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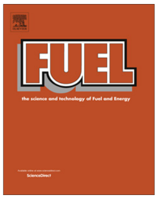

Molecular dynamic simulation of spontaneous combustion and pyrolysis of brown coal using ReaxFF

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HIGHLIGHTS

- Combustion and pyrolysis of brown coal was studied using reactive force field.
- During combustion, the yield of gaseous products were more in fuel lean conditions.
- Potential energy of the system decreases with increase in temperature.
- Effect of temperature was more pronounced as compared to density during pyrolysis process.
- Both combustion and pyrolysis process followed exothermic and endothermic path.

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ABSTRACT

Brown coal is a soft sedimentary organic rock which is complex in nature and is the main source of energy production. In this work, we have studied the combustion and pyrolysis of brown coal using reactive molecular dynamic (MD) simulation. To make the large scale (above 1000 of atoms) reactive system practical, ReaxFF MD system was used which is 100 times faster than the methods of quantum mechanics (QM). To examine the pyrolysis/combustion process and initiation mechanism of brown coal, a fuel lean ($\phi = 2$), fuel rich ($\phi = 0.5$) and stoichiometric ($\phi = 1$) conditions were used in this work. The temperature used was high as per experimental reported condition so as to enable chemical reaction within a computationally affordable time. It was observed that the combustion of brown coal was initialized by thermal degradation subsequently forming small fragments. As the brown coal molecule oxidizes or thermally decomposes, hydrogen is abstracted and reacts with oxygen to form large amount of H_2O molecules. Furthermore, the combustion of coal was also studied in the same conditions namely fuel rich, fuel lean and stoichiometric. Potential energy gradually decreases at high temperature while it was the reverse in pyrolysis. It was found that the effects of densities are lesser as compared to temperature. Some important intermediate like formaldehyde (HCHO) generated during the simulation reaction agreed well with the experimental data reported in literature.

1. Introduction

Coals are generally complex in structure. Its contain mainly carbon and large number of oxygen, phenol, carboxyl, carbonyl, ether and hydroxyl groups as well as gaseous products like CO_2, CO, SO_2, N_2, and H_2O [1,2]. During the oxidation and pyrolysis processes large numbers of hydrocarbons, alternative fuels and bio-chemicals are produced. For electricity production, coal combustion fuels are used as a primary source [3]. Rapid loss of moisture and devolatilization occurs during the coal combustion process. High pressure pyrolysis of hydrocarbon decreases the volatile mater and increase the H/C and O/C ratio which is beneficial for the spontaneous heating of coal at low temperature. Pyrolysis temperature is one of the key parameter to describe the physical and chemical properties of the char atomic structure. From the chemical analysis of char, it is observed that atomic ratio of H/C and O/C significantly decreases with increasing pyrolysis temperature [4–13]. At low temperature, coal oxidation is an important source of spontaneous combustion of coal contributing to greenhouse gases emission. The reaction mechanism explains the details of the consumption of oxygen and formation of the gas and solid phase oxidation products. The solid oxidation products like aliphatic and aromatic compounds and gaseous products such as CO, CO_2 and H_2O are formed during the reaction [14–18]. Experimental measurements examining pyrolysis has provided the analytical structural information of brown coal [19,20]. Variation of temperature range and the residence time in the thermal decomposition of n-dodecane gave

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major intermediate such as hydrogen, ethylene and also gave the kinetic parameters for the formation of benzene. Therefore, the chemical kinetics and the thermodynamics models are the two important major factors which describe the detailed analysis of the pyrolysis and combustion reaction mechanism of $C_{12}H_{26}$ which contains 1282 species and 5030 elementary reactions [21]. Although the char models were effective for the studies of the pyrolysis reaction, but the description of the structural model of char is complicated and time consuming due to its complexity in structure. Therefore the inorganic complexes have been described with the help of both experimental as well as small scale modelling for low rank coal and char containing inorganic complex [22–24].

Subsequently, kinetic chemical models were developed, but its validation with experimental results was found to be very expensive and time consuming. Therefore, simulation methods are preferred to examine the details reaction mechanism of the pyrolysis and combustion process. The molecular dynamic (MD) simulation provides a fundamental reaction mechanism using a representative structure of brown coal. Reactive force field is then used to describe the detailed fundamental understanding of the formation, transition and dissociation of the chemical bond during the reactive MD simulation which is accurately close to quantum mechanics (QM) [25].

For large scale systems (i.e. above 1000 atoms) reactive chemical system, ReaxFF [26] has developed different types of reactive force field in order to describe the bond order, bond distance, bond dissociation energy of the atomic structure. This allows us to describe complex reactions of hydrocarbons [27,28]. Several ReaxFF models have been developed for different materials and applications [26,29–32]. The ReaxFF reactive force field has earlier analyzed kinetics and initial reaction mechanism for different hydrocarbon, fuel, oxidation, combustion and pyrolysis of coal [25,33–36]. Further, the time scale of reactive dynamics simulations is 100 times faster than the commonly used quantum mechanics (QM). Thus, a reactive simulation used at a temperature range much larger than normal experimental/industrial conditions help us to enable chemical reactions within a computational affordable time [35–37].

