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# ReaxFF and DFT study on the sulfur transformation mechanism during the oxidation process of lignite

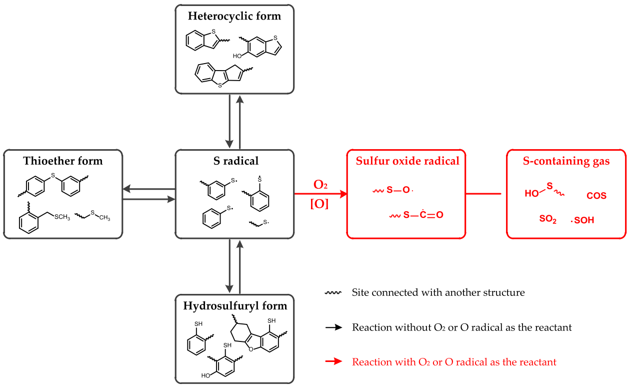
Guang-Yue Li, Feng Wang, Jie-Ping Wang, Ying-Ying Li, An-Qi Li, Ying-Hua Liang *

*College of Chemical Engineering, North China University of Science and Technology, Tangshan 063009, PR China*

## HIGHLIGHTS

- S-transformation mechanisms in the $O_2$-atomsphere pyrolysis of lignite are simulated by ReaxFF molecular dynamics.
- The ReaxFF simulation results show good agreements with previous experimental results.
- Different forms of S atoms transform to each other with sulfur radicals as their intermediates.
- $O_2$ molecules react with sulfur radicals and transform them to S-containing gases.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Two structural models for lignite and $O_2$-lignite systems were constructed to investigate the impact of $O_2$ atmosphere on the sulfur transformation in the lignite oxidation process. Reactive force field molecular dynamics was employed to simulate the reaction process of the two models at 1000–2000 K, and then the obtained reaction pathways were further confirmed by density functional theory. By analyzing simulation trajectories with C++ program, we have obtained the existing forms, distributions and elementary reactions of sulfur during the pyrolysis and oxidation processes. Different forms of sulfur transform into each other through sulfur radical intermediates in the pyrolysis process. The added $O_2$ molecules or the oxides produced by $O_2$ can react with sulfur radicals, forming sulfur oxide radical intermediates (such as R–S–O· and R–S–C–O·). The sulfur atoms in these intermediates transform into small sulfur-containing gas molecules. Thus, sulfur atoms in lignite are finally removed by $O_2$ molecules during the oxidation process.

## 1. Introduction

Gasification is one of clean utilization technologies of lignite, in which lignite always reacts with air or $O_2$ gas [1]. After gasification, sulfur in lignite is mostly converted into S-containing gas pollutants (such as $SO_2$), which has a number of adverse effects on our respiratory system. To reduce air pollution, we should well understand the sulfur transformation during the industrial processes of lignite and develop more rational conditions for the thermal utilizations of lignite.

When heated up under gasification conditions, lignite would firstly undergo initial oxidation process [2,3]. In this step, $O_2$ reacts with the semicoke (the pyrolysis product of lignite) and mainly

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* Corresponding author.
*E-mail address:* yhliang@ncst.edu.cn (Y.-H. Liang).

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produces CO, $H_2$ and hydrocarbons. Previous experiments confirmed that the initial oxidation process is helpful for the sulfur transformation from the solid residue to the volatile products [4,5]. Liu et al. [6] have studied sulfur transformation of a few S-containing compounds in the oxidation process based on the results of thermogravimetric analysis and mass spectrometry. They found that $O_2$ could remove sulfur atoms with less carbon loss at a lower temperature. Based on this conclusion, the oxidation process of coal has attracted the interests of researchers [3,7]. For example, Guo et al. [7] have studied effects of both pyrolysis temperature and $O_2$ concentrations on desulfurization efficiency of Huozhou coal, and found that 70% of sulfur could be removed under a proper condition. However, previous studies cannot provide a detailed sulfur transforming mechanism for the oxidation process of coal. This was because it is difficult to experimentally distinguish the reactive and short-lived S-radical intermediates among a large amount of other intermediates in the coal pyrolysis process.

Recently, molecular dynamics (MD) method with reactive force field (ReaxFF) [8] is applied to many thermal conversion processes of coal. It could simulate the formation of radicals, bond cleavages, cross-linking reactions and interactions between coal and other molecules. All of these are helpful for the study on the thermal reaction mechanisms of coal. For example, Zhan et al. [9] have carried out ReaxFF simulations to investigate the thermal decomposition mechanism of a subbituminous coal. In their simulations, the cleavage of weak C–C and C–O bonds is considered to be the initial steps during the pyrolysis process. Yan et al. [10] have simulated the spontaneous combustion reaction of lignite by ReaxFF. They found that this process is likely caused by $O_2$, which captured the hydrogen atom in hydroxyl and carboxyl groups. Our group also simulated the pyrolysis process of the metal-ion-exchanged lignite [11] and the hydrothermal treatment of lignite [12]. All of the above ReaxFF studies agreed well with previous experimental observations, and explained the mechanism of corresponding reactions at the molecular level. ReaxFF has great potential in the study on the thermal reaction mechanism of coal [13,14]. Moreover, the reliability of MD studies depends crucially on the force field. Quantum chemical calculations, such as density functional theory (DFT) [15,16], are needed for the ability to reproduce the reaction energies of the pathways observed in the ReaxFF simulations. Because of expensive costs, the local structure obtained from ReaxFF results [9,17] or very small model molecules [18,19] are usually used in the DFT calculations.

