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ReaxFF simulations of hydrothermal treatment of lignite and its impact on chemical structures

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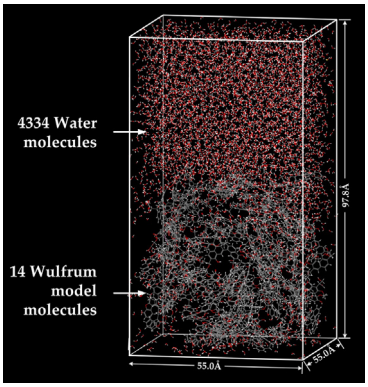
HIGHLIGHTS

- Hydrothermal treatment mechanism of lignite is simulated by ReaxFF molecular dynamics.
- The simulation results show good agreements with previous experimental results.
- Water molecules destroy intermolecular hydrogen bonds and coordination in lignite.
- Metal atoms in lignite are removed by water molecules at high temperatures.
- The hydrogen atom plays a key role in both releasing oxygen-containing groups and inhibiting cross-linking reactions.

GRAPHICAL ABSTRACT



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ABSTRACT

Two structural models for pyrolysis and hydrothermal treatment of lignite were constructed to investigate the impact of water at high temperature on the structure and reaction processes of lignite. The chemical model proposed by Wolfrum was used as the structural unit of the two models. Reactive force field molecular dynamics was employed to simulate the reaction process of the two models at 1000–3000 K over a period of 300 ps. The characteristics observed in the simulation agree well with the known characteristics of the lignite structure and reactions. The effects of temperature on the product distributions, intermolecular interactions and elementary reactions were analyzed. We found that the temperature should be controlled in an appropriate range in hydrothermal treatment to reach maximum ratio when extracted by organic solvents. The added water molecules can form hydrogen bond with O-containing groups and complexes with metal atoms, destroying intermolecular interactions in lignite. The hydrogen radicals from water molecules can inhibit cross-linking reactions between relatively small fragments, thereby decreasing molecular weights distribution of lignite. Furthermore, water molecules are also favorable to releasing O-containing groups and metal atoms at high temperatures. This work is an intensive study on hydrothermal-treatment mechanism at high temperatures at the atomic level. These conclusions could be helpful for the clean coal technology of lignite.

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1. Introduction

Coal is one of the most important fossil fuels, which can be divided into different categories according to coal ranks [1]. Lignite is considered as the lowest rank of coal due to its relatively low heat content. Lignite usually contains a relatively large quantity of water, sulfur and metal elements. So, direct combustion of lignite would produce a large amount of pollutants, include dust, sulfur dioxide, nitric oxides and so on [2]. Application of coal-cleaning methods to lignite can increase its heat content and make it more environmentally friendly. A number of physical, chemical and biological pretreatment methods [3] can effectively remove the water content, ash content, pyritic sulfur, and trace elements associated with major inorganic elements.

Hydrothermal treatment is one of the pretreatment methods for lignite [3]. Unusually, coal and water are mixed at the ratio from 1:1 to 1:2 and are hydrothermally treated at high temperature and high pressure in an airtight reaction vessel [4–12]. Recently, Fu et al. studied the effects of thermal and hydrothermal treatments on properties of two low-rank coals [7]. Hydrothermal treatment was carried out at temperatures from 150 °C to 300 °C with autogenously pressure from 0.8 MPa to 9.2 MPa. Shui et al. found that hydrothermal treatment could increase the extraction yields of bituminous coals in the carbon disulfide/N-2-pyrrolidinonein mixed solvent [11,12]. The decrease of total oxygen and hydroxyl oxygen in hydrothermal treatment was responsible for the enhancement of solubility. Our group also found that effects of hydrothermal treatments of low rank coals are related with temperature, pH of the water, etc. [13]. Besides, it is found that hydrothermal pretreatments of lignite could increase its calorific value, and further improve its combustion efficiency [3]. The removal of mineral matter could also reduce its sulfur dioxide emissions. Meanwhile, swelling behavior of lignite could be restrained and extraction yield in organic solvents is increased after hydrothermal treatment. Partial water, volatile matters, metal elements and ash contents is removed. Researchers have speculated the reasons for the above phenomena in hydrothermal treatment. It is thought that structures of lignite are changed when lignite and water are co-pretreated hydrothermally. At high temperatures, oxygen content is decreased and hydrogen content is increased [12] According to these experimental results, it is not enough to propose a mechanism of hydrothermal treatment of low-rank coals. This is because the thermal reactions of coal, including hydrothermal treatment, involve a large amount of free radicals as intermediates [14]. The concentrations, categories of radicals and their elementary reactions in the reaction process will greatly influence the compositions and structures of the final products. However, impacts of radicals on coal structures and its reaction mechanism in hydrothermal treatments have been ignored in the above experiments. Due to their high reactivity and very short lifetime, there are only a few measurement techniques for radicals, such as electron paramagnetic resonance (EPR) [15] and rapid condensation [16]. By EPR, the total concentration of radicals can be obtained, but their categories cannot be determined. By rapid condensation, only inactive big molecular radicals can be detected, but active small molecular radicals are ignored. Herein, experimental works are not sufficient to obtain impacts of radicals on reaction mechanisms in hydrothermal treatment. Detailed theoretical investigations are needed to study theses proposed mechanisms.

