Analysis of Pressurized Pyrolysis Behavior of Yichun Coal at Different Temperature with Gas Chromatography and Mass Spectromter

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Abstract. The fast pyrolysis connected with gas chromatography/mass spectrometer is used to explore the pyrolysis process of Yichun raw coal, and the influence of different pyrolysis temperatures on the composition and distribution of pyrolysis products under high pressure is investigated. Studies have shown that as the temperature increases, the number of volatile substances gradually decreases, which indicates that high pressure inhibits the production of volatiles. In addition, aromatic hydrocarbons in pyrolysis volatile substances dominate, and as the pyrolysis temperature increases, their content gradually increases. The volatile substances transform towards low carbon number compounds with the increment of temperature.

Keywords: Coal, pressurized fast pyrolysis, product composition, product distribution.

1. Introduction

China is a country with more coal, less oil and poor gas, and the proved coal reserves account for 13.3% of the coal reserves in world. The research report of "China's Sustainable Energy Development Strategy" points out that the proportion of coal will not be less than 50% until 2050, which shows that the basic position of coal in the national economy of China will be stable and irreplaceable for a long time [1]. The reasonable, efficient and clean utilization of coal is an urgent problem to be solved. In various conversion and utilization technologies of coal, such as combustion, gasification and liquefaction, pyrolysis plays a very important role and affects the subsequent chemical reaction process [2]. Therefore, detailed research on the coal pyrolysis is helpful to the optimization and development of related coal clean and efficient conversion technologies.

In the past, researchers focused on coal pyrolysis at atmospheric pressure. However, coal pyrolysis often faces some changes under atmospheric pressure. In addition, in recent years, the development and application of coal utilization technologies, such as Integrated Gasification Combined Cycle technology (IGCC) and pressurized fluidized-bed technology has attracted more attention, which was characterized by high gasification efficiency, low pollutant emission, and high reaction intensity. Terry F. points out that volatile substances produced by pyrolysis are affected by pressure. Furthermore, the composition and distribution of volatiles has changed [3]. Similarly, the structure and morphology of coal-char under high pressure are quite different from those under atmospheric pressure. Natalia Howaniec finds that carbon particles obtained by pressurized pyrolysis have the...
characteristics of high surface area and uneven surface [4]. Scholars, such as Wu show that coal-char is greatly affected by the pyrolysis pressure, which is mainly reflected in the high porosity of carbon particles under high pressure [5].

The investigation of pressurized pyrolysis of coal mainly focuses on the weightlessness of raw coal and the physical and chemical characteristics of coal-char, while ignoring the composition and distribution of volatile substances generated by pressurized pyrolysis of coal. The utilization of fast pyrolysis-gas/mass spectrometry (Py-GC/MS) can overcome the shortcomings of the above research method. Firstly, the fast pyrolysis device as a precision instrument has the characteristics of high heating rate, which is in line with actual working conditions [6, 7]. In addition, the volatiles produced by pressurized pyrolysis pass through the high-temperature pipeline directly into the GC-MS for the detection of detailed molecular structure [8]. On this basis, Py-GC/MS is used to explore the influence of different pyrolysis temperatures on the fast pressurized pyrolysis behavior of Yichun coal and the composition and distribution of pyrolysis volatile products.

2. Experiments

2.1. Experimental samples

Yichun coal used in experiments is a typical coal in China. The proximate analysis and ultimate analysis are obtained according to the national standards GT/T 212-2008 and GT/T 476-2001 respectively. The specific results are shown in Table 1. It can be seen from Table 1 that the content of fixed carbon and volatile of Yichun coal are both high, and the ash content is relatively low. In addition, the content of C in Yichun coal can reach 80.01%. The selected coal sample is ground and sieved to \(48 \times 10^{-3} - 75 \times 10^{-3}\) mm, and dried at 100 degrees for 2 hours for pretreatment. The processed coal sample is sealed and is stored for standby.

| Sample  | proximate analysis | ultimate analysis |
|---------|-------------------|-------------------|
|         | \(M_{\text{ad}}\) | \(A_{\text{ad}}\) | \(V_{\text{ad}}\) | \(FC_{\text{ad}}\) | \(C\) | \(H\) | \(O^*\) | \(N\) | \(S\) | \(C/H\) | \(O/H\) |
| Yichun coal | 7.68 | 7.36 | 39.85 | 45.11 | 80.01 | 5.07 | 12.88 | 1.11 | 0.94 | 1.32 | 0.16 |

Note: by difference

2.2. Experimental method

The fast pressurized pyrolysis experiments of Yichun coal are conducted on the fast pyrolysis-gas-mass spectrometer (Py-GC/MS). During the preparation process of experimental samples, quartz wool, Yichun coal and quartz wool were put into the zinc tube in sequence. Among them, the quality of raw coal is between 0.3-0.4mg. At the beginning of the experiment, the sample is put into the cracking probe and the cracking probe is placed into the valve box. The system pressure is maintained at 3MPa and the purge gas flow is 50ml/min. When the system is stable, the pyrolysis temperature, heating rate and residence time are set by the CDS program. The GC/MS real-time software will automatically record the mass spectra of volatile substances obtained by pressurized pyrolysis. Therefore, the fast pressurized pyrolysis of Yichun coal at different temperatures (600°C, 700°C, 800°C, 900°C, 1000°C) is explored, while the pressure is 3MPa, the heating rate is 3000°C/s and the residence time is 30s.

