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Study of coal hydropyrolysis and desulfurization by ReaxFF molecular dynamics simulation

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HIGHLIGHTS

- Hydropyrolysis of coal was studied using reactive force field and compared with pyrolysis.
- Hydrogen plays a role to weaken the C—S bond and serves as H radical provider during hydropyrolysis.
- Hydrogen has positive effects on the gas production and desulfurization.
- Desulfurization rate increases first and then decreases with the rise of temperature or pressure.

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ABSTRACT

Based on the Wiser Coal Model, the process of coal hydropyrolysis was studied by molecular dynamics simulations with reactive force field (ReaxFF). The gas production and organic sulfur removal were analyzed. The related reaction mechanism and factors were discussed. It turns out that hydropyrolysis, relative to pyrolysis, could increase the gas yield and improve the removal rate of organic sulfur up to 80%. With the rise in temperature or pressure, the desulfurization rate increases first and then decreases. Adding hydrogen could weaken the C—S bonds in thiophene (ring), thiophenol (R–S–H), phenyl sulfide (R–S–R), then the bond-dissociation energy declines and the bonds are easier to break, so the hydropyrolysis could effectively improve the desulfurization rate. The simulated temperature-dependence of desulfurization rate is in agreement with the reported experimental tendency.

1. Introduction

Coal plays a key role in the world's energy resource, and it supplies 70% of total energy consumptions in China in 2009 [1]. Conventional utilization of coal fails to meet human needs for environmental and economic benefits, so people turned to produce new technologies of coal conversion and utilization. From 1970s, hydropyrolysis technology has attracted great attention in pursuing energy-efficient production of light hydrocarbon-rich gaseous products [2–4] and high efficient desulfurization of purification [5–7].

In 1970s, Wiser's research group [3] conducted a series of experiments on the coal hydropyrolysis and pyrolysis, they found that the light hydrocarbon and tar products significantly increased in hydropyrolysis than pyrolysis. And then Collin et al. [2] studied distillate constituent of hydropyrolysis using the same experimental method. In 1990s, Li's group [8] investigated the influence of different reaction conditions on the desulfurization of hydropyrolysis in a pressurized fixed bed, the results showed the desulfurization rate of hydropyrolysis enhanced 80% related to pyrolysis in nitrogen atmosphere. Yoneyama et al. [9] studied the effect of water on coal hydropyrolysis without catalyst, the results indicated that pyrite in coals acted as the catalyst and played an important role in synergistic effect between hydrogen and water on the conversion of coal. Luo et al. [6] studied formation of gaseous sulfur species during the steam hydro-gasification process by experiments.

Considerable research has been conducted on the hydropyrolysis by experiments. Owing to the limitation in experimental analysis, e.g. it is hard to observe the process and confirm the intermediate, the effects of hydrogen on the reaction mechanism of gas production and desulfurization have not yet been discovered.

In recent years, researchers have applied molecular dynamics (MD) and quantum chemical calculation to coal pyrolysis

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[10–12] for the possible reaction pathways. The ReaxFF reactive force field, capable of describing bond breaking, bond formation, and chemical reactivity, has been developed to be an effective method for complicated chemical reactions under various conditions. Salmon and van Duin et al. [13] used ReaxFF reactive MD to investigate the thermal decomposition of pure coal, and they found that the decarboxylation and dehydroxylation of the lignin side chain of morwell brown coal model involves the formation of double bonds conjugated with the aromatic rings. It was also found that gaseous hydrocarbons were generated by cleavage of C—C bonds of the lignin side chain. Zhang's group [14] combined ReaxFF MD with the density functional theory (DFT) to investigate the mechanisms of coal pyrolysis in supercritical water (SCW). Their results implied that SCW can induce the cleavage of the C—C bond in aromatic rings and cyclic structures, which decreases the cracking energy of C—C bond and enhances the reaction of aromatic ring openings. They also revealed interaction mechanism between SCW and coal. Chen et al. [15] also applied ReaxFF MD simulations to lignite methanolysis in supercritical methanol (SCM) with a unimolecular model compound, and their results indicated that the SCM donated hydrogen to other intermediate radicals, which promoted linkage cleavage when compared to common methanol. To date, however, no theoretical study has been reported on the coal hydropyrolysis.

In this paper, the reaction mechanism of coal hydropyrolysis was investigated by ReaxFF MD simulations to reveal the effects of hydrogen on gas production and desulfurization. The influences of temperature and pressure on the rate of desulfurization were further studied. Our work is expected to be beneficial to optimizing the conversion and utilization of coal.

