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Molecular dynamic investigation on hydrogen production by polycyclic aromatic hydrocarbon gasification in supercritical water

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ABSTRACT

The decomposition of polycyclic aromatic hydrocarbon (PAH) is the rate-determining step for coal gasification in supercritical water (SCW). Anthracene, which is the simplest PAH, was selected as the model compound to investigate the gasification characteristics. The reactive force field method combined with the method of density functional theory was utilised to investigate the SCW gasification process of anthracene, and the process was also compared with steam gasification and pyrolysis. Compared with pyrolysis, SCW effectively weakened the C(ring)-C(ring) bond energy in anthracene and decreased the energy barrier of the ring-opening reaction by 558.22 kJ/mol. The effect of SCW on the anthracene gasification was revealed. This effect proved that supercritical water accelerated the gasification rate and increased the hydrogen yield. The SCW molecule was converted into H radical-rich water clusters, which contributed to the main source of H_2 production.

Introduction

The utilization method based on coal burning causes serious pollution problems. The efficient and clean utilization of coal is a major issue that is yet to be resolved at present [1,2]. Over the past few decades, the supercritical water (SCW) gasification of coal has become a research hotspot. This method is considered effective and clean with high carbon conversion and can convert coal into small molecules of gas [3,4]. Many researchers have studied the process of SCW gasification and have mainly focused on various feed stocks, the reactor design, and major thermodynamic analysis. The group of Bi [5–10] completed a series of pyrolysis experiments based on a variety of feedstock [5–7,9,10] gasification in SCW They developed coal gasification in SCW with a short-running process, but the carbon conversion was higher than that in pyrolysis in N_2. The group of Guo [3,4,11–13] contributed to optimization of the reactor and proposed a SCW fluidized bed reactor to eliminate the plugging problem and therefore realise continuous and stable operation. They also investigated and numerically simulated various reactors based on gasification kinetics. The group of Vostrikov [14–17] established a semi-continuous reactor for coal gasification and investigated the kinetic characteristics based on a homogenous non-reactive core and porous pore model. These above investigations showed that the product distributions of coal gasification in SCW are obviously different from those of

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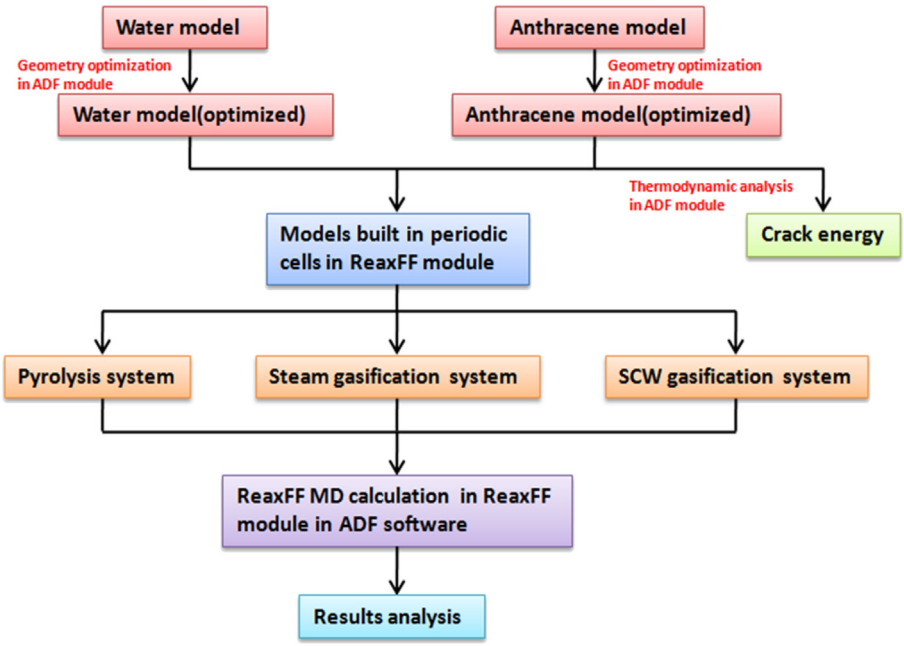

Fig. 1 – Molecular dynamics calculation flow chart.

steam gasification and pyrolysis. A SCW environment can effectively increase the yield of small molecules, especially H_2 [17].

SCW has been reported to act as solvent and as reactant in the reaction process [18–20]. However, the effects of SCW on the reactions are yet to be comprehensively determined because of the unique characteristics of SCW. Hence, we need to be cautious in improving the yield of hydrogen in the coal gasification process in SCW. Liu and his colleagues [21] used a series of quantitative chemical calculation methods to study the possible reaction pathways between the carboxyl aromatic ring and hydroxyl aromatic ring with a brown coal model. However, their results did not involve SCW. The group of Zhang [22–25] simulated the molecular dynamics to study the effects of SCW on the cracking of a linear chain, aromatic ring openings and H_2 production with the three-dimensional Wiser model. These above-mentioned contributions helped to reveal the mechanism and to promote the optimization of the reactor based on the SCW reaction environment.

Polycyclic aromatic hydrocarbons (PAHs) are the main intermediate products of the biomass, petroleum and coal chemistry industries [26,27]. PAHs are also believed to be the rate-determining step in the thermal chemistry conversion process. As a typical and the simplest PAH, anthracene shares numerous common characteristics with coal and oil [22,28–35]. Thus, anthracene is chosen as the model compound of PAH in this study. The method of reactive force field (ReaxFF) coupled with density functional theory (DFT) is used to investigate SCW gasification process of anthracene, and the process is also compared with traditional pyrolysis and steam gasification to investigate the effects of SCW on the gasification process.

Computational method

Simulation details

The calculations were performed using the DFT and ReaxFF methods of the Amsterdam Density Functional (ADF) software supplied by SCM Inc. And the overall approach was shown in Fig. 1. Firstly, the anthracene model and the water model were optimized using the ADF module in the ADF software. The model optimization and thermodynamic analysis of anthracene were conducted using DFT. The DFT calculations were at the level of the generalized gradient approximation using the Becke–Lee–Yan–Parr function [22,36]. The DZP basis set was applied in this study. For comparison, three reaction systems were designed. These systems are listed in Table 1. The initial structures of the steam gasification system, supercritical water gasification system and pyrolysis system were built using the ReaxFF module in ADF software. Periodic boundary

Table 1 – The parameter setting of three simulation systems.

System	Anthracene (molecules)	Water (molecules)	Density/g·cm $^{-3}$	Pressure/MPa
Pyrolysis	50	0	0.58	0.1
Steam gasification	50	500	0.039	0.1
SCW gasification	50	500	0.38	25