Recently, for hydrocarbon combustions, researchers have expanded the force field for sulfur and nitrogen containing hydrocarbon. ReaxFF have been found to correctly simulate pyrolysis and combustion of coal molecules and hydrocarbon containing sulfur and nitrogen functionality [32]. Castro-Marcano et al. [38,39] used ReaxFF for Illinois No. 6 coal to analyze the pyrolysis simulations on a large-scale molecular model based on experimental data to investigate the effect of sulfur content on the pyrolyzed coal structure. Recently the ReaxFF MD simulations gave a detailed behavior of the thermal decomposition of algaenan of biopolymer. It further elucidated the mechanism observed in the pyrolysis experiments of algae [40]. In this present work, ReaxFF was used to perform the initiation mechanism of spontaneous combustion and pyrolysis of brown coal. Till date we did not find studies on the initiation process for brown coal. Further in order to benchmark our predictions, we also compared the results on the products formed in intermediate stages.

2. Computational details

2.1. ReaxFF force field

ReaxFF [26] is based on the covalent formalism [41] and the bond order principle which relates the bond energy to bond lengths, valence angles and torsion angle [42]. It was developed to efficiently simulate molecular dynamics of large scale chemical systems containing more than thousand atoms. Generally, the ReaxFF is the boundary between quantum mechanics (QM) and classical mechanics models based on the semi-empirical interaction potential. The total potential energy of the system is described by Eq. (1) [26] which is associated with different partial energy contributions:

$$\begin{aligned} E_{system} &= E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} \\ &\quad + E_{vdWaals} + E_{Coulomb} \end{aligned} \tag{1}$$

where E_{system} is the potential energy of the system which describes the interaction between the particles of the systems. The interaction potential can be divided into non-reactive and reactive potentials. The non-reactive potential simulates transition state and barrier energy in a reaction; whereas reactive potential has a ability to simulate reaction between particles by bond formation and dissociation between the particles accurately. The reactive potential is more expensive then the non-reactive potential. E_{bond} represents the bond energy due to the interatomic distance between a pair of atoms. It calculates the bond order between the interatomic distances, which is given by Eq. (2) [26],

$$\begin{aligned} E_{bond} = &-D_e^{\sigma} \cdot BO_{ij}^{\sigma} \cdot \exp\left[p_{be,1}\left(1 - \left(BO_{ij}^{\sigma}\right)^{p_{be,2}}\right)\right] - D_e^{\pi} \cdot BO_{ij}^{\pi} \\ &- D_e^{\pi\pi} \cdot BO_{ij}^{\pi\pi} \end{aligned} \tag{2}$$

where BO'_{ij} is the bond order between a pair of atoms which is obtained directly from the interatomic distances. If a pair of atoms like carbon–hydrogen or hydrogen–hydrogen is observed then only sigma bond is considered; whereas for carbon–carbon, where bond order of three results in one sigma and two π bonds.

$$\begin{aligned} BO'_{ij} &= BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \\ &= \exp\left[p_{bo1} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{bo2}}\right] + \exp\left[p_{bo3} \cdot \left(\frac{r_{ij}}{r_o^{\pi}}\right)^{p_{bo4}}\right] \\ &\quad + \exp\left[p_{bo5} \cdot \left(\frac{r_{ij}}{r_o^{\pi\pi}}\right)^{p_{bo6}}\right] \end{aligned} \tag{3}$$

E_{over} and E_{under} represents over- and under-coordinated energy, respectively. After the correction of the original bond order, a degree of over coordination may remain in the molecules. Therefore to handle this error an over coordination has been used and is given by,

$$E_{over} = p_{over} \cdot \Delta_i \cdot \left(\frac{1}{1 + \exp(\lambda_6 \cdot \Delta_i)}\right) \tag{4}$$

where $\Delta'_i = \sum_{j=1}^{nbond} BO'_{ij} - Val_i$ is the degree of deviation for the sum of the corrected bond orders around an atomic center.

$$E_{under} = -p_{under} \cdot \frac{1 - \exp(\lambda_7 \cdot \Delta_i)}{1 + \exp(-\lambda_8 \cdot \Delta_i)} \cdot f_6(BO_{ij,\pi}, \Delta_j) \tag{5}$$

where $f_6(BO_{ij,\pi}, \Delta_j) = \frac{1}{1+\lambda_9 \cdot \exp\left(\lambda_{10} \cdot \sum_{j=1}^{neighbors(i)} \Delta_j \cdot BO_{ij,\pi}\right)}$

Other terms, including E_{val} is the valence angle energy for valence angle i–j–k, where i, j, k are location for three atoms. If one of the two bonds in the angle break, the valence angle energy disappears smoothly. The energy contribution from valence angle term goes to zero as the bond orders in the valence angle goes to zero. The valence angle energy term is given by [26],

$$\begin{aligned} E_{val} = &f_7(BO_{ij}) \cdot f_7(BO_{jk}) \\ &\cdot f_8(\Delta_j)\left(k_a - k_a \exp\left[-k_b(\Theta_0 - \Theta_{ijk})^2\right]\right) \end{aligned} \tag{6}$$

where $f_7(BO_{ij}) = 1 - \exp\left(-\lambda_{11} \cdot BO_{ij}^{\lambda_{12}}\right)$

$$\begin{aligned} f_8(\Delta_j) = &\frac{2 + \exp(-\lambda_{13} \cdot \Delta_j)}{1 + \exp(-\lambda_{13} \cdot \Delta_j) + \exp(p_{v,1} \cdot \Delta_j)} \\ &\times \left[\lambda_{14} - (\lambda_{14} - 1) \cdot \frac{2 + \exp(\lambda_{15} \cdot \Delta_j)}{1 + \exp(\lambda_{15} \cdot \Delta_j) + \exp(-p_{v,2} \cdot \Delta_j)}\right] \end{aligned}$$