**Construction of Dongqu No. 2 Raw Coal Model and Characterization of Methane Formation by Pyrolysis Simulation**

Abstract: Application13C-NMR data were used to extract the skeleton information of coal macromolecules, and the macromolecular structure model of Dongqu No. 2 was constructed. The macromolecular structure model was simulated by single and five macromolecules respectively. After the simulation, the kinetic parameters were combined. Pyrolysis simulation was performed for analysis. The results show that in a single macromolecular simulation, the bond length and bond level affect the chemical reaction environment, which is the main factor of CC fracture in the model. In the molecular cluster simulation of 5 macromolecules, the reaction types of methane formation are mainly 3 Species: (1)Before the system simulates stable temperature rise, the system energy increases sharply.C atoms and the main chain at the edge of the molecular group are cleaved off; (2)systemStable warming medium (<2600K), andThe benzyl group attached to the aromatic nucleus on the pyrolysis fragment of the molecular group; (3) systemStable temperature rise (>2600K),The cyclopentane on the main chain fragment of the molecular group is thermally broken, causing the methyl group at the end of the branch to fall off to form methane.。 At the same time, the pyrolysis test is used to analyze the formation of methane and the pyrolysis simulation, and provide theoretical support for the pyrolysis reaction of coal from the microscopic point of view.

The pyrolysis of coal is an important step in the thermal conversion process of coal cleaning, gasification, liquefaction, etc. It is of great significance to study the pyrolysis of coal for the production of coal industry. The construction of the coal structure model has been studied, and the Fuchs of the University of Pennsylvania in 1942[1]After constructing the first coal structure model, it laid a solid foundation for scholars to study coal structure. With the development of testing technology and testing theory and computer technology, the data of industrial structure, elemental analysis, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and other characterization of coal structure are more accurate and credible. The necessary verification calculations can also be performed based on scientific calculation software. Hatcher [2], Jia Jianbo [3], Xiang Jianhua [4-5], Wu Li [6], Zhan-Ku Li [7], Ma Yanping [8] test data from FTIR, XPS, 13C NMR, combined with coal macromolecules The theory of structural model has successively constructed an increasingly reliable coal macromolecular structure model, which provides a theoretical model basis for coal pyrolysis simulation and adsorption simulation. In the pyrolysis of coal, Zeng Fangui[9] Using thermogravimetry-mass spectrometry to perform pyrolysis simulation experiments on low rank coals, the methane formation rate curve was obtained, and four types of methane generation reactions were calculated using quantum chemical theory. The main research method for analyzing coal pyrolysis; Li Meifen[10] The pyrolysis simulation experiments of seven low metamorphic coals were also carried out by thermogravimetry-mass spectrometry. The relationship between the pyrolysis characteristics and the first coalification transition was studied. The characteristic temperature parameters of hydrogen generation and Kinetic parameters can provide reference for parameter analysis of methane generation;Feng Han[11] The thermal decomposition and precipitation gas characteristics of five lignites from Yunnan Province in southwestern China were studied. The functional groups have significant effects on lignite weight loss and gas phase product evolution. The theory of low temperature pyrolysis is not only for CO.2, CO, H2O is applicable and can also be extended to other pyrolysis products of coal;A. Arenillas[12] The pyrolysis behavior of anthracite and three different volatile matter bituminous coals in the optimization system based on calcium oxalate was studied. The transient evolution process of volatile organic compounds was described, and the coal rank changes were dependent on different functional groups. Sexual conclusionMingjie Gao[13] The super coal macromolecular pyrolysis simulation was carried out with ReaxFF MD, revealing the basic law that the main reaction of methane and other gases in the early stage of coal pyrolysis is closely related to carboxyl and methoxy groups; Dikun Hong[14] Using the same method to align the east coal for pyrolysis simulation reveals the secondary reaction mechanism of tar, which provides a new theoretical support for pyrolysis simulation. The work of the predecessors is mainly to analyze the pyrolysis test of coal or the pyrolysis simulation test of coal macromolecules. For this reason, we try to combine the pyrolysis simulation test of coal macromolecules with the pyrolysis test of coal, and its main products. Methane is analyzed and a certain correspondence is found between the two.

