



Development, validation and application of the ReaxFF reactive force field to hydrocarbon oxidation kinetics

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Investigation of Methane Oxidation at different temperatures and the effect of Argon dilution: A ReaxFF Molecular Dynamics Study

Report for AFOSR grant FA 9550-17-1-0173

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1. Introduction

A major contributor to the global shift towards alternative and clean-burning fuels is the depletion of fossil fuels. The extraction and use of fossil fuels also pose a long-term threat to the environment. Methane captures the interest of many researchers as one of the alternative fuels as a main constituent of natural gas which produces significantly lower amount of hazardous air pollutants than oil and coal. Accordingly, there is a surge in the demand and global consumption of natural gas for power generation due to its abundancy, relatively low prices and environmental benefits. Furthermore, a recently developed Hybrid Chemistry¹ (HyChem) model for the design of jet fuels describes the combustion of larger hydrocarbon components as a two-step process. First, the complex hydrocarbon molecules convert into smaller components namely ethylene (C_2H_4), methane (CH_4), propene (C_3H_6), iso-butene ($i-C_4H_8$), 1-butene ($1-C_4H_8$), benzene (C_6H_6), toluene (C_7H_8) and hydrogen (H_2) through pyrolysis within the high temperature preheat zone. In the next step these decomposed fragments undergo oxidation in the flame zone to convert into final combustion products. With this new approach, combustion of conventional/alternative distillate fuels is largely governed by smaller hydrocarbons requiring a detailed oxidation mechanism of these components. Hence in order to develop detailed understanding of the oxidation mechanism of large hydrocarbon fuels we need to bridge the gap in our understanding

of the combustion properties of small intermediates such as CH_4 . Methane is one of most widely studied hydrocarbon fuels in a variety of conditions such as shock tubes^{2,3}, laminar flow reactors⁴, etc. But there is still some gaps in the understanding of oxidation mechanism specially at high pressure and intermediate temperature regime.²

The objective of the present work is to apply a computational approach to examine the dependency of overall methane oxidation behavior on different temperature/pressure regime. ReaxFF is a computationally feasible method compared to QM which can simulate large reactive systems with high accuracy. Therefore, ReaxFF provides a convenient method for the investigation of detailed oxidation reactions at the atomic level. ReaxFF C/H/O description has been developed to address the combustion of large and small hydrocarbon systems including processes as pyrolysis and oxidation⁵⁻⁹. The next sections describe the methodology implemented in this study, the results and discussion of methane oxidation and the conclusions of this study.

In addition, most of the engine studies of methane oxidation use dilution with monoatomic/diatomic or polyatomic gases to influence the parameters of combustion and control the temperature of flame¹. Studies conducted in shock tubes in high-temperature and pressure zones typically use argon or nitrogen to optimize shock wave behavior². However, the measured ignition delay times in the presence of different types of inert diluent gases has been shown to differ under some experimental conditions³. This raises concern about whether the use of diluents have any effect on the underlying chemistry of combustion. Hence in order to develop detailed understanding of the effect of inert diluent gas on the oxidation mechanism of methane we need develop an atomistic level of understanding of the mechanism.

The objective of the present work is to apply a computational approach to examine the dependency of methane oxidation pathways on the presence of varying degrees of argon gas. The next sections describe the methodology implemented in this study, the results and discussion of methane oxidation and argon dilution and the conclusions of this study.

2. Methodology

The simulations presented in this study are all performed with ReaxFF reactive force field based molecular dynamics (ReaxFF-MD) method. The next three sections present a brief introduction to the ReaxFF, description of methodology and CVHD method implanted in ReaxFF-MD for low temperature oxidation simulations.

