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Research article

A reactive molecular dynamics study of CH_4 combustion in $O_2/CO_2/H_2O$ environments

Dikun Hong[a], Xin Guo[a,b,*]

[a] State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, 1037 Luoyu Street, Hongshan, Wuhan, Hubei 430074, China

[b] Shenzhen Institute, Huazhong University of Science & Technology, Shenzhen, Guangdong 518000, China

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ABSTRACT

CH_4 oxidation in $O_2/CO_2/H_2O$ environments was studied using reactive molecular dynamics (ReaxFF-MD) method with the aim to investigate the chemical effects of CO_2 and H_2O under different conditions. The influence of molar heat capacity and thermal radiation of CO_2 and H_2O were eliminated, which estimated that only chemical effects were taken into account. The results showed that high concentration of CO_2 inhibited the reaction rate of CH_4 at low temperatures, but advanced CH_4 oxidation rate at high temperatures because of CO_2 reactivity expressed by $CO_2 + H \rightarrow CO + OH$ (R1). The presence of H_2O promoted the oxidation rate of CH_4 even at low temperatures. Reacting with O and H radicals through $H_2O + O \rightarrow OH + OH$ (R2) and $H_2O + H \rightarrow H_2 + OH$ (R3) dominate the effect of H_2O. Furthermore, the interaction between CO_2 reactivity and H_2O reactivity was studied in $O_2/CO_2/H_2O$ combustion under fuel rich condition. It was shown that the presence of 30%H_2O promoted the conversion rate of CO_2 at relatively low temperatures by providing more H radicals for R1, therefore enhanced CO production. However, an inhibition effect of H_2O on CO_2 conversion rate was found at high temperatures. R3 tended to occur at high temperatures, which would compete with R1 and thus the production of CO was suppressed. The main elementary reactions for CO_2 and H_2O were studied by analyzing the computed trajectory of the systems during ReaxFF-MD simulations. Finally, the effects of oxygen concentration on $CH_4/O_2/CO_2/H_2O$ systems were also studied. The results showed that the effect of CO_2 and H_2O were less pronounced with increasing O_2 concentration.

1. Introduction

Combustion of fossil fuels or any carbon containing materials releases carbon dioxide, which is recognized as the most important greenhouse gas emitted to the atmosphere ultimately leading to climate change. Recently, significant process has been made in different CO_2 capture technologies. Among those, one promising option is oxy-fuel combustion, which involves the combustion of the fuel with pure oxygen and recycled flue gases instead of air as in traditional combustion. Considering the economy of oxy-fuel combustion technology, wet flue gas recirculation is usually used for industrial applications. During oxy-combustion with wet flue gas recirculation, the level of CO_2 and water vapor in the furnace gases are much higher than that in conventional air-fired combustion. Oxy-fuel combustion has been found to differ from air combustion in several ways, including reduced flame temperature [1], delayed flame ignition [2], reduced NO_x and SO_x emissions [3,4]. Many of these effects can be explained by differences in gas properties between recycled flue gases and N_2: (1) lower thermal diffusivity, (2) higher molar heat capacity, (3) chemical effects, and (4) modified radiative heat transfer. Until now, numerous works have been performed concerning on the physical and chemical effects of CO_2 on fuel combustion at different conditions [1–13]. Glarborg et al. [9] studied the oxidation of CH_4 experimentally in an atmospheric-pressure flow reactor under the conditions of high CO_2 concentration at the temperatures range 1200–1800 K. Results indicated that the presence of CO_2 competes with O_2 for H radicals through the reaction of $CO_2 + H \rightarrow CO + OH$ (R1) which significantly leads to the increase of CO concentration during O_2/CO_2 combustion. Watanabe et al. [10] performed a CH_4 flat flame experiment to study the chemical effect of high concentration of CO_2 on CH_4 oxidation in fuel-rich O_2/CO_2 combustion. They concluded that CO_2 mainly takes part in the reaction of R1 and the chemical effect of CO_2 advances CH_4 oxidation. CO_2 reactivity reduced the H/OH ratio by converting H to OH and thus the formation of H_2 was inhibited while the production of H_2O was

* Corresponding author at: State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, 1037 Luoyu Street, Hongshan, Wuhan, Hubei 430074, China.
E-mail address: guoxin@mail.hust.edu.cn (X. Guo).

