Quantum chemical simulation of methane production by coal hydrogenation pyrolysis

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Abstract. In this work, molecular mechanics, molecular dynamics and semi-empirical quantum chemistry of the Wiser molecular structure model of bituminous coal were studied by molecular simulation. The molecular structure model was optimized and the geometrical configuration of the structural model was analyzed. The bond length and bond cleavage energy of different types of bonds were obtained, and the weak bonds and possible fragments were revealed by a series of simulation. The reaction mechanism of methane production from debris of hydrogenation pyrolysis was studied by transition state theory. The results showed that the energy of the optimal structure of Wiser molecular model of bituminous coal was 704.517 kcal/mol, and the arrangement of aromatic layers was approximately parallel. The initial cleavage of the Wiser model mainly occurs in the coal structure of the relatively high degree of cross-linking and the C-C bond connected to carbonyl carbon. The three-dimensional structure of Wiser model was broken and then generated a large number of debris, the groups of methyl were removed from debris molecules under hydrogen atmosphere, and then methyl radicals and hydrogen radicals combined to form methane.

1. Introduction
At present, the world faces a very difficult task of energy saving and emission reduction, in which the responsibility of coal industry is particularly difficult, and the environmental problems caused by coal direct combustion have no effective cure [1]. Therefore, how to develop the clean utilization of coal is an important problem to face. In this paper, based on the recent demands of coal clean utilization, a quantum chemical simulation study of coal pyrolysis to methane was put forward. Based on the existing coal pyrolysis technology, the change of coal structure model, reaction formation mechanism and molecular dynamics quantum chemical simulation of coal pyrolysis were studied using MS software.

2. Simulation details
In this paper, the mechanism of methane production from coal hydrogenation pyrolysis is studied by selecting the Wiser bituminous coal model of “the molecular hydrocarbon generation structure evolution of vitrinite and the mechanism of energy barrier control” [2].

2.1. Construction of macromolecular structure model of coal
We created a new project in MS software, and then opened the Visualizer module, and draw the diagram of wiser model structure, as shown in Figure 1 (left). Using the molecular mechanics method, the coal structure was optimized and the Forcite module in the Materials Studio software was used. In order to search for the minimum energy configuration of coal structure, the initial molecular
mechanics simulation was performed before annealing dynamics simulation, and the global optimization was performed on the entire potential energy surface, and a global minimum configuration was obtained [3].

2.2. Quantum chemical simulation of coal macromolecular model
Using the VAMP module in Materials Studio 8.0, Geometry Optimization was used to obtain the bond lengths and cracking energy of different types of bonds, revealing the weak bonds and possible debris molecules [4]. Finally, the reaction mechanism of coal fragment molecular hydrogenation pyrolysis to methane was studied by the transition state theory [5].

3. Results and discussions
As shown in Figure 1, the structure diagram after optimization can be found that the structure of the molecular mechanics optimization has changed obviously, the spatial distribution was more reasonable, the structure was more compacted and has a good three-dimensional conformation, and the energy was more stable than before. The energy of the optimal structure of Wiser molecular model of bituminous coal was 704.517 kcal/mol, and the arrangement of aromatic layers was approximately parallel.

![Figure 1. The model of bituminous coal geometry before and after optimization.](image)

As shown in Figure 2 comparing with the energy image obtained, it is easy to find that after the optimization of annealing kinetics, the large molecular model of bituminous coal has obvious bending deformation, and the bridge between each aromatic sheet has strong torsion, so that the parallelism between the layers was enhanced and a good three-dimensional sense was presented.

![Figure 2. The model of bituminous coal annealing optimization.](image)
Through the analysis of bond length, bond angle and charge distribution of bituminous coal structure model, it is easy to draw the conclusion that the bond length of C-O bond is smaller than that of C-C bond. In the coal model structure, the ether oxygen bonds linked to the fatty carbon and oxygen atoms and the C-C bond are weak bond strength, which is easy to fracture during the pyrolysis of coal, and the activity is relatively high [6]. After the initial pyrolysis, the spatial structure of the coal structure model is destroyed, it is easy to crack to generate a large number of reaction debris, and the reaction process will have CO, CH$_4$ and other gas generation, as shown in Figure 3.

Figure 3. The fragment formed in bituminous coal pyrolysis.

Figure 4. The reactive model compounds.

The transition state energy of the fragment structure R1 is shown in Figure 5.

Figure 5. The transition state energy of bituminous coal structure.

It is shown in Figure 5 that the activation energy of the first step reaction is less than the activation energy of the second step (ΔE$_1$ < ΔE$_2$), therefore, the second step requires greater energy, and the second step is much slower than the first step. The second step is the key to the total reaction rate, called the reaction rate determination step [7].

Figure 6 shows the reactant products and transition states of the structural fragment R1. As shown in Figure 6, the main pathway of methane generation by the fragmentation of structural fragments is hydrogen bond breaking to generate hydrogen radicals and then the reactants generate methyl radicals...
via the hydrogen radical’s standard addition, and finally the methane is generated by the combination of methyl radicals and hydrogen radicals.

![Chemical structure](image)

**Figure 6.** The reactant product and transition state.

4. Conclusions
The Wiser structure model of bituminous coal was applied, and its structure was optimized and simulated by MS software. The structural debris generated during coal pyrolysis was obtained. Then the reaction mechanism of methane production from coal hydrogenation pyrolysis was simulated by the transition state search. The following conclusions are drawn:

1. The results of molecular mechanics optimization and molecular dynamics simulation showed that the minimum energy was 704.517 kcal/mol. In the macromolecular structure of coal, the stability of the whole macromolecular skeleton was mainly from the non-bond energy in the structure, and the non-bond energy was mainly dominated by van der waals energy. The hydrogen bond energy in the non-bond energy mainly comes from the intermolecular interaction. Due to the π-π interaction between the aromatic lamellae in the molecule, the structural model showed that the aromatic lamellae were arranged in an approximate parallel manner.

2. The primary pyrolysis of bituminous coal mainly occurs in the position of high cross-linking degree of coal structure and C-C bond which connect with carbonyl carbon atoms, after the initial cracking, the three-dimensional structure of coal is broken, and a large number of reactive fragments are generated.

3. The way of coal hydrogenation pyrolysis to methane is mainly divided into the following two aspects. The first pyrolysis of coal to produce free radical debris, in the process will have a part of methane production. The main pathway of methane production from the fragmentation of structure is generate hydrogen free radical by fracture of hydrogen bond, and then the reactants generate methyl free radicals via the standard-based addition of hydrogen radicals, and then the methane is generated by the combination of methyl free radicals and hydrogen radicals, and then the reactants generated methyl free radicals by the standard radical addition of hydrogen radicals, finally the methane is generated by the combination of methyl free radical and hydrogen free radical.

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