2.1 ReaxFF introduction

ReaxFF^{10,11} or reactive force field is a second-generation empirical potential model which can accurately describe the smooth formation and dissociation of bonds between the atoms in a given system. ReaxFF determines the system connectivity from bond orders calculated from interatomic distances in conjunction with the bond order-bond energy relation. The bond order relationship in ReaxFF also has a significantly long-range thus allowing improved structures and energies for transition states. Hence the major advantage of using ReaxFF is its capability to simulate chemical reactivity and reaction kinetics without any precondition during MD simulations. With ReaxFF, the total potential energy of the system (E_{system}) is generally expressed as a sum of several partial energy contributions:

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{lp} + E_{val} + E_{tor} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

The first six terms, namely E_{bond} (bond energy), E_{over} and E_{under} (atom over- and under-coordination penalty energy), E_{lp} (lone-pair energy), E_{val} (valence angle energy), and E_{tor} (torsion angle energy) represent the bond-order dependency of the potential energy. These terms are updated with every iteration and their contribution approaches zero with bond breaking. The non-bonded van der Waals interactions and Coulombic interactions are represented in the total energy as E_{vdWaals} and E_{Coulomb} respectively. These energy terms are calculated between every atom pairs regardless of their connectivity and are shielded at short range to eliminate excessively strong repulsions. A more detailed description of the ReaxFF potential functions can be found in the work by van Duin et al.¹⁰

2.2 Simulation details

Methane oxidation. To study the methane oxidation, we employed molecular dynamics simulations using the ReaxFF CHO-2016 force field¹². The system containing methane/oxygen mixture is generated by placing 200 CH₄ molecules and 400 O₂ molecules in a box of size 51.03 Å x 51.03 Å x 51.03 Å. The box is set up ensuring periodicity in all three directions. The box dimension, number of molecules and their mole fractions are configured such that the system describes a stoichiometric methane/oxygen mixture (equivalence ratio $\phi=1$) with a density 0.2 g/cm³. The simulation procedure started with the minimization of the whole system using conjugate gradient minimization scheme. Next the system is equilibrated for 100 picoseconds at 1500 K using a time step size of 0.25 fs as shown in Figure 1. For temperature restraint, a Berendsen thermostat with a temperature damping constant of 100fs is used. The equilibration and MD simulations were performed with the canonical ensemble where the system has constant number of atoms (N) in a constant volume (V) and temperature (T), alternatively known as NVT-MD. The temperature range was selected from 2500K to 4000K with a 500K interval. The

simulations are run for 800ps with a time step of 0.1fs. In order to eliminate statistical uncertainty, ten different cases of simulations are performed with each having a different initial configuration.

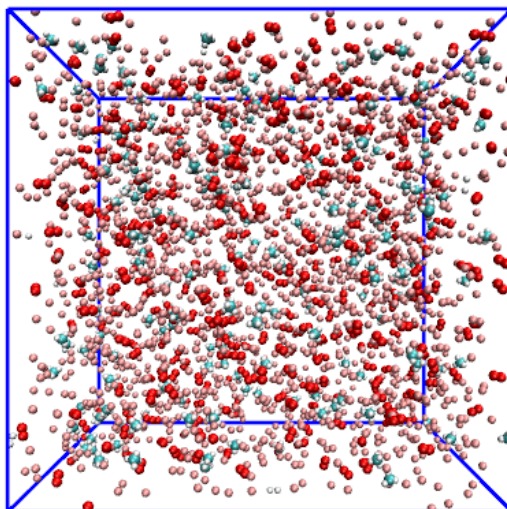


Figure 1: Snapshot of representative system of equilibrated methane and oxygen (total 1800 atoms) with density 0.2 kg/dm³.

Argon dilution effects. To study the methane oxidation with argon dilution, we employed molecular dynamics simulations using the ReaxFF CHO-2016 force field¹¹. The system containing methane/oxygen/ argon mixtures are generated by placing 200 CH₄ molecules, 400 O₂ molecules and different amount of argon in a box of size 51.03 Å x 51.03 Å x 51.03 Å. Table 1 lists the dilution ratio we used during the simulations. The box is set up ensuring periodicity in all three directions. The box dimension, number of molecules and their mole fractions are configured such that the system describes a stoichiometric methane/oxygen mixture (equivalence ratio $\phi=1$) with a density 0.2 g/cm³ without considering argon dilution. The simulation procedure started with the minimization of the whole system using conjugate gradient minimization scheme. Next the system is equilibrated for 100 picoseconds at 1500 K using a time step size of

0.25 fs as shown in Figure 1. For temperature restraint, a Berendsen thermostat with a temperature damping constant of 100fs is used. The equilibration and MD simulations were performed with the canonical ensemble where the system has constant number of atoms (N) in a constant volume (V) and temperature (T), alternatively known as NVT-MD. The temperature range was selected from 2500K to 4000K with a 500K interval. The simulations are run for 800ps with a time step of 0.1fs. In order to eliminate statistical uncertainty, ten different cases of simulations are performed with each having a different initial configuration.

