Study on the Formation Mechanism of the Pyrolysis Products of Lignite at Different Temperatures Based on ReaxFF-MD

Xin He, Hongqing Zhu, Yujia Huo, and Wei Wang

ABSTRACT: The internal part of coal that is not in contact with oxygen will undergo pyrolysis reaction due to heat conduction, and the active groups generated can reverse-aggravate the degree of coal spontaneous combustion. At present, a few studies have been conducted on the pyrolysis mechanism of coal at different temperatures by using mutually validated experimental and simulation methods, resulting in the mismatch between the microscopic mechanism and macroscopic characteristics. In this paper, DH lignite is taken as the research object, and its macromolecular model is established. The pyrolysis reaction of lignite is studied by the experimental methods of coal pyrolysis index gas collection and detection experimental and thermogravimetric analyses and the simulation method of ReaxFF-MD. The influence of temperature on lignite pyrolysis is explored by analyzing the distribution of products at different temperatures and the formation mechanism of typical products, so as to reveal the microscopic mechanism of lignite pyrolysis. The results show that 110−500 K of experimental temperature corresponds to 1400−2400 K of simulation temperature. CO2 and C2H4 are the main gas products during pyrolysis simulation. Carboxyl and ester groups are the main source of CO2, which gradually increases with the rise of temperature. Since CO2 can be reduced to produce CO, H2O, and C2H2O at high temperatures, the yield decreases when the temperature is higher than 2000 K. C2H4 is derived from the decomposition of long-chain aliphatic hydrocarbons, and its yield fluctuation rises with the rise of temperature. The formation of H2O and H2 mainly occurs in the secondary pyrolysis stage. When 1400 K < T < 2100 K, the primary pyrolysis is the main reaction, where the weak bridge bonds and macromolecular structure undergo cleavage to form gas products and tar free radical fragments. When T > 2100 K, the secondary pyrolysis reactions were significant. Tar free radicals and char undergo decomposition, hydrogenation, and polymerization reaction, gas products and tar free radicals increase, and the char yield decreases compared with the primary pyrolysis stage, so 2100 K is the key temperature of the pyrolysis reaction. The research is of great importance in improving the accurate control of coal spontaneous combustion.

1. INTRODUCTION

Coal is the main traditional energy source, which dominates the world’s energy consumption, especially in China.1 Lignite is a kind of widely used low-rank coal that has large reserves, low cost, high chemical reactivity, and low pollution.2,3 However, it also has some defects, such as low calorific value, high moisture content, and high spontaneous combustion tendency.4 The process of coal spontaneous combustion is very complex. For a long time, scholars at home and abroad have carried out a lot of research on the mechanism of coal spontaneous combustion, and the coal oxygen composite theory has been most widely recognized.5,6 However, the internal part of coal that is not in contact with oxygen will undergo pyrolysis reaction due to heat conduction, and the active groups generated can reverse-aggravate the degree of coal spontaneous combustion.7−9 Therefore, it is necessary to conduct scientific research based on the inherent mechanism of pyrolysis. The analysis of the pyrolysis chain reaction process on this basis also plays an important role in improving the accurate control of coal spontaneous combustion disaster, which is the key to the safe production of coal mines.