2. Coal model and simulation method

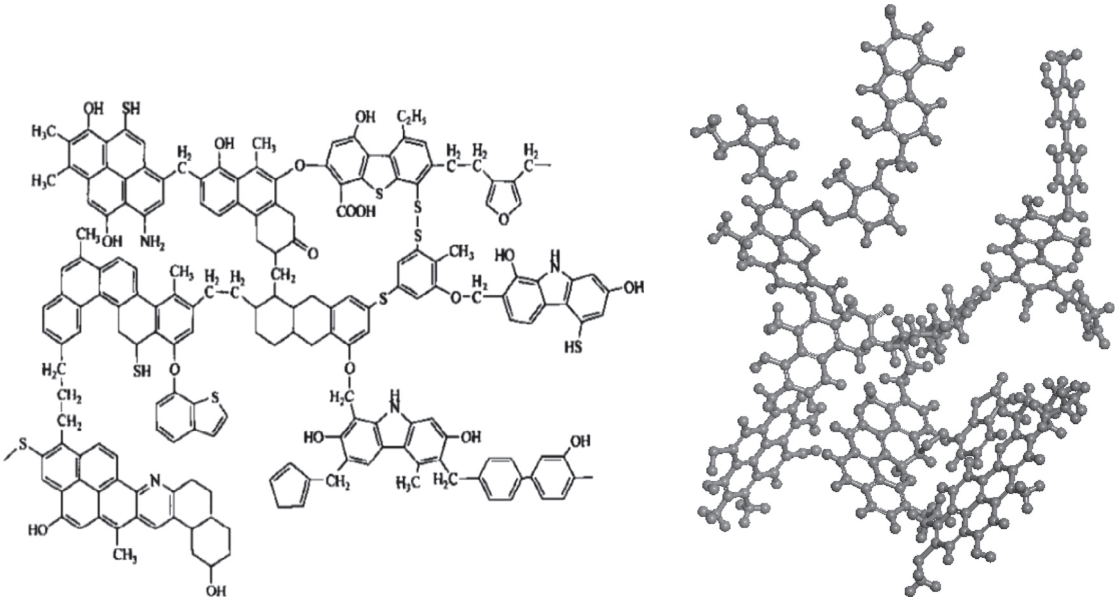
A large number (>134) of molecular representations for coals that span the rank range had been proposed over the past seven decades [16]. Among them, the Wiser Coal Model [17] (Fig. 1a) was accepted due to its good representation of the macromolecular part of coal structure, and its chemical formula is $C_{190}H_{166}N_5O_{19}S_9$. The three-dimensional coal model (Fig. 1b) in this work was optimized from the Wiser Coal Model.

For comparison, we designed four reaction systems as listed in Table 1 and Fig. 2. Periodic boundary conditions in all directions were applied to eliminate possible surface effects. The initial density of four systems was set as 0.3 kg/m^3. Nitrogen was added to reaction system S2 and S4 as inert gas, relative to hydropyrolysis systems S1 and S3. The geometric relaxation was conducted on the systems as follows: Firstly, the temperature of the system was slowly raised from 0 k to 300 K with a rate 3 K/ps. Then, an annealing cycle ran from 300 K to 600 K using NVT ensemble (constant atomic number, volume and temperature) for 60 ps. The equilibrium structures obtained after NVT-MD simulation were set as the initial models for the following simulations.

ReaxFF was developed by van Duin ACT and his group [18]. It is an empirical reactive force field that can describe bond formation and charge transfer for complex reactive molecular systems based on the bond order. ReaxFF reactive force field method has demonstrated good agreements with quantum chemistry methods in reproducing the potentials of alkanes and aromatic hydrocarbon with oxygen, nitrogen, and sulfur [19–23]. The initial reaction mechanisms and kinetics associated with hydrocarbon [19,24–26], soot [13,27], and coal [28–31] pyrolysis process have been studied using ReaxFF MD simulation. Recently, the reports of the coal pyrolysis process in SCW [14] and SCM [15] validate the applicability of ReaxFF to the coal–gas interaction systems.

Table 1
Parameters of reaction systems.

Systems	Coal	Addition	Geometries(nm)	Density (kg/m^3)
S1	5	100H$_2$	4.416 × 4.416 × 4.416	0.3
S2	5	100N$_2$	4.666 × 4.666 × 4.666	0.3
S3	5	400H$_2$	4.491 × 4.491 × 4.491	0.3
S4	5	400N$_2$	5.291 × 5.291 × 5.291	0.3



(a) 2-D Wiser Coal Model

(b) 3-D coal model after optimization

Fig. 1. Wiser Coal Model.