Table 1: Molecular configuration of methane/oxygen/argon systems used in ReaxFF-MD simulations

CH₄ molecule #	O₂ molecule #	Ar molecule #	CH₄ mole fraction (χ_{CH_4})	O₂ mole fraction (χ_{O_2})	Ar mole fraction (χ_{Ar})
200	400	200	0.25	0.50	0.25
200	400	600	0.17	0.33	0.50
200	400	1800	0.08	0.17	0.75

2.3 Introduction to CVHD

Despite the availability of numerous experimental data for methane oxidation at high temperature/pressure conditions, typically in rapid compression machines and shock tubes^{ref}, most of the experiments do not go well beyond the temperature of 2000K¹³. On the other hand, owing to the high computational cost, it is currently not feasible to run reactive molecular dynamics simulations for a timescale of more than a couple of nano-seconds. Furthermore, to ensure the occurrence of significant reactions, the temperature is usually ramped up to very high values to facilitate bond-breaking and bond formation. However, recently few methods^{14,15} to accelerate reactions have been developed to perform ReaxFF-MD simulation at a lower

temperature region for which experimental data is available. In order to access the relatively lower temperature domain ($<2000\text{K}$) and longer time-scale we have also employed a recently developed procedure called CVHD^{16,17} (collective variable-driven hyperdynamics) in the present work. The method of CVHD, which is an extension of the hyperdynamics method, adds a suitable self-learning bias potential to the potential energy surface of the system. The simulated physical time called hypertime is the product of MD simulation time and the boost factor.

ReaxFF-MD simulations for methane-oxygen mixtures with configurations mentioned in Section 2.2 have been also performed implementing CVHD method with the parameters mention in reference¹⁷. The range of temperatures for these NVT simulations were 1200K, 1400K, 1600K and 1800K.

3. Results and Discussion

3.1 Fuel decomposition and overall product analysis

The oxidation of methane observed in this ReaxFF-MD study occurs primarily in two stages. During the first one the thermal decomposition of methane molecules results into formation of CH_3 radicals. The second step involves the conversion of CH_3 into some of the major final products such as CO_2 , H_2O , CO etc.

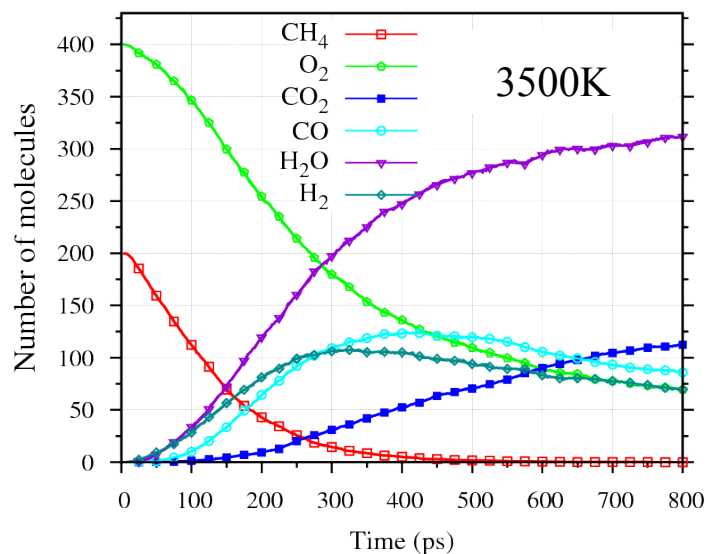


Figure 2: Time evolution of fuel decomposition and major products observed during ReaxFF-MD simulation of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm^3 at a temperature of 3500K.