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Apart from CO_2, H_2O also plays an important role on the combustion characteristics of fuel in $O_2/CO_2/H_2O$ environments. Riaza et al. [14] reported that higher ignition temperatures and lower coal burnout values were observed after the addition of steam in oxy-fuel combustion atmospheres under the experimental conditions due to the higher losses of heat by thermal radiation. Gil et al. [15] found that the replacement of 10% and 20% of CO_2 with H_2O in oxy-fuel combustion of the coal resulted in an increase in the rate of mass loss and a decrease in the burning time, no significant differences being observed between the two steam concentrations. Zhao et al. [16] reported that the chemical kinetic effect of steam addition promoted the OH radical production for the same maximum flame temperature due to the decomposition reaction of steam and consumption reactions of OH radical. Alzueta et al. [17] studied the effect of H_2O concentrations on the oxidation of CO for a CO_2 concentration of 0% and 25%, respectively. The results indicated that water vapor mainly takes part in the reactions of $H_2O + O \rightarrow OH + OH$ (R2), $H_2O + H \rightarrow H_2 + OH$ (R3) and H_2O also acts as a very efficient collision partner in $H + O_2 + M \rightarrow HO_2 + M$ (R4) which competes with the main chain branching reaction $H + O_2 \rightarrow OH + O$ (R5).

Adequate researches have been done for studying the individual influence of CO_2 or H_2O during oxy-fuel combustion as summarized above. During oxy-fuel combustion with wet flue gas recirculation, the fuel would be burned in an $O_2/CO_2/H_2O$ atmosphere. Both CO_2 and H_2O have significant chemical effect on fuel combustion. The reactivity of CO_2 is mainly expressed by R1, and H_2O may also react with H radicals through R3. In addition, the reactivity of H_2O is largely determined by the specific conditions such as temperature, H_2O concentration and so on [17]. The existence of H_2O provides more H radicals which would promote the reaction rate of R1. On the other hand, H_2O could also compete with CO_2 for H radicals which would inhibit the reaction rate of R1. Therefore, the interaction between CO_2 reactivity and H_2O reactivity needs to be further studied in $O_2/CO_2/H_2O$ combustion under different conditions. The volatiles are important for ignition, burnout, and pollutant emissions during fuel combustion. As an important component of volatiles, CH_4 combustion is the main topic of this study.

The statistics and analysis of the distributions of H/O/OH radicals and intermediates which are difficult to detect and replicate by experiments alone are important for understanding the chemical effect of CO_2 and H_2O during CH_4 combustion in $O_2/CO_2/H_2O$ environments. Therefore, an accurate and computationally feasible method is urgently needed. In general, density functional theory (DFT) [18] can investigate chemical reaction with high accuracy, but it is computationally intensive and expensive for large reactive systems. On the other hand, Classical molecular dynamics (MD) [19] can be used for modeling large-scale system, but it cannot describe bond breaking and bond formation in the chemical reactions. Recently, reactive force field (ReaxFF) derived from DFT has been developed for describing complex chemical reactions with accuracy close to quantum mechanics (QM) but with significantly reduced computational costs and can describe the effect of temperature and pressure. ReaxFF-MD method has been proved feasible for studying CH_4 combustion systems [20–24]. The chemical effects of H_2O during O_2/H_2O combustion with a high concentration of steam have also been studied by our recent research using ReaxFF-MD method and a better understanding of the initial or fundamental chemical events regarding the intermediate and radical distributions responsible for CH_4 combustion in the O_2/H_2O environment was obtained [25].