In this paper, the large-molecular structure model of Dongqu No. 2 was constructed. After pyrolysis simulation analysis of this model, the pyrolysis test and verification of the sample were carried out by thermogravimetry-mass spectrometry, which provided a deeper level for the pyrolysis process of coal. understanding. This work is based on the ReaxFF reaction force field in the ADF integration software. The model is subjected to thermal reactivity simulation of a single macromolecule with a simulated termination temperature of 3000K. In the simulation process, according to the position of different types of chemical bond cleavage in the pyrolysis process, the process of side chain functional bond cleavage at different temperatures is obtained, and the pyrolysis process of coal is described from a microscopic point of view. Because coal is in agglomerated form[15]Exist, the pyrolysis of a single molecule in the pyrolysis process will be affected by other molecules. In this work, the thermal reaction simulation of a molecular group consisting of five macromolecules is carried out simultaneously, the termination temperature is 3000K, and the molecular group pyrolysis simulation process is analyzed. The type of reaction in methane formation provides a theoretical basis for the source of methane in coal pyrolysis. In addition, this work also includes pyrolysis experiments using a thermogravimetric-mass spectrometer (TG/MS) to obtain the weight loss curve during pyrolysis of the sample.[16]And methane precipitation rate curve[9]The relationship between the two is analyzed to obtain the relationship of methane production under simulated and experimental conditions.

**1 sample and test**

The fresh coal sample was collected from the No. 2 coal seam of the No. 2 coal in the Gujiao mining area of Xishan Coalfield, Taiyuan, Shanxi, and the raw coal of the No. 2 coal of the Dongqu (the maximum reflectivity of the vitrinite group)Industrial analysis, elemental analysis, for 1.81%)13C nuclear magnetic resonance test.

Industrial analysis and elemental analysis (Table 1): The test was carried out using the German ELEKRTO-AUTOMATIK Vario EL elemental analyzer, which was weighed in a dry environment during the test.0.2g sample, industrial analysis and determination according to the national standard "Industrial Analysis Method for Coal" (GB/T212-2008), elemental analysis and determination according to the national standard "Determination of carbon and hydrogen in coal" (GB/T476-2008). The test values of C, H, N, and S are the average of two parallel sample tests, and the O element content is calculated by subtraction.

13C nuclear magnetic resonance (13C-NMR) test: The test was carried out using a Varian INOVA 300 type superconducting nuclear magnetic resonance apparatus from Agilent Technologies, USA. The test environment is: cross-polarization (CP) technology with TOSS suppression sideband, ZrO with an outer diameter of 6mm2The rotor, the magic angle is 6 kHz,13The C detection nuclear resonance frequency is 76.425 MHz, the spectral width is 3000 Hz, the pulse width is 4 μs, the sampling time is 0. 05 s, the cyclic delay time is 4 s, the scanning is 6000 times, and the contact time is 5 ms.

Single coal macromolecular pyrolysis simulation: simulation using ADF/ReaxFF module in chemical material calculation software of Dutch SCM company[17-21]Firstly, hydrotreating the macromolecular structure model of Dongqu No. 2 coal, selecting Velocity Verlet+Berendsen ensemble, simulating the lowest energy configuration under normal temperature and normal pressure conditions, and then lattice at side length 5nm·5nm·5nm Randomly put in an optimized Dongqu No. 2 coal macromolecular structure model, set the simulation step number to 400,000 steps before the simulation of pyrolysis, simulate the heating rate at 25K/ps under normal pressure, and increase the temperature from 297K to 3000K. The length is 0.25fs, the reaction field is HE.ff, and the thermal reactivity simulation of the macromolecule is calculated, and finally the molecular dynamics parameters of the model and the reaction relationship between the chemical bonds are obtained.

Coal molecular group pyrolysis simulation: This pyrolysis simulation is based on a single molecular pyrolysis simulation, also using Velocity Verlet+Berendsen ensemble, randomly placed in the lattice of 5nm·5nm·5nm side length 5 optimized The macromolecular structure model of Dongqu No. 2 coal, the energy minimum simulation of this system (Fig. 7), the simulated step number is 400,000 steps before the simulation pyrolysis, and the simulated heating rate is 25K/ps under normal pressure, and the temperature is raised from 297K. 3000K, the time step is 0.25fs, the reaction field is HE.ff, and the thermal reactivity simulation calculation of the molecular group is performed.