Figure 2 represents the overall summary of the ReaxFF-MD simulations of methane-oxygen mixture with an equivalence ratio of 1. The plot shows the time evolution of decomposition of fuel molecules and major species including CO₂ and H₂O which are the final products of combustion observed at 3500K. The decomposition of both fuel and oxidizer occurs nearly instantaneously with the beginning of the simulation and with almost similar rate till 450ps. Nearly all of the CH₄ molecules are decomposed within this simulation time but oxygen molecules continue to decrease at a slightly slower rate. The production of H₂ and H₂O begins immediately after fuel and oxidizer starts reacting, due to the availability of H, O and OH radicals which is later discussed. CO production was observed to follow H₂/H₂O production and reaches the peak at the same time when all the fuel molecules are decomposed. The production of CO₂ begins around 100ps and slowly begins to overtake CO production near the end of the simulation indicating the onset of complete combustion.

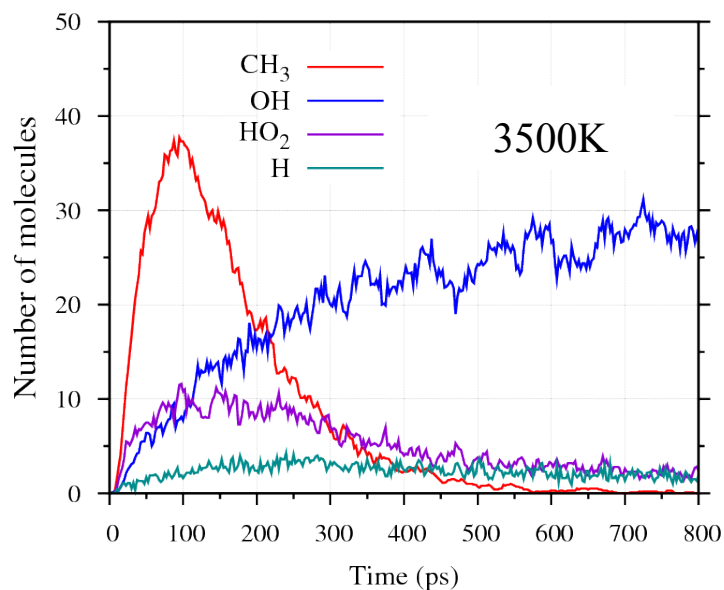


Figure 3: Time evolution of major radicals observed during ReaxFF-MD simulation of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm^3 at a temperature of 3500K.

Figure 3 shows the major radical species produced during methane oxidation at 3500K and their evolution with time. The two most prominent ones are CH_3 and OH radicals indicating the onset of chain branching reactions from fuels molecule and oxidizer. Initially, for a brief while more HO_2 production is observed than OH production, as a result of the H radicals colliding with O_2 molecules. But HO_2 is unstable at this high temperature and soon reacts with H radicals to produce OH radicals. As a result, after about 110ps, it can be observed that OH production overtakes HO_2 production.

3.2 Formation mechanism and reaction pathways of CH_3 radicals

ReaxFF-MD simulations carried out for methane-oxygen mixtures at different temperature revealed that the initial formation of methyl radical (CH_3) consists of four major pathways:

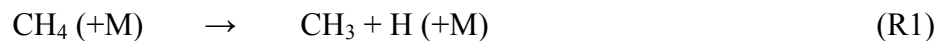




Figure 4 shows the total number occurrences for each type of reaction at two different temperatures, 2500K and 4000K. The detection of chemical reactions is carried out with an interval of 0.05ps. In order to eliminate reversible reactions, the numbers reported in Figure 3 are calculated by subtracting the number of backward reactions from the number of forward reactions. The reaction R1 is the chain initiating step where hydrogen dissociation from CH₄ molecule leads to the formation of CH₃. Other initiation mechanisms for the conversion of methane to methyl radical also occurs due to the attack of O₂, and active radicals (OH and H) which are represented reactions R2, R3, and R4. From Figure 4, among the overall observed pathways of methane decomposition, R1 represents the most probable one and therefore represents the rate determining step¹⁸.