Coal pyrolysis refers to a series of physical and chemical changes that occur when coal is heated under an isolated atmosphere or inert atmosphere. The organic matter in coal can be pyrolyzed to produce char, tar, and gas. The chemical process of coal pyrolysis is very complicated, mainly involving bond breaking, vaporization, and polyreaction. These reactions...
form three parallel reaction sequences: the thermal decomposition of surface functional groups forms gas; the degradation of macromolecules produces smaller fragments and then leads to evolution into tar; volatile substances and tar are transported to the outside of coal particles through the mass transport process, and the remaining solid product is char. In the previous research on coal pyrolysis behavior, scholars have carried out a large number of experimental studies. Mandapati and Ghodke evaluated the applicability of the commonly used pyrolysis kinetic model of lignite from India through mass loss experiments and gas evolution experiment under different conditions. Xu et al. use a self-researched fixed bed reactor, TG, GC, GC/MS, BET, SEM, FTIR, and chemical means. The morphology and functional structure changes of semichar were investigated. They found the optimum reaction conditions for the formation of tar and pyrolytic gas. Liu et al. carried out a pyrolysis test in a quartz tube reactor. The structural characteristics and thermal weight loss of coal were analyzed by elemental analysis, $^{13}$C-NMR, FTIR, and chemical means. The morphology and functional structure changes of semichar were investigated. They found the optimum reaction conditions for the formation of tar and pyrolytic gas. Liu et al. carried out a pyrolysis test in a quartz tube reactor. The structural characteristics and thermal weight loss of coal were analyzed by elemental analysis, $^{13}$C-NMR, FTIR, and TG. They studied the relationship between structural characteristics and product distribution of lignite and concluded that the formation of pyrolytic products is related to the breaking of chemical bonds and the decomposition of functional groups. Scholars use TG, GC, and MS analysis equipment to analyze and study the weight loss characteristics and gas production law of pyrolysis reaction through experimental research methods and use elemental analysis, $^{13}$C-NMR, FTIR, and other detection methods to study the structural change characteristics of coal samples in pyrolysis reaction. In recent years, on the basis of macro-experiments, scholars have studied the micro-mechanism of pyrolysis behavior on the molecular scale through molecular dynamic simulation. ReaxFF is a force field method developed in recent years to describe the activity of breaking bonds, bonding, and chemical reactions. It is an effective method to study complex phenomena such as complex chemical reactions under extreme conditions. It can almost reproduce the accuracy of quantum mechanics in the reaction system, including reactants, transition states, and products. Liu et al. studied the pyrolysis process of perfluorinated ketones at different temperatures (300–5000 K) by using ReaxFF. Salmon et al., Yan et al., and Chen et
### 2. RESULTS AND DISCUSSION

#### 2.1. Comparison between Simulation Results and Experimental Results

Figure 1a shows the concentration change curves of CO$_2$, CO, and C$_2$H$_4$, which is from DH lignite pyrolysis and the molecular number of C$_2$H$_4$ from ReaxFF-MD. A large amount of CO$_2$ and CO is detected in the temperature range of 40–440 °C, and the concentration is directly proportional to the temperature. C$_2$H$_4$ is produced at 110 °C, and the concentration is also directly proportional to the temperature. In the process of experiments, CO$_2$ and CO can form from desorption and chemical reaction at the same time. Therefore, C$_2$H$_4$ is selected as the reference gas and the corresponding relationship between experiment and simulation temperatures is determined according to the temperature point generated. The temperature of coal pyrolysis experiment is usually less than 1300 K. However, the reaction rate is increased by selecting temperatures higher than normal experimental conditions according to the harmonic transition state theory and the principle of time temperature equivalence. This is to observe the chemical reaction process more clearly in the simulation time. The ReaxFF-MD simulation temperature is increased to 1300–2400 K and C$_2$H$_4$ is formed at 1400 K. When it reaches 2400 K, the concentration of C$_2$H$_4$ increases continuously, and the change trend is similar to the experimental value. It can be preliminarily considered that the experimental and simulated temperature ranges correspond well.

Figure 1b shows the comparison diagram of DH lignite pyrolysis TG curve and ReaxFF-MD results. TG shows the change curve of the thermal weight loss of coal sample under a N$_2$ atmosphere of 30–900 °C and DTG reflects the change trend of TG. The TG decreases rapidly below 150 °C, which is mainly due to the evaporation of water and the desorption of adsorbed gas in the coal. When the temperature reaches 300 °C, it is in the active decomposition stage of pyrolysis reaction, and the thermogravimetric phenomenon is obvious. When the temperature is higher than 700 °C, the TG tends to be stable. To more accurately determine the corresponding relationship between simulation and experimental temperature thresholds, ReaxFF-MD simulation is also carried out at 2600, 2800, and 3000 K. It can be seen that the result of ReaxFF-MD at 1400–1800 K is higher than that of the TG, which is mainly due to the physical desorption of adsorbed gas in the drying and degassing stage of pyrolysis reaction, but there is only chemical reaction in the simulation results. In the range of 1800–2200 K, the simulated value is lower than that of experiment. At this time, the pyrolysis is in the decomposition stage and the chemical reaction increases. There are many influencing factors that can lead to the incomplete reaction in the experiment, such as particle size, heating conditions, and so on. When the simulation temperature is above 2300 K, the simulation results are in good agreement with the experimental results. Based on the above analysis, 110–500 °C of experiment corresponds to...
1400–2400 K of simulation. Therefore, through the comprehensive comparative analysis of gas chromatography and thermogravimetric data, it can be considered that the ReaxFF-MD method is effective to analyze the reaction mechanism in the early stage of coal pyrolysis.