3. Results and discussion

3.1. The effect of reaction temperature on the pressure pyrolysis process of Yichun coal

Temperature is one of the key factors affecting the chemical reaction and determines the speed of the pyrolysis reaction of macromolecular polymers.
Figure 1. Total ion chromatogram of the volatiles for Yichun coal at different temperatures under 3Mpa.

Fig.1 is the total ion chromatogram of volatile substances at different temperatures obtained from Yichun coal pyrolysis at 3MPa. Among them, the abscissa is the retention time of spectral peak, and the ordinate indirectly represents the relative abundance of the pyrolysis products. When the pyrolysis temperature is 600°C, 700°C, 800°C, 900°C and 1000°C, the quantities of volatile substances detected are 355, 250, 215, 203 and 96, respectively, which means that at 3MPa, as the pyrolysis temperature increases, the number of volatile substances detected shows a downward trend. The decrease in the number of pyrolysis products is due to the double effects of pressure and temperature on the pyrolysis. On the one hand, the increment of pyrolysis temperature is beneficial to the acceleration of pyrolysis process. During the pyrolysis process, the sample particles are heated to break and decompose to form molecular fragments with different molecular weights. The higher the temperature, the more violent the reaction between molecular fragments. Moreover, larger molecular structural substance is easier to volatilize into the gas phase. Furthermore, the covalent bonds in coal can basically be broken at high temperature, and the secondary reaction of primary volatiles will also intensify, which leads to an increase in the number of pyrolysis products. On the other hand, the evaporation is one of the main mechanisms for the release of volatile substances. The properties of coal-tar itself determines that its vapor pressure is relatively low and coal-tar is easy to release at low pressure, which indirectly indicates that the volatilization of coal-tar under high pressure will be significantly inhibited. Some literature points out that the residence time of volatile substances in coal is prolonged under high pressure conditions [9, 10]. On this basis, the secondary reactions of coal-tar, such as redeposition reaction and repolymerization reaction, will improve the possibility of converting coal-tar into coal-char and light coal-gas. In addition, the small molecular compounds produced by the secondary cracking may adhere to the surface of the coal-char, resulting in a decrease in the yield of volatiles [11]. Therefore, the coal pressurized pyrolysis is subject to the competition mechanism of pressure and temperature. As the temperature increases, the reduction of volatile substances is closely related to the dominant advantage occupied by pressure.

3.2. Effect of reaction temperature on the composition and distribution of pyrolysis products
In order to understand the effect of different temperatures on the relative content during the pressurized pyrolysis, the pyrolysis volatile substances are divided into aliphatic hydrocarbons, aromatic hydrocarbons, phenols, alcohols, N-containing compounds, and O-containing compounds (except phenols, alcohols) and others. Moreover, the area normalization method is used to obtain the relative content of each component.
Fig. 2 shows the relative content of different products obtained from the Yichun coal pyrolysis at different pyrolysis temperatures under 3MPa. It can be seen from Fig. 2 that the highest content of different components at different pyrolysis temperatures is significantly different. The content of aliphatic hydrocarbons gradually decreases with the increment of pyrolysis temperature, reaching a maximum of 40.58% at 600°C. This is because the chemical structure with weak bond energy breaks at low temperature, leading to the gradual release of small molecule compounds embedded in coal. In addition, the fracture of branches in aromatic compounds and the escape of small molecular compounds with high vapor pressure under high pressure are also reasons for the increase in the content of aliphatic hydrocarbons. When the pyrolysis temperature is too high, the tendency of secondary reactions and cyclization reactions occurred in the aliphatic hydrocarbons gradually increases, resulting in a decrease in the relative content of aliphatic hydrocarbons. During the coal pyrolysis, there are many ways to generate aromatic compounds. The increase in pyrolysis temperature not only promotes the cleavage of bridge bonds to generate more aromatic hydrocarbons and phenolic precursors, but also facilitates the cracking of phenolic compounds and the secondary reaction of phenolic hydroxyl groups [12]. Therefore, the influence of pyrolysis temperature on the type and number of broken bridge bonds and subsequent secondary reactions directly leads to a rocket-like increase in the content of aromatic compounds. Phenols are an important part of volatile products. With the gradual increase of pyrolysis temperature, phenols decrease from 15.69% to 1.58%, which result from that phenol is easy to decompose and transforms into aromatic compounds at high temperature.

In order to have a deeper understanding of the composition and distribution of pyrolysis products, the relative content of the pyrolysis products is calculated according to the carbon number distribution, as shown in Fig. 3.