At relatively low temperature (2500K), the thermal decomposition of CH₄ is the prominent one with very few occurrences of the bimolecular reactions. But at a very high temperature of 4000K, R4 becomes the second most dominant reaction due to the production of H radical through hydrogen abstraction from either CH₄ or other intermediate species discussed in the next section.

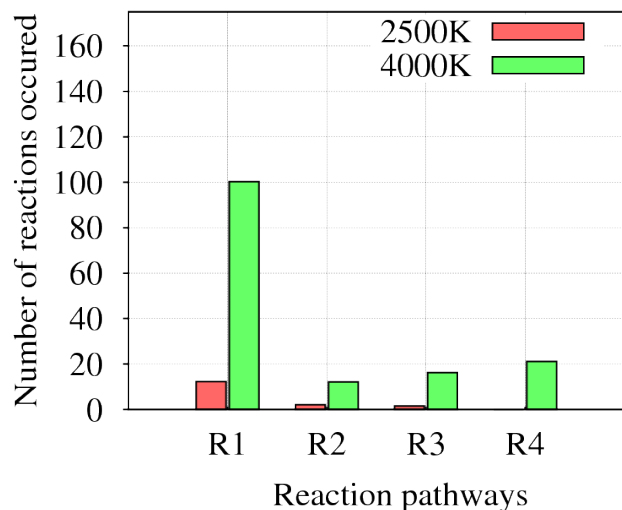


Figure 4: Number of occurrences of methyl producing reactions observed during ReaxFF-MD simulation of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm^3 at temperatures of 2500K and 4000K.

3.3 Conversion of CH_3 radicals into final products of combustion

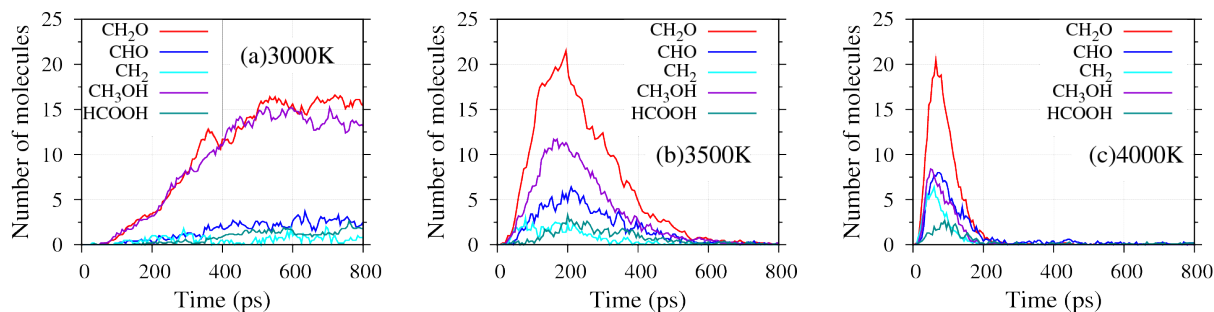
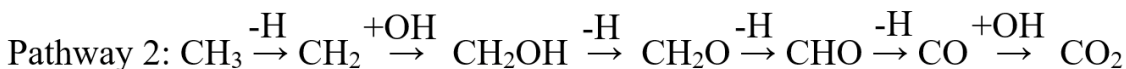


Figure 5: Time evolution of major intermediate radicals observed during ReaxFF-MD simulation of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm^3 at temperatures of (a)3000K, (b)3500K, and (c)4000K.

To study the production of CO_2 and CO during the combustion of methane-oxygen performed by ReaxFF-MD simulations, we looked at the second stage of reactions occurred after fuel molecules are mostly decomposed. Figure 5 shows the major intermediate species observed at different temperatures as they are generated and dissociated over time. At relatively lower temperature ($<3000\text{K}$) the dominant pathway for oxidation of CH_3 radicals is to be attacked by O_2 or highly reactive O and OH radicals gradually built up in the system (Figure 3). In most of

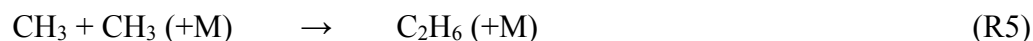
the cases, the reaction generates methanol (CH_3OH) which goes through a few H abstraction reactions to produce CHO (Figure 5). The intermediate species during these steps with the largest concentration is CH_2O , which is a crucial element during methane oxidation¹⁹.