2.2. Pyrolysis Products of Lignite. The ReaxFF-MD pyrolysis simulation of the lignite molecular model can observe the structure change in the ps range and predict the chemical reaction process. The structure change and the crushing process of lignite in the early stage of pyrolysis were studied in this paper, and the evolution of gas, tar, and char was analyzed.

The pyrolysis products are mainly divided into gas, tar, and char. According to the mass distribution of char and tar used in previous CPD models, it can be divided into char with more than 40 carbon atoms, heavy tar with 14–40 carbon atoms, and light tar with 5–13 carbon atoms. In addition, the fragments with less than 4 carbon atoms are considered as gas in this case, divided into organic gas and inorganic gas. Later, the product evolution trend analysis and RPWs analysis of 2300 K are carried out, so 2300 K is also selected for product analysis. It can be seen from Table 1 that there are 28 kinds of pyrolysis products and 68 molecular fragments under the environmental parameters of 2300 K and 100 ps. The mass fractions of inorganic gas and organic gas are 5.41 and 10.30%, respectively, mainly CO₂, H₂, H₂O, and C₂H₄. The mass fractions of light tar and heavy tar are 5.88 and 38.84%, respectively. The char content is 39.57%. Some representative molecular diagrams of pyrolysis products are listed in Table 2.

| Categories          | Structure                  | Inorganic gases       | C₁-C₄ compounds      | CH₂=CH₂       | CO₂, H₂O, H₂ | CH₂=O       | (C₂H₄)   | CH₂=C=O       | (C₂H₆O)   |
|---------------------|----------------------------|-----------------------|----------------------|--------------|-------------|-------------|-----------|--------------|-----------|
| C₁-C₄ compounds     |                            |                       |                      | CH₂=CH₂      | CO₂         | CH₂=O       | (C₂H₄)   | CH₂=C=O       | (C₂H₆O)   |
| C₅-C₁₃ compounds    |                            |                       |                      | C₆H₁₂O₆      |              |             |           |              |           |
| C₁₄-C₄₀ compounds   |                            |                       |                      | C₁₆H₁₂O₁₃     |              |             |           |              |           |
| C₄₁- compounds      |                            |                       |                      | C₄₁H₂₇O      |              |             |           |              |           |

CO₂ and C₂H₄ are the main gas products of DH lignite pyrolysis at 2300 K. Figure 2 shows the generation of typical gas products in the initial stage of pyrolysis at 2300 K. A large amount of CO₂ and C₂H₄ can be produced at the initial stage, which is closely related to the characteristics of lignite with more oxygen-containing functional groups (OCFGs) and a

Figure 2. Species analyses for ReaxFF-MD simulations of the initial stage of pyrolysis at 2300 K.
longer alkane chain structure. The main source of CO₂ is the decarboxylation of carboxyl and ester groups. With the progress of pyrolysis reaction, the number of CO₂ molecules decreases and then continuously increases. The mechanism will be analyzed in Section 2.4.2. The main source of C₂H₄ is the cleavage of the –C=O or C=C bond in the side chain of fat and the formation of C=C. H₂O and H₂ are typical gas products of pyrolysis reaction at 2300 K. The formation of H₂O is due to the fracture of –C=O to form –C=O·, which combines with H· to form –C=C=O and then hydrogenates to form H₂O. The formation of H₂ mainly comes from the H· of R–H and Ar–H.