In this paper, the chemical role of CO_2 and H_2O on CH_4 oxidation during $O_2/CO_2/H_2O$ combustion was studied using the reactive molecular dynamics simulation method. CH_4 oxidation in O_2/N_2 combustion was also studied for comparison. Simulations were performed under well-defined reaction conditions to reduce the effects of molar heat capacity and thermal radiation in order to ensure that only chemical effects are significant. Furthermore, different conditions were taken into account concerning the influences of temperature and stoichiometries. An atomistic description of the details of the critical initiation reactions was observed directly during analysis of the computed MD trajectory of the model system allowing us to systematically describe the initial or fundamental chemical events responsible for the interaction between CO_2 reactivity and H_2O reactivity during CH_4 combustion in $O_2/CO_2/H_2O$ environment.

2. Computational methods and simulation details

2.1. ReaxFF reactive force field

The reactive force field derived from the calculations of quantum chemical can be used in molecular dynamics simulations of large systems. A parameter of bond orders calculated from the distance between a pair of atoms is adopted to describe the bond cleavage and formation during ReaxFF-MD simulations. The total potential energy of simulated system can be described by the following equation [26]:

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{tors} + E_{conj} + E_{vdWaals} + E_{Coulomb} \quad (1)$$

in which E_{bond} represents the bond energy between a pair of atoms, it can be calculated by Eq. (2) [26]:

$$E_{bond} = -D_{\varepsilon}^{\sigma} \bullet BO_{ij}^{\sigma} \bullet exp(p_{b\varepsilon,1}(1 - (BO_{ij}^{\sigma})^{p_{b\varepsilon,2}})) - D_{\varepsilon}^{\pi} \bullet BO_{ij}^{\pi} - D_{\varepsilon}^{\pi\pi} \bullet BO_{ij}^{\pi\pi} \quad (2)$$

where BO_{ij} denotes as the bond order between a pair of atoms. Only sigma bond is taken into account when describing H—H or C—H bond, whereas one sigma and two π bonds are considered when describing C—C bond. The bond order is given by Eq. (3) [26]:

$$BO_{ij} = BO_{ij}^{\sigma} + BO_{ij}^{\pi} + BO_{ij}^{\pi\pi} \quad (3)$$

E_{over} and E_{under} correspond to the atom under-coordination and over-coordination, respectively. Other terms, including E_{val}, E_{pen}, E_{tors}, E_{conj}, $E_{vdWaals}$, and $E_{Coulomb}$ are the valence angle term, penalty energy term, torsion angle energy, conjugation effects to molecular energy, non-bonded van der Waals interactions and Coulomb interactions, respectively. A more detailed description of these terms can be found in previous work by Banerjee [27]. In our simulations, The ReaxFF parameters for C/H/O/N compounds (see Supplementary data) used in our simulations have been identified accurately for hydrocarbon oxidation process, as shown in the previous studies [26,28].

2.2. Simulation details

In this work, a wide range of input conditions for the $CH_4/O_2/CO_2/H_2O$ mixtures were studied. First, all the systems were minimized at 5 K for 100 ps with constant number of atoms in a constant volume with control of the total energy, denoted as NVE-MD, for the purpose of detecting and subsequently correcting the overlap of assembly of atoms. Then, these systems were equilibrated at 1000 K for 100 ps with constant number of atoms in a constant volume with control of the temperature, denoted as NVT-MD, to distribute the extra degree of freedom i.e. kinetic energy to the potential energy contribution. These two processes were carried out with Compass force field using the Forcite Module in Materials Studio (MS) [29]. Finally, a series of NVT-MD simulations at temperatures range from 2400 to 3200 K under different CO_2 and H_2O concentration and stoichiometries were performed using ReaxFF force field for a total simulation time of 1000 ps with a time step of 0.1 fs. The temperature was controlled using the Berendsen thermostat [30] with a 0.1 ps damping constant. The product distributions were analyzed from trajectories after ReaxFF simulations using a bond-order cutoff of 0.3 Å. The density used in the simulations is 0.15 kg/dm^3. A summary of all the input conditions can be seen in