However, as the temperature increases, we see that some of the CH_3 radicals are converted into CH_2 radicals through H abstraction before oxidation. At 4000K, the CH_2 radical peak can be seen around 100ps. The formation of CH_2 at very high temperature creates another pathway for CH_2O and CHO formation through combination with OH radicals. At moderately high temperatures (2500K and 3000K), the formation of CH_2 is very low and CH_3OH formation dominates. The two different reaction networks for CHO and CO_2 formation is listed below:



3.4 Formation of C_2 - C_3 hydrocarbon species

An important step for the PAH and soot formation during oxidation of rich hydrocarbon fuels is the recombination reactions of carbon containing fragments to produce species with C_2 or higher number of carbon atoms²⁰. In the present study at high temperatures ($>2500\text{K}$), a significant intermediate step for the conversion of fuel into final products is observed to be the growth of C_2 - C_3 containing molecules and their subsequent oxidation. The primary species in this group are C_2H_6 , C_2H_4 , C_2H_5 and C_3H_4 . The formation of C_2H_6 involves the recombination reaction for methyl radicals,



Subsequent H abstraction reactions of ethane (C_2H_6) lead to the formation of ethyl radical (C_2H_5) and ethylene (C_2H_4). Figure 6 shows the time evolution of the total number of C_2 - C_3 containing molecules at a range from relatively low (2500K) to very high temperature (4000K). At 2500K, negligible amount of C_2 - C_3 species is observed which can be attributed to the presence of very small number of methyl radicals in the system. However, as the temperature is increased (>2500K) a significantly higher amount of C_2 - C_3 species is produced in the system. This is because at higher temperatures, the initial rapid decomposition of methane leads to a large and rapid built up of CH_3 radicals (Figure 3) in the system. The large amount of methyl radicals followed by a higher kinetic energy increases the collision probability between them. As the temperature increases, the C_2 - C_3 species start to be consumed by the reactions with H, O and OH radicals. A complete understanding of CH_4 oxidation mechanism would also require further look into the oxidation of C_2 - C_3 species present in the system.

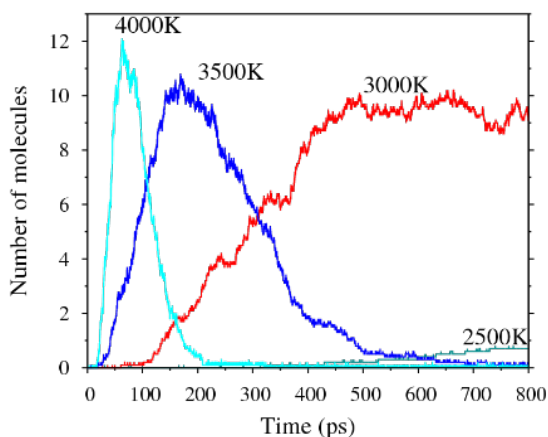


Figure 6: Time evolution of C_2 - C_3 species observed during ReaxFF-MD simulations of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm^3 at a temperature range of 2500K-4000K.

3.5 Oxidation of CH₄/O₂ mixture at lower temperatures using CVHD

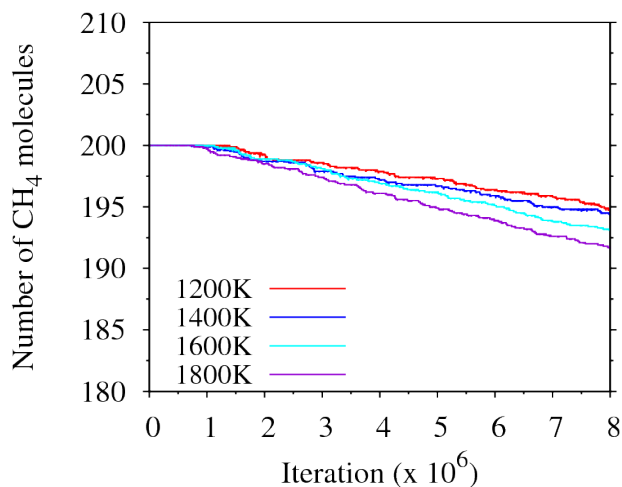


Figure 7: Time evolution of fuel decomposition observed during ReaxFF-MD simulations of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm³ at a temperature range of 1200K-1800K.