2.3. Effect of Temperature on Pyrolysis Products. 2.3.1. Effect of Temperature on Char, Tar, and Gas Content in Pyrolysis. Figure 3 shows the mass fraction distribution of char, tar, and gas products from DH lignite pyrolysis. It can be seen from the figure that no pyrolysis occurred in coal at 1300 K. When the temperature reaches 1400 K, coal molecules have been pyrolyzed to produce a small amount of inorganic gas and organic gas, such as CO₂ and CₓHᵧ, and no tar. The mass fraction of char is about 98.88%. Heavy tar and light tar appeared at 1700 and 1800 K, respectively. Until the temperature rises to 2100 K, the yield of char decreases, but those of tar and gas increase. It can be considered that the coal is in the primary pyrolysis process, and the weak bridge bond and macromolecular structure in coal form gas and tar free radical fragments. When 2100 K < T < 2400 K, the content of char continues to increase, but the change of tar is on the contrary and the yield of gas changes little. This phenomenon shows that the tar polymerization occurs at this time and the pyrolysis is in the secondary stage.

According to the results of product distribution, 2100 K may be the transition temperature between the primary pyrolysis and the secondary pyrolysis. To determine the turning point more intuitively, 41.12% of 2000 K and 39.57% of 2300 K with a similar char yield are selected to study the complex chemical reaction mechanism of lignite pyrolysis. Figure 4 shows the variation trends of gas, tar, and char with those two temperatures. It can be seen from Figure 4a that the char at 2000 K shows a step-by-step downward trend, but the trends of tar and gas are on the contrary. However, as shown in Figure 4b, the char yield rapidly decreased by 90.35% and the decomposition is the main reaction within 60 ps at 2300 K. After 60 ps, the yield of char increased and that of tar decreased, but the yield of gas remained almost unchanged. It shows that polymerization is the main reaction type between char and tar.

Therefore, the ReaxFF-MD results show that the pyrolysis of DH lignite can be divided into two stages: (1) when 1400 K < T < 2100 K, the coal is in the primary pyrolysis process, and the weak bridge bond and macromolecular structure in the coal decompose to produce small molecular gas and tar free radical fragments; (2) when T > 2100 K, tar free radical fragments and char undergo decomposition, hydrogenation, and polymerization reactions. The small molecule gas and tar free radical fragments increase, and the char yield decreases compared with the primary stage. It is in the second pyrolysis reaction stage.

2.3.2. Effect of Temperature on Char Characteristics. The H/C and O/C of char can reflect the pyrolysis degree of coal to a certain extent. It can be seen from Figure 5 that the H/C and O/C of char from the pyrolysis of DH lignite at different temperatures.
temperatures continue to decrease with the increase in temperature, which is caused by the release of alkanes and the conversion of oxygen in OCFGs (such as carboxyl, ester, etc.) into tar and gas during pyrolysis. When 1400 K < T < 1900 K, H/C is basically unchanged compared with raw coal, while O/C is lower than that. It is indicated that the OCFGs in coal are easier to fracture than aromatic alkanes and aliphatic hydrocarbons. With the increase in simulated temperature, when 1900 K < T < 2100 K, H/C fluctuates and decreases in the range of 0.84–0.88, but O/C remains nearly constant. When T > 2100 K, those two kinds of parameters decrease rapidly, indicating that a high temperature makes char molecules release a large number of alkane chains and decompose stable OCFGs, and increase the aromaticity and polymerization degree. It conforms to the characteristics of the secondary pyrolysis reaction.

2.3.3. Effect of Temperature on Typical Gas Distribution. Figure 6 shows the distribution of typical gas in DH lignite pyrolysis, mainly CO2, C2H4, H2O, and H2. Because carboxyl and ester groups are easily decomposed at lower temperatures, CO2 is the gas with the highest yield below 1900 K. With the increase in temperature, the yield of CO2 rises in a wavelike manner. When the temperature is above 2200 K, the yield of CO2 decreases, and the mechanism is analyzed in Section 2.4.2. C3H4 is the gas with the highest yield above 2000 K, and its formation is attributed to the fracture of a weak C–C bond in the alkane chain. In the simulated temperature range, the yield of C2H4 fluctuates with the increase in temperature. In the pyrolysis process, H· reacts with hydroxyl to generate H2O. Since the coal sample is deacidified and does not contain hydroxyl, the output of H2O is low. The H2O generated at 2000 K comes from the rupture of an ether bond (–O–) to form hydroxyl. Some ester groups break and combine with H· to generate H2O, which is also related to the decrease in CO2 output at 2400 K. The formation of H2O mainly comes from the secondary pyrolysis stage. H2 is generated at 2100 K, and its production increased rapidly in the secondary pyrolysis stage.