TG/MS test: The instrument used in the pyrolysis test is a thermal analysis-quadrupole mass spectrometer of the type 447Z F3-QMS403 D from NETZSCH, Germany. The thermogravimetric test is carried out in a dry environment, and 10 mg of the original coal sample of Dongqu No. 2 is weighed. The vacuum condition of the instrument is raised from 313K to 1273K, the heating rate is 10K/min, the test atmosphere is nitrogen, the purge gas flow rate is 80 mL/min, the shielding gas flow rate is 20mL/min, and the instrument can measure the gas product mass range of 1u. -300u.

**2 Model construction and experimental analysis**

**2.1 Model Construction and Correction of Dongqu No. 2 Coal**

**2.1.1 Model construction**

Characterizing coal structure13C-NMR data for analysis, reference Jia Jianbo[3]Xiang Jianhua[4-5]Et al. The coal macromolecular chemical structure model construction method, the macromolecular structure model of Dongqu No. 2 raw coal was constructed by simulating the connection of aromatic structural units, fat structures and other functional groups in the structure.

Use the Origin 7.5 software pair13The C-NMR original spectrum was subjected to peak-saturation (Fig. 1). According to the chemical shift of each functional group and its relative content, twelve major structural parameters such as fatty carbon and aromatic carbon in Dongqu No. 2 coal were calculated (Table 2).

**2.1.2 Model correction**

According to the structural parameters of Dongqu No. 2 coal, combined analysis13The ratio of carbon to pericarbon of Dongqu No. 2 coal aromatic bridge obtained by C-NMR spectrum:

Calculated, by the different combinations of individual aromatic groups, get the closestThe type and number of aromatic structures corresponding to the values (Table 3), the number of aromatic carbons in the large molecular structure model of Dongqu No. 2 coal was calculated to be 117.

From the definition of aromaticity combined with Table 2, the aromatic carbon ratio of the macromolecular model to be constructed is calculated to be 0.67, and the number of carbon in the macromolecular structure model of Dongqu No. 2 coal is calculated to be 174, and the combined elemental analysis data (Table 1) ) Derivation, Num(C:H:N:O)= (90.31 / 12): (4.66 / 1): (1.56 / 14): (2.91 / 16). In summary, the molecular formula of the Dongqu No. 2 coal macromolecular model is。

According to the above analysis, the occurrence pattern of various elements and the number of functional groups in the macromolecular structure model of Dongqu No. 2 coal were calculated. The coal macromolecular structure model was constructed by ACD/C NMR software, and each carbon atom was calculated by gNMR software. After the chemical shift, the predicted spectrum is compared with the experimental nuclear magnetic spectrum in the Origin software. If the difference between the two is large, the work of structural model modification and spectral comparison is repeated until the experimental nuclear magnetic spectrum and prediction are performed.13The C-NMR spectra were matched and matched (Fig. 2) to obtain the most suitable macromolecular average structure model. The factors affecting the determination of hydrogen in the analysis of sample elements are numerous and complex, so the hydrogen content in the model is used as the final result. The molecular formula of the corrected coal macromolecule is。 The macromolecular structure model of Dongqu No. 2 coal (Fig. 3) is connected by a fat carbon bond or a carbon bond directly connected to two aromatic rings, and consists of a main chain with an aromatic ring as the main skeleton and three sides with strong cross-linking action. Chain composition[3-5, 8, 22-23]。

**2.2 Pyrolysis Simulation of Dongqu No. 2 Coal Structure Model**

**2.2.1 Simulation analysis of single coal macromolecular pyrolysis**

The lowest energy configuration was calculated during the pyrolysis simulation of a single coal macromolecule (Fig. 4). After the simulation was completed, the energy at the beginning and end of the two time points (Table 4) was selected for comparison.