Figure 7 shows the decomposition of CH₄ molecules observed in ReaxFF-MD simulations with implemented CVHD parameters at a temperature range of 1200K to 1800K. The reported number of molecules are averaged from 10 different simulations as before. Unlike ReaxFF-MD simulations at higher temperatures, methane decomposition does not start immediately after the start of the simulation. This is due to the buildup of CVHD bias until the system is close to observing a transition state. The earliest CH₄ decomposition is observed at a temperature of 1800K after nearly 0.5x10⁶ iterations resulting from C-H bond dissociation, while for the lowest temperature (1200K) it takes about 1x10⁶ iterations. Afterwards, the fuel molecules continue further breakdown at a steady pace until the end of the simulation. Although the total amount of decomposed CH₄ molecule is very low compared to previously mentioned high temperature ReaxFF-MD runs, the qualitative trend of temperature dependency is transferred well in the low temperature regime.

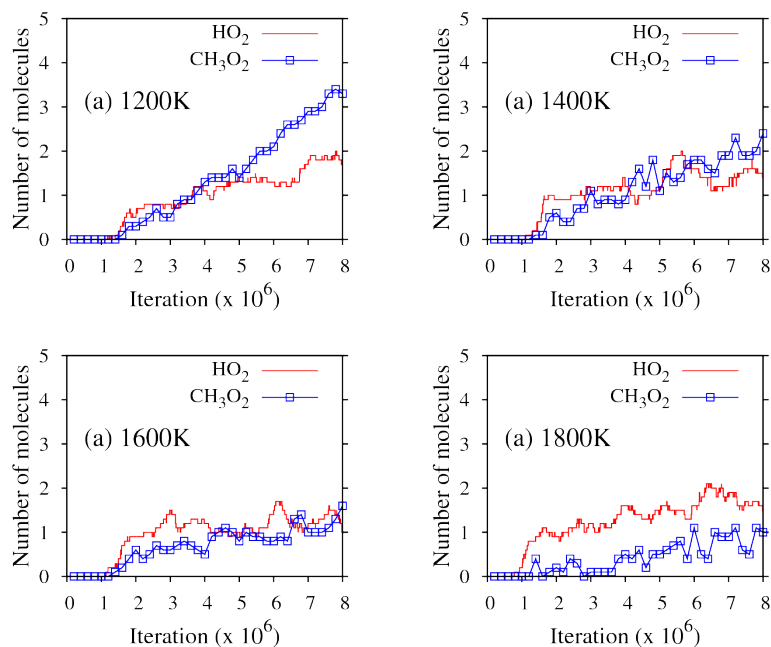


Figure 8: Time evolution of the number of CH₃O₂ and HO₂ molecules observed during ReaxFF-MD simulations of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm³ at a temperature range of 1200K-1800K.

Figure 8 shows the time evolution of the major radicals and intermediate species observed during CVHD implemented ReaxFF-MD simulations. Among the radicals and intermediate species generated at low temperatures such as 1200K, CH₃O₂ was observed to be the most prominent radical. This methyl-peroxy radical is generated through the combination reaction of CH₃ and O₂. It is also one of the most significant flame propagation reactions occurring during the combustion of CH₄, specially at high pressure and low temperature condition^{21,22}. At this low temperature simulations, few number CH₃ radical have been formed overall, the majority of which has been converted to CH₃O₂. This leaves a very low probability of a CH₃O₂ radical to find another CH₃ radical in the system to generate CH₃O and further propagate the branching. Further study is required to increase the system size which can generate a sufficient number of CH₃ radical pool to

The major difference observed during low temperature ReaxFF-MD simulations of methane combustion from its high temperature counterpart, is that CH_3O_2 was observed to be a much more stable radical. During the entire duration of the high temperature ($>2000\text{K}$) oxidation, CH_3O_2 radicals were generated in a very negligible amount. The formation reaction is endothermic and hence dissociates almost immediately. The most common pathway for CH_3O_2 disappearance is to produce two CH_3O radicals followed by successful collision with another CH_3 radical.