2.4. Formation Mechanism of Pyrolysis Products. 2.4.1. Formation Mechanism of Char and Tar. Based on the above analysis and ReaxFF-MD pyrolysis simulation trajectory file, it can be judged that the primary pyrolysis process starts with the fracture of an alkyl ether bridge bond, marked as “②” in Figure 7. Then, the fracture of a C–O bond with a low bond dissociation energy (262.15 kJ/mol) and a few C–C bonds (“⑥”) follows. Later, the decomposition of carboxyl and ester functional groups (“③”) promotes the formation of CO2 and generates H· (“⑥”). At the same time, the methylene radical (−CH2) in the alkane chain decomposes to produce C2H4 (“⑥”). With the progress of the reaction, more C–C bonds break and form tar, char fragments, and gas.

When T > 2100 K, the reaction is in the secondary pyrolysis stage. The polymerization reaction occurs between tar fragments, free radicals, and char. The new or larger volumes of char molecules and intermediate products are generated. The secondary RPWs of typical heavy tar and char at 2300 K are listed according to the ReaxFF-MD simulation trajectory file, as shown in Figure 8. P1–P3 is the chain RPW of char molecules during the secondary pyrolysis and the reaction process of decomposing tar molecules and gas small molecular fragments.

P1 reaction shows that the C=C and C–C bonds of the char molecule C63H77O31 (shown as bond 1-1, bond 1-2, and bond 1-3 in Figure 8) are broken to form the methylene radical (−CH2), heavy tar C26H17O4, and light tar C3H4O, respectively. Subsequently, the methylene radical (−CH2) condenses with the methyl (−CH3) of the tar molecule of C80H63O3 (bond 1-4), forming new C69H55O4 and H·. P2 reaction shows that the C–C bond of the heavy tar molecule C43H32O breaks (bond 2-1), C=C is formed, and then C3H4 is formed. The methyl (−CH3) on the benzene ring condenses with the methyl of C65H49O10 of the P1 reaction product to form C=C (bond 2-2), resulting in C115H95O10 and the hydrogen radical H·. P3 reaction shows a polyyreaction between the P1-decomposing product heavy tar C26H17O4, the P2 polyyreaction product C115H95O10, and the heavy tar molecule C33H32O. First, the C–O bond (bond 3-1, bond 3-2, and bond 3-4) and C–C bond (bond 3-2) break to form C2H4, C6H10, C2H2O, and -OH. Then, the C=C bond (bond 3-5, bond 3-6, and bond 3-7) breaks off and condensates with the methylene radical (−CH2) to form the C=C bond (bond 3-8 and bond 3-9) to generate the char molecule C160H120O13 and H·.
Figure 7. Formation mechanism of the primary pyrolysis.

P4 gives the RPW of the intermediate C₂H₃O in P3. It can be seen that the C−O bond (bond 4-1) in the heavy tar C₃₄H₃₇O₃ breaks to form a new heavy tar C₃₂H₃₅O₉, which is accompanied by the formation of acetylene alcohol (CH≡C−OH) and aldehyde hydroxyl (−CHO) or H₂O and carbonyl (−C=O).

2.4.2. Formation of CO₂. During the pyrolysis of DH lignite, a large amount of CO₂ is generated at the primary stage. Feng et al. also found that CO₂ was generated very early in the pyrolysis, mainly from the decarboxylation reaction of carboxyl and ester groups. The reaction equations are shown in formulas 1 and 2. The simulation in this study also verified the formation mechanism of CO₂. Figure 9 shows the process of decomposition of carboxyl and ester groups to form CO₂. In Figure 9a, −COOH loses −H to form −COO−, and then decarboxylation occurs to generate CO₂; in Figure 9b, the ester group first breaks the C−O bond to form −COO−, and then the reaction process is similar to that of the carboxyl group to produce CO₂.

2.4.2.2. Formation of C₂H₄. As a common indicator gas for coal spontaneous combustion prediction, C₂H₄ is mainly generated through the decomposition of long-chain aliphatic hydrocarbons. During the pyrolysis of DH lignite, −CH₃ is formed due to the fracture of the C−O bond, followed by decomposition reaction to generate C₂H₄ as shown in Figure 11, and the reaction equation is shown in formula 3.