It can be seen from Table 4 that the total energy before and after the single molecular dynamics simulation is reduced from -36384.39 kcal/mol to -43087.92 kcal/mol, and the bond energy is reduced from -62408.01 kcal/mol to -69678.87 kcal/mol. Both the torsional energy and the van der Waals force are reduced accordingly. The reason for this phenomenon is that various functional group fragments are generated inside the system during the pyrolysis process, resulting in a reduction in the total energy, bond energy, torsion energy, and van der Waals force of the system. Small, and the atomic energy of the system increases from 782.27 kcal/mol to 960.86kcal/mol, and the charge energy increases from 806.09 kcal/mol to 901.39kcal/mol, indicating that the macromolecule is cleaved into fragments under the programmed temperature simulation conditions in this system. The stability of the post system is enhanced.

After the macromolecule is hydrotreated in the lattice to obtain the lowest energy configuration, the pyrolysis reaction of the single macromolecule is simulated. The reaction process is: the process of the first macromolecular fragment falling off from the main structure (Fig. 5\_a) At around 603K, at this time, due to the increase of the internal temperature of the system, the total energy of the macromolecule in this chemical environment increases, and the relatively active C on the main chain of the macromolecular structure model.73-C45The bond breaks, causing N to be contained135,O179Two branched molecular fragments are detached from the backbone, resulting in two macromolecular fragments.

The second fragment is detached from the first macromolecular fragment (Fig. 5\_b). The process occurs at about 707K. At 603K, the macromolecular fragment detached from the main chain has two branches, and two branches are connected at this temperature. The fatty carbon bond C84-C82 breaks, causing the cross-linking of the two branches to decrease. In this chemical environment, the relatively active C83-C78 breaks, causing the branch containing O179 to fall off from the fragment just detached from the main chain. .

The process of the third piece falling off the structure (Fig. 5\_c) occurs around 975K. In this chemical environment, it may be due to O.170With O181The role of the surrounding C is relatively active, causing C at this time164-C154A fracture occurred (Fig. 6) to produce a p-methylphenol.

The process of the fourth piece falling off the main structure (Fig. 5\_d) occurs around 1020K, and after the second piece falls off, C85-C80The fragmentation produces a molecular fragment and dimethylnaphthalene. It can be seen that most of the primary bond cleavage during coal pyrolysis occurs in a relatively low temperature environment (<1100K).

**2.2.2 Simulation analysis of coal molecular mass pyrolysis**

The lowest energy configuration can be calculated during the molecular mass pyrolysis simulation of the five coal structure model molecules (Fig. 7). After the simulation is completed, the methane generation process and the precipitation rate curve are obtained (Fig. 8), and the start and end are selected. The energy at time points (Table 4) was compared.

It can be seen from Table 5 that the total energy before and after the molecular group dynamics simulation is reduced from -215469.43 kcal/mol to -215606.38kcal/mol, and the bond energy is reduced from -298394.73kcal/mol to -298501.77kcal/mol. Both the torsional energy and the van der Waals force are correspondingly reduced. The reason for this phenomenon is that the molecular group generates various functional group fragments in the pyrolysis process under the corresponding chemical environment, resulting in the total energy, bond energy, and torsion energy of the system. Van der Waals' power can be reduced, and the corresponding atomic energy and charge energy of the system increase. The result corresponds to the energy changes before and after the single molecular dynamics simulation, and it conforms to the basic principle of system energy conservation.

It can be seen from the methane generation rate curve in the pyrolysis simulation process (Fig. 8) that methane starts to precipitate from about 2200K, and the precipitation rate reaches the maximum at 2580K, and the final temperature of the pyrolysis final temperature is 3000K. During the pyrolysis process, the potential energy of the system (Fig. 9) is rapidly increased due to the action of the force field and the rapid temperature change at the beginning of the simulation. The system energy in the NVT ensemble increases rapidly, which is manifested by the rapid increase of the potential energy of the system. After a short period of time, the system pyrolysis reaction is stable, the potential energy of the system decreases rapidly, and the subsequent overall trend tends to increase with time.

inLarge molecular structure model of Dongqu No. 2 coalIn the pyrolysis simulation process, the methane generation pathway (Fig. 10) is mainly the primary or secondary shedding of methyl groups on several major side chain functional groups of the coal structure in the ReaxFF force field system.

