differential Thermal Gravimetric (TG)curves. From Fig. 2, It can be seen that the maximum weight loss rate of Yanzhou coal was up to 0.26%/ °C, which was much higher than that of its THF-extracted residue (0.11%/ °C). The weight loss rate interval of its THF-extracted residue was wider than that of Yanzhou coal. This was because some easy-break bonds of Yanzhou coal became further weakened and were more prone to breakage at low temperatures due to solvent extraction, leading to the forward weight loss rate interval. In addition, the pyrolysis process of its THF-extracted residue was promoted by solvent extraction in the high-temperature range, resulting in the backward weight loss rate interval. So it is the two reasons that lead to the wide weight loss rate interval.

As shown in Fig.2, the corresponding temperature to the maximum weight loss rate of Yanzhou coal and its THF-extracted residue was almost the same. This illustrated that although small molecular compounds in coal were partly removed, and some chemical bonds have been more or less weakened after solvent extraction,

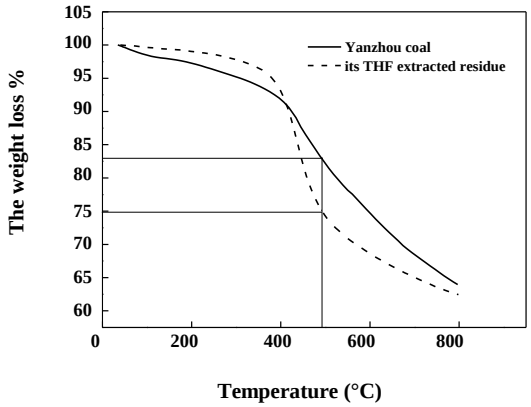

Fig. 1: TG curves of Yanzhou coal and its THF extracted residue.

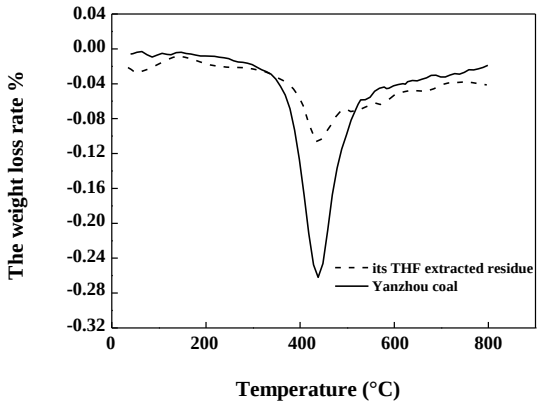

Fig. 2: DTG curves of Yanzhou coal and its THF-extracted residue

however, the main structure of coal has not been destroyed. Thus, the reaction temperature of the high-temperature fast liquefaction of coal can be used as a reference for the liquefaction reaction temperature of primitive coal.

The pyrolysis characteristics parameters of Yanzhou coal and its THF-extracted residue were shown in Table 1. As shown in Table 1, the liquefaction reaction temperature of Yanzhou coal and its THF extracted residue was 389-490 °C and 380-525 °C, respectively. Therefore, 490 °C was determined as the liquefaction reaction temperature of Yanzhou coal because 490 °C was the upper limit temperature of the thermal decomposition of Yanzhou coal, where the bridge bonds between the molecular structure units of the coal could be broken at the extreme. The width of the temperature range of the coal pyrolysis reaction temperature for Yanzhou coal was 101 °C (T_f-T_b), while the width of the THF extracted residual was 145 °C (T_f-T_b), In addition, the maximum T_m of Yanzhou coal and its THF extracted residue was 439 °C and 437 °C, respectively, and the difference of them was only 2 °C, which has once again illustrated that although some weak chemical bonds of coal have been damaged during the THF extraction, the destructive effect on the coal main structure was limited. And thermal decomposition of the main structure of coal still played a decisive role in the coal active thermal decomposition zone of coal.

T_b: the starting temperature of pyrolysis reaction; T_m: the temperature of maximum weight loss rate; T_f: the termination temperature of intense pyrolysis reaction; R_m: the maximum weight loss rate of pyrolysis reaction; V_f: the loss weight of the final temperature of pyrolysis reaction.

The T_m and the maximum weight loss rate were determined on the basis of the peak point of DTG curve.

The value of V_f was obtained from two kinds of samples' *TG* curves at 800 °C. The solution method of T_b and T_f is shown in the literature [29].

CONCLUSIONS

In this paper, the effect of small molecule compounds on the pyrolysis behavior of coal was discussed for the first time by comparing TG and DTG curves of Yanzhou coal and its THF-extracted residual. The results showed that both total weight loss and weight loss rates of the Yanzhou coal decreased after THF extraction, suggesting that the pyrolysis behavior of coal was influenced to a certain extent. Compared with the Yanzhou primitive coal, its THF-extracted residue could occur pyrolysis at low temperatures. The degree of thermal decomposition of Yanzhou coal and its THF-extracted residual was almost the same. The reaction temperature of the high-temperature fast liquefaction of its THF-extracted residue can be used as a reference for the liquefaction reaction temperature of the primitive coal.

The pyrolysis characteristics parameters of Yanzhou coal and its THF extracted residue showed that the maximum temperature of weight-loss rate for Yanzhou Coal and its THF extracted residual is 439 °C and 437 °C, respectively. Their liquefaction reaction temperature of them is 389-490 °C and 380-525 °C, respectively.

Table 1: Pyrolysis characteristics Parameters of Yanzhou coal and its THF extracted residual

Samples	T_b/ ºC	T_m/ ºC	T_f/ ºC	R_m(%/ºC)	V_f/%
Yanzhou coal	389	439	490	0.27	37.42
its THF-extracted residual	380	437	525	0.11	36.13

The research results of this paper can offer a theoretical basis for the effect of small molecule compounds of another coal type on the pyrolysis behavior of coal, which can give some help to the further perfection of the theory of the pyrolysis behavior of coal, and its application. And it is further helpful to study the mechanism of the theory of the pyrolysis behavior of coal.

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