3.6 Fuel decomposition and initial product analysis with Ar dilution

We compared the oxidation of methane observed in this ReaxFF-MD study with various degrees of argon dilution. We also observed, similar to methane/oxygen simulations in our previous study, that the combustion occurs primarily in two stages: the formation of CH_3 radicals and the conversion of CH_3 into some of the major final products such as CO_2 , H_2O , CO etc.

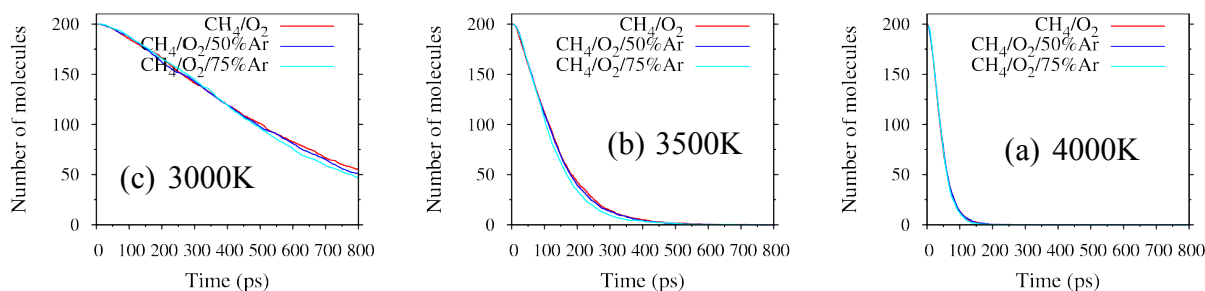


Figure 9: Time evolution of fuel decomposition and major products observed during ReaxFF-MD simulation of methane-oxygen-argon in a stoichiometric mixture at a temperature of 3500K.

Figure 9 represents the overall summary of the ReaxFF-MD simulations of methane-oxygen-argon mixture with an equivalence ratio of 1. The plot shows the time evolution of decomposition of fuel molecules observed at temperatures ranging from 2500K to 4000K.

Although, we did not observe very significant change overall in the decomposition of fuel molecules, during the entire simulation we did see minor influence of argon in number of fuel molecules decomposed (~5%).

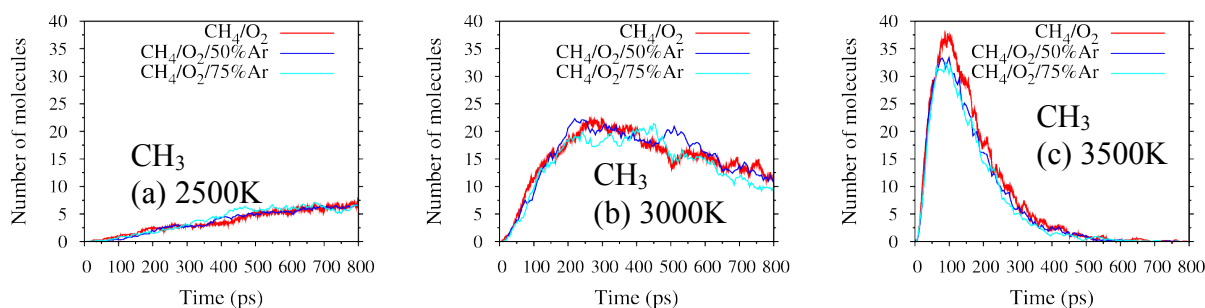


Figure 10: Time evolution of CH_3 radicals observed during ReaxFF-MD