In this work, a combined ReaxFF and DFT study are applied to investigate the sulfur transforming mechanism in the oxidation process of lignite. By searching different forms of S atoms and S-containing elementary reactions, we will obtain effects of added $O_2$ molecules on the S transformation in the oxidation process of lignite. This work will be helpful for understanding the mechanism of sulfur transformation of lignite and relative utilization processes such as gasification.

## 2. Computational details

### 2.1. Construction of lignite and lignite-$O_2$ models

The lignite model proposed by Wolfrum [20] is chosen as the structural unit. This model molecule includes thiophenol, thioether and thiophene forms of S atoms, which is beneficial to simulate the transformation between different S forms in lignite. We modified unstable structures (anti-aromatic and nonplanar structure) in the structural unit, and removed metal atoms due to limitations of the force field (see Figs. S1 and S2, *Supporting Information*). The final structure of the structural unit ($C_{225}H_{182}N_4O_{36}S_3$, abbreviated as **W**) is shown in Fig. 1.

The molecular structure of **W** is optimized by Dreiding force field [21] of LAMMPS program [22,23] and shown in Fig. 2a. Then, 14 **W** molecules are put into a periodic 55.00 × 55.00 × 55.00 Å box to build a lignite model (**L**, see Fig. 2b) by the Packmol program [24]. The density of **L** is close to that of lignite ($\sim$0.5 g/cm$^3$). Another model containing 14 **W** molecules and 424 $O_2$ molecules (**LO**, see Fig. 2c) was built in a 55.00 × 55.00 × 110.00 Å box for the oxidation process of $O_2$-lignite system. Thus, there are 14 thiophenol forms, 14 thioether forms and 14 thiophene forms of sulfur atoms in the starting configuration of both **L** and **LO**. The number of $O_2$ is calculated by the density ($1.3092 \times 10^{-3}$ g/cm$^3$) of $O_2$ at room temperature and pressure [25]. Then, three steps were performed to relieve intermolecular stresses in the two models: (1) heated from 0 K to 900 K with the NVT ensemble, (2) compressed at 10 MPa and decompressed process at 0.1 MPa with the NPT ensemble, and (3) annealed to 298 K with the NVT ensemble. At last, **L** and **LO** was energy minimized with non-reactive ReaxFF before MD simulations.

### 2.2. Convergence test of ReaxFF simulation

Parameters reported by van Duin and Kamat [26] are used in the following ReaxFF simulations of both two models. In the ReaxFF simulations, one trajectory for each simulation could not provide reliable results. To achieve meaningful statistical data, the number of trajectories should be sufficient. Herein, following ReaxFF simulations were performed to verify the convergence. We obtained the relationship between the reaction distribution and the trajectory number of **L** at 2000 K (see Fig. S3, *Supporting Information*). When the trajectory number was more than three, the molecular distributions became almost stable. Results of calculation for the three trajectories agree well with those for the calculation of four and five trajectories. That is, over three trajectories could give converged results for the subsequent analysis. To improve the accuracy, calculations of four trajectories were used in the following ReaxFF simulations at each temperature. All the simulation results are obtained by sum up the results of four trajectories.

### 2.3. ReaxFF simulation parameters

According to our previous work [27], the simulation temperature is set to 1000–2000 K, which is much higher than that in the real pyrolysis process. This treatment overcomes the difficulty of extrapolating tests at shorter times to real-world conditions. It is well grounded in theory [28] and can be applied to the macromolecule simulations such as coal [10,29]. The bond order cutoff and nonbonded cutoff were 0.3 and 10 Å. The time step was 0.25 fs. We traced all S atoms in **L** and **LO**. According to previously reported works [30–33], the simulation trajectories were analyzed by C++ programs for classifying existing forms and elementary reactions with marked S atoms in the two models (Fig. S4, *Supporting Information*).

In the actual oxidation process, such as gasification, the $O_2$ gas or air flows react with the lignite and take the gas products away. That is to say, $O_2$ gas acts as both the reactant and the carrier gas. The reaction system would not reach equilibrium at this condition. We would think shorter simulations would get closer to real oxidation condition. We have performed ReaxFF simulations of both **L** and **LO** at 2000 K for 1 ns, and found that **L** reached equilibrium at $\sim$410 ps and **LO** reached equilibrium at $\sim$780 ps (kinetic energy, potential energy and total molecular number remain unchanged). Within 200 ps, the concentration of main product CO in **LO** reached its maximum (Fig. S5, *Supporting Information*). The oxidation reaction would be stopped when the CO concentration approaches a maximum value in the real situation. It is obvious that $O_2$ is