In the SCM MOVIE, the methane generation method is tracked. The first methane molecule generation (Fig. 10\_a) is around 312K, and the source is C.130-C89Breaking of the bond leads to C130After the methyl group is detached, it combines with hydrogen ions to form methane. At the beginning of the simulation process, due to the rapid increase of the potential energy of the system, the molecular clusters composed of the five macromolecular models in the system are drastically changed, making the C at the edge of the molecular cluster relatively unstable.130Shedding forms a benzyl group to form a methane.

The second methane molecule formation (Fig. 10\_b) is around 1036K, the source is the side branch chain breaking from the molecular group, and the C on this branch163-C161Breaking of the bond leads to C176The methyl group is detached from the quaternary benzene ring to form a benzyl group to form methane.

The third methane molecule is produced (Fig. 10\_c) at around 1794K, and the source is cyclohexane C in the molecular structure.28-C8，C8-C6Key break, C8-C4After the bonds are connected, the force field at this temperature causes C to8Methane is formed after detachment from the side chain fragment.

The fourth methane molecule formation (Fig. 10\_d) is around 2543K, and the source is C on the side chain fragment in the molecular group.180-C158，C180Forming benzyl to form methane after detachment from the side chain.

The fifth methane molecule formation (Fig. 10\_e) is around 2600K. The source is C123-C121 on the side chain fragment in the molecular group. Since C123 is closer to O179, the electronegativity of O is larger than that of C. In this chemical environment. The action of the force field and O causes C123 to fall off the side chain to form benzyl to methane.

The sixth methane molecule formation (Fig. 10\_f) is around 2610K. The source is C142-C42 on the main chain of the molecular structure. The C42-C40 breaks under this condition, resulting in the distance between C142-C42 and the relatively stable C27. The increase causes C142 to detach from the main chain fat fragment to form methane.

The seventh methane molecule formation (Fig. 10\_g) is around 2897K. The source is C40-C39 on the main chain of the molecular structure. Under the simulated conditions, the molecular backbone breaks to form a main chain fragment. At this time, C44-C40, C42 -C40 has been broken, C40 methyl group is exposed to the most unstable distal end of this molecular fragment, C40-C39 is broken, and C40 is detached from the main chain fat fragment to form methane.

After this, the second simulated reaction process (Fig. 10\_h) is around 2906K. At this time, the methane labeled in the figure decomposes to form a methyl group and a hydrogen ion due to the influence of the force in the chemical environment.

The last reaction to regenerate methane (Fig. 10\_i) is around 2960K, when the molecular group has been cleaved into one more molecular fragment, in this chemical environment C131-C93Break, make C131Methane is formed by detaching from a side chain fatty group in the molecule.

The bond length and bond level characterization of the CC bond from methyl group to methane (Table 6) shows that the bond length of the CC bond that breaks to form a methyl group is large, and the bond level is not much different. The basic principle is that the bond length in the process of generating methane is the main factor affecting the formation of methyl group by CC bond cleavage, and the bond level is a secondary factor.

From the simulation of molecular coal pyrolysis of five coal structure models, the first is that the potential energy of the system rises, so that the most active methyl group at the edge of the molecular group falls off to form methane, and then in the molecular group composed of five coal structure model molecules before 1020K. The main structure undergoes thermal cracking reaction, the main side chain functional groups are successively detached from the molecular group, and the shed side chain functional groups are also subjected to secondary cleavage due to their own chemical environment, and then the corresponding methyl groups are successively detached to form methane during heating. It is worth noting that in the process of methane formation, especially around 2900K, some methane will decompose into methyl and hydrogen ions under high temperature, and the amount of hydrogen ions and methyl groups will change slightly. The reaction produces a higher methyl activity and regenerates methane in subsequent reactions.

**2.3 Thermogravimetric-mass spectrometry analysis of samples**

The sample weight loss and weight loss rate curve (Fig. 11) and the methane precipitation rate curve (Fig. 12) were obtained through experiments.