Nowadays, the molecular dynamic (MD) simulations [17,18] based on reactive force field (ReaxFF) have been successfully applied to simulate complex systems, such as the coal macromolecules. By ReaxFF, Wei et al. have investigated the pyrolysis mechanism of lignite in the supercritical methanol solvent [19]. They found that the pyrolysis of lignite is initiated by ether linkage cleavage, followed by carbon skeleton rearrangement and hydroxyl migration. Both the product species and the initiation reactions predicted by ReaxFF agreed well with previously reported work [20]. Li et al. have performed ReaxFF MD simulations of initial pyrolysis process of bituminous coal [21,22]. The product profile tendency and the sequence of gas generation in the simulations were consistent with experiments. Our group has also simulated the pyrolysis mechanism of ion-exchanged lignite by ReaxFF, and has explained the catalytic mechanism of metal ions [23]. So, ReaxFF simulations of coal reactions could successfully explain mechanisms of complex reactions of coal macromolecules in molecular level. If the results are converged in numerical calculations and are consistent with the experimental results at the same time, ReaxFF simulation can adequately address the reaction details of hydrothermal treatments. However, detailed mechanisms of hydrothermal treatment of lignite studied by ReaxFF MD have never been reported yet.

In this study, we investigated the mechanism of hydrothermal treatment of lignite by a series of ReaxFF MD simulations. A metal-containing chemical model developed by Wolfrum [24] was selected as the structural unit in these simulations with some modifications. In ReaxFF, an atom is treated as a single particle, and a chemical bond is treated as a "spring". Unlike quantum chemical methods [25,26], ReaxFF does not involve electrons or high spin states of metal atoms in the model molecule. By observing product and element distributions, intermolecular interactions and elementary reactions at different simulation temperatures, we can obtain the detailed process of reaction between lignite and water molecules at the molecular level. In particular, impacts of hydrothermal treatment on the chemical structures of lignite are discussed. We believe our theoretical work could aid in understanding experimental results of coal hydrothermal treatments and be helpful for the clean coal technology of lignite.

2. Simulation details

2.1. Three-dimensional model construction

The chemical model provided by Wolfrum is selected to depict the structural units of lignite. This model revealed interconnections among various structural components, such as lignin, humic acid and aromatic ring in lignite structure [24,27,28]. It is one of the few models which contain coordinated metal atoms. Furthermore, different types of functional groups with oxygen lead to high reactivities of this model. We have modified some unreasonable or unstable substructures in this model, and further changed N and S atoms due to limitations of the force field. The final structure of the chemical model used in this article (molecular formula $C_{227}H_{177}O_{44}AlCaFe$, abbreviated as **W**) is shown in Fig. 1. Since all S and partial N atoms are changed to O atoms, more O-containing reactions and no N- and S-containing reactions may be observed. These changes have not induced new types of functional groups in the model, and would not affect the mechanism of the hydrothermal treatment. More detailed modifications can be found in Figs. S1 and S2 of Supporting Information. Dried products after pyrolysis or hydrothermal treatment, the inorganic ash content of lignite could not be considered in this work.

The initial conformation of **W** molecule was optimized by the Dreiding force field [29] in the LAMMPS program [30,31] (see Fig. 2a). Subsequently, 14 **W** molecules were added to a $55.00 \times 55.00 \times 55.00$ Å cell to construct a three-dimensional lignite model (**M1**, see Fig. 2b) by the Packmol package [32]. Considering the water molecules in the hydrothermal treatment, we built another 3D model containing 14 **W** molecules and 4334 water molecules (**M2**, see Fig. 2c) in a $55.00 \times 55.00 \times 97.80$ Å cell. The density of the added water molecules in the top of the cell is 1.000 g/cm^3. The weight ratio of **W** molecules and water molecules