Fig. 3. Carbon number distributions of volatiles at different temperatures under 3MPa.
Fig. 3 is the carbon number distribution of volatile substances at different reaction temperatures under 3MPa. It can be seen from Fig. 3 that volatile substances are mainly distributed between C\textsubscript{2}-C\textsubscript{22} and C\textsubscript{27}. Considering that small molecule compounds cannot enter and be detected by GC-MS, there is no distribution of C\textsubscript{1} compounds. C\textsubscript{2} compounds are only related to N-containing compounds or other compounds. With the gradual increment of pyrolysis temperature, the pyrolysis degree of coal deepens and the secondary cracking rate of coal-tar increases, generating a large number of low-carbon compounds, mainly between C\textsubscript{6}-C\textsubscript{8}. Among them, C\textsubscript{6} compounds are mainly aliphatic hydrocarbons. Furthermore, and the content of C\textsubscript{6} compounds gradually increases with the increment of the pyrolysis temperature, which is due to the release of embedded small molecules in coal. Of course, the second cracking of macromolecular substances, straight-chain aliphatic hydrocarbons and long-chain fatty acids also plays an important role. However, the content of C\textsubscript{7} and C\textsubscript{8} compounds increases firstly and then decreases, and C\textsubscript{7} and C\textsubscript{8} compounds with relatively high content is mainly obtained at 700°C or 800°C. C\textsubscript{9}-C\textsubscript{12} compounds are mainly aromatic hydrocarbons, phenols, and a small amount of aliphatic hydrocarbon compounds. Aromatic hydrocarbons are mostly branched benzene rings and substances with more than two benzene rings. With the gradual increment of the pyrolysis temperature, the cleavage of the cross-linked aromatic ring structure and the bridge bond accelerate, generating more aromatic compounds. The increasing trend of C\textsubscript{8} compounds is also related to the cyclic dehydrogenation of alkenes. However, as the temperature continues to rise, the dehydroxylation reaction of phenolic substances has caused the content of C\textsubscript{8} compounds to decrease. In addition, the change trend of compounds with high carbon number is also very obvious, showing a downward trend and reaching the highest at 600°C. For example, C\textsubscript{18}-C\textsubscript{21} compounds are mainly composed of polycyclic aromatic hydrocarbons, supplemented by a small amount of macromolecular aliphatic hydrocarbons. The increase in temperature is conducive to the conversion of macromolecular compounds obtained from coal pyrolysis to small molecular compounds. From the perspective of the overall carbon number distribution of volatile substances, the content of compounds with low-carbon number is generally greater than that with high-carbon number compounds, which further confirms that as the temperature increases, the volatile substances produced by pressurized pyrolysis are gradually move closer to small molecular compounds.

It can be seen from Fig. 2 that volatile substances are mainly aromatic hydrocarbons. In order to better understand the effect of pyrolysis temperature on the coal pressurized pyrolysis behavior, the aromatic compounds in volatile substances were integrated according to the carbon number distribution.

![Figure 4](image-url)  
**Figure 4.** Carbon number distributions of aromatics in the volatiles at different temperatures under 3Mpa.

It can be seen from Fig. 4 that the aromatic compounds in the volatile substances are mainly concentrated between C\textsubscript{6}-C\textsubscript{19}, C\textsubscript{20} and C\textsubscript{22}. Among them, C\textsubscript{6} is the benzene series with the least carbon...
atoms. $C_{20}$ and $C_{22}$ are benzene series with a series of branched aliphatic hydrocarbons, and $C_{20}$ compounds only appear at 600°C and 700°C. At 600°C, aromatic compounds are mainly concentrated in $C_7$-$C_{10}$. Among them, C8 benzene series is a benzene ring with two methyl groups or one ethyl group or one vinyl group. As the temperature gradually rises, the branches on the benzene ring are broken to form the benzene or $C_7$ benzene series, which is also the reason why the $C_7$ benzene series content gradually rises at 700°C and 800°C. In addition, the cracking reaction of branched chain occurs in $C_7$ compound to form a single benzene ring. Therefore, the content of $C_7$ compounds shows a downward trend when the pyrolysis temperature is higher than 800°C. Simultaneously, the increasing trend of the content of benzene is very obvious. Of course, the increase of benzene content is also closely related to the dehydroxylation reaction of phenolic compounds. Similarly, the breaking reaction of branched chain in $C_9$ benzene series is the same as that in $C_8$ benzene series. From an overall point of view, the content of aromatic compounds gradually decreases with the increase of carbon number, which is related to the secondary cracking of macromolecular benzene series.

4. Conclusion

In this paper, the fast pyrolysis-gas/mass spectrometer is used to investigate the pressurized pyrolysis behavior of Yichun coal from the point of view of reaction temperature. The main conclusions are as follows: 1) Pressure will inhibit the production of volatiles. With the increase of temperature, the number of volatile substances detected was 355, 250, 215, 203 and 96, respectively, showing a gradual decrease; 2) Aromatic hydrocarbons dominate in volatile substances, and with pyrolysis temperature rises, its content shows a gradually increasing trend; 3) Volatile substances develop towards a low carbon number as the temperature rises.

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