It can be seen from the above figure that the reaction before 600K is to remove the adsorbed water and adsorbed gas from the sample by heat removal. [24]The sample began to react violently with pyrolysis from 600K. The weight loss of the sample was obvious and reached the maximum weight loss rate of 0.08%/K at 785K. At this time, the macromolecular structure of the coal depolymerized and decomposed, and a large amount of volatile gas was produced. During 600K to 785K, the sample weight loss rate was 5.92%, 5.02% at 785K to 866K, the sample pyrolysis tar yield increased before the 785K maximum weight loss rate, and the tar amount decreased after 785K to generate a large amount of gas, with increasing temperature. The weight loss rate of the sample is reduced, and the volatile matter is completely precipitated. In this process, the main reaction is a secondary reaction of the pyrolysis product, and a methane-based gas is precipitated.

There are three main types of reactions in coal pyrolysis.Methane and methane radicals are formed by secondary cleavage of long-chain aliphatic hydrocarbons and cleavage of short aliphatic chains, methoxy groups, alcohol functional groups, and methyl groups in methyl ester fat side chains linked by hetero atoms; The methyl group linked to the naphthene and the naphthenic structure is formed at the high temperature stage by the cleavage of the CC bond; and the methyl group released by the alicyclic structure formed by the condensation polymerization of the aromatic structure in the coal is formed.

It can be seen from the methane evolution rate curve that the methane precipitation rate starts to increase gradually at 680K, and decreases until the maximum value is 820K. The maximum methane precipitation temperature 820K is greater than the maximum weight loss temperature 785K. The reason for the analysis may be that the free radical generated by bridging in the coal reaches a maximum at 820K, and then a sharp drop is generated to generate a large amount of hydrogen and the active semi-coke is hydrogenated.Methane。

Comparative pyrolysis simulation and experimentMethane precipitation temperature (Figure 13), in pyrolysis simulationThe initial temperature of methane precipitation was 2200K, and the termination temperature was 2900K. In the pyrolysis test.The initial temperature of methane precipitation is 680K, and the termination temperature is 1220K. Combined with the corresponding relationship of other temperature points, it can be seen that the simulation and test are in progress.The temperature point at which methane is precipitated has a good linear correlation.

**3 conclusions**

Pass onConstruction of a large molecular structure model of Dongqu No. 2 coal, for a single macromolecular structurePyrolysis simulation, obtaining information on the chemical bond cleavage in the structure under specific temperature conditions,Molecular group consisting of 5 macromolecular structuresThe pyrolysis simulation obtained a methane production rate curve. CombineCharacterization and simulation results analysis of the large molecular structure model of Dongqu No. 2 coal, the main conclusions are as follows:

(1) Calculating the ratio of aromatic bridge carbon to pericarbon in the process of constructing the macromolecular model of Dongqu No. 2 raw coal0.35, the aromatic carbon ratio is 0.67,The experimental spectrum is basically consistent with the simulated spectrum, so the structure of the macromolecular model is relatively reasonable.Molecular formula。

(2) Dongqu No. 2 raw coalDuring the pyrolysis simulation, under relatively low temperature conditions (<1100K), the main functional groups in the coal undergo a cleavage reaction, and the corresponding side chain functional groups are detached from the main chain, and with the temperatureWhen it rises, the chemical environment in the system tends to be stable.

(3) Pyrolysis simulationThere are three main ways to generate methane: before the system simulates stable temperature rise, the system energy increases sharply.C-rings and the main chain at the edge of the molecular group are cleaved off;systemStable warming medium (<2600K), andThe benzyl group attached to the aromatic nucleus on the pyrolysis fragment of the molecular group; systemStable temperature rise (>2600K),The pyrolysis of cyclopentane on the backbone segment of the molecular group opens, causing the methyl group at the end of the branch to fall off to form methane.There may be a reaction in which methane is dehydrogenated to a methyl group by the chemical environment surrounding the oxygen atom.

(4) During the pyrolysis testThere are three main ways to generate methane, andPyrolysis simulationThe path of methane production corresponds.

(5) For samplesThe simulated pyrolysis product methane was analyzed. The initial temperature of methane precipitation was 2200K, and the termination temperature was 2900K. The simulation was linearly related to the temperature point of methane precipitation. The pyrolysis simulation method was to investigate the methane generation during coal pyrolysis.The route provides an effective means.