2.4.2.3. Formation of H₂O. From the pyrolysis simulation results of DH lignite at different temperatures, it can be seen that H₂O appears in the pyrolysis products with T > 2000 K, which mainly belongs to the secondary pyrolysis stage. There are three RPWs of H₂O. Figure 12a shows that −COOH breaks the C−O bond to form −OH and combines with free H· to form H₂O. After the ester group breaks C−O, it becomes −COO· and combines with free H· to form COOH, which then breaks the C−O bond to form −OH and combines with H· to form H₂O, as shown in Figure 12b. The above two RPWs are similar to CO₂ consumption pathways, which verifies the above view. Figure 12c shows that the breaking of the −C−O bond to form phenolic hydroxyl (−OH), combined with H· to generate H₂O, is the main RPW of DH lignite pyrolysis to generate H₂O.

2.4.2.4. Formation of H₂. H₂ is produced at 2100 K, which belongs to the secondary pyrolysis stage. The generation of H₂ comes from free H·. Two sources of H· are listed in Figure 13, which are R−H and Ar−H. H· interacts to form H₂. It conforms to the characteristics of secondary pyrolysis reaction.

3. CONCLUSIONS

To explore the structural change and crushing process of lignite in the early stage of pyrolysis at different temperatures, DH lignite is used as the research object. The pyrolysis reaction of lignite is studied by the experimental methods of coal pyrolysis index gas collection and detection experimental and TG analyses and the simulation method of ReaxFF-MD. The following conclusions are obtained:

(1) The concentration changes of CO, CO₂, and C₂H₄ in the range of 40−440 °C were determined by coal pyrolysis index gas collection and detection experiment. C₂H₄ was selected as the reference value and compared with the ReaxFF-MD simulation results. It was...
determined that 110—500 °C of experiment corresponds to 1400—2400 K of simulation.

(2) The pyrolysis products of lignite can be divided into gas, tar, and char according to the number of C atoms. CO2, C2H4, H2O, and H2 are the typical gas products in pyrolysis of the DH lignite molecules. CO2 and C2H4 are the main gas products, among which the formation is closely related to the structural characteristics of more OCFGs and the alkane chain length of lignite. The formation of tar and char comes from C—O and C—C fracture with a low bond dissociation energy.

(3) Temperature has a great influence on the type and content distribution of pyrolysis product. At 1400 K < T < 2100 K, DH lignite is mainly a primary pyrolysis reaction, which is characterized by the decomposition of weak bridge bonds and macromolecular structure in coal to produce small molecular gas products and tar free radical fragments. The secondary pyrolysis stage is after 2100 K. The tar radical fragments and char undergo decomposition, hydrogenation, and polymerization, the small molecular gas and tar radical fragments increase, and the char yield decreases compared with the primary pyrolysis stage.

The OCFGs in coal are easier to break than aromatic alkanes and aliphatic hydrocarbons. The change trend of H/C and O/C of char conforms to the reaction type law of the primary pyrolysis and secondary pyrolysis. The change trend of O/C shows that a high temperature decomposes the stable OCFGs.

CO2, C2H4, H2O, and H2 are typical gas products. Among them, the output of CO2 increases with the increase in temperature and decreases when the
temperature is higher than 2200 K. C₂H₄ production keeps growing with the temperature increase. H₂O and H₂ appear at 2000 and 2100 K, which are mainly in the secondary pyrolysis stage.

(4) In the second pyrolysis stage, the reaction mechanism of char molecules under the combined action of decomposition reaction and polyreaction is as follows: char + tar → char + tar + intermediate products + free radicals. Carboxyl and ester groups are the main sources of CO₂ generation. CO₂ disappears at a high temperature to form CO, H₂O, and C₂H₂O. C₂H₄ comes from the decomposition of long-chain aliphatic hydrocarbons.

The RPWs of H₂O include carboxyl, ester, and phenolic hydroxyl formed by −C−O− bond breaking, which confirm the phenomenon of CO₂ disappearance. The formation of H₂ mainly comes from the H· of R−H and Ar−H.

This study is conducive to find the key points of the early pyrolysis reaction sequence of lignite molecules, accurately cut off its chain reaction process, and hinder the further development of coal spontaneous combustion disaster. Even more, it can provide theoretical guidance for the accurate prevention and control of coal spontaneous combustion disaster.

4. EXPERIMENTAL AND SIMULATION METHODS

4.1. Experimental Methods. 4.1.1. Sample Preparation. DH lignite was selected as the research object, and large fresh coal samples were crushed and sieved to prepare two kinds of samples to be tested: (1) One hundred fifty grams of coal particles with five particle sizes of 1.25–1.6, 1.6–2, 2–3.5, 3.5–5, and 5–7 mm was screened and fully mixed into 150 g of coal samples to be tested, which were evenly divided into three groups for temperature-programmed and gas chromatography experiment. (2) Thirty milligrams of 60–80 mesh pulverized sample was screened for thermogravimetric test.

4.1.2. Experimental Details. 4.1.2.1. Coal Pyrolysis Index Gas Collection and Detection Experiment. The experimental system is shown in Figure 14, including the gas supply system, gas generation system, and gas detection system. The gas supply system includes high-pressure gas cylinders for storing N₂, H₂, and automatic air source, which are supplied through the pyrolysis reaction process of a tube furnace and the detection work of a gas chromatograph. The gas generation system is mainly for the pyrolysis reaction of coal samples in the tube furnace and collects the pyrolysis gas. Fifty grams of particle coal sample was placed in an adiabatic reactor, and the N₂ flow rate of the temperature programmed instrument was
set at 60 mL/min. The temperature was kept at 30 °C for 30 min; after that, the furnace temperature was raised to 440 °C at 3 °C/min. The coal temperature was monitored in real time during the heating process. At the beginning of 30 °C, pyrolysis gas was collected into the gas collection bag every 20 °C until the coal temperature rose to 440 °C. The gas detection system was used to analyze the collected pyrolysis gas, and the gas analysis was carried out by a gas chromatograph, which was supplied with N₂, H₂, and air. The sampling time and the type and concentration data of index gas were recorded.

4.1.2.2. Thermogravimetric Analysis. Thermogravimetric analysis (TG) was used to study the mass loss of coal during heating up. The thermogravimetric experiment was carried out in a N₂ gas environment by using a synchronous thermal analysis instrument. Ten milligrams of pulverized coal samples was put into the crucible sample chamber in each group of experiments, the heating rates was set at 2 K/min, and the N₂ flow rate was 60 mL/min in the range of 30−900 °C. According to the change of sample quality with temperature during heating up, the TG and DTG curve can be obtained.

4.2. Simulation Methods. 4.2.1. Molecular Structure Model of Lignite. The organic compounds in lignite are composed of various aromatic units with alkyl side chains and OCFGs such as hydroxyl, methoxy, carbonyl, and carboxyl groups,45−48 which are usually connected by oxygen bridges. In this paper, the macromolecular structure model of lignite constructed by our team was used for pyrolysis research,39−41 as shown in Figure 15. The chemical formula of a single coal molecule in the model is C_{215}H_{191}O_{30}N, which contains 24 OCFGs, including 2 carboxyls (−C==O), 16 ether bonds (−C−), 1 carboxyl (−COOH), and 5 esters (−C(==O)−O−). The unit cell size is 24.2 Å × 24.2 Å × 24.2 Å and the density of the system is 1.15 g/cm³.

4.2.2. Simulation Parameter Setting. The molecular dynamic (MD) method was applied to simulate the pyrolysis process of the lignite molecular model at different temperatures, and ReaxFF was selected to keep the number of particles, volume, and temperature constant (NVT). The temperature was controlled from 300 K to 1300 K by a Berendsen thermostat with 0.1 ps damping constant49 and a heating rate of 100 K/ps. It is worth noting that the simulation was carried out after the system was balanced for 20 ps. The total simulation time is 100 ps, the time step is 0.1 fs, and one frame is the output every 100 steps. To evaluate the relationship between the pyrolysis degree and the temperature, 11 temperature points were selected for simulation at 1300−2400 K with an interval of 100 K.24 To determine all possible RPWs in ReaxFF-MD simulation, each reaction system was simulated several times, and the trajectories of each atom (every 0.1 fs) were analyzed to find the corresponding relationship between the temperature and the number of fragments produced by pyrolysis and the molecular species. The intermediate configuration was deduced to obtain the most favorable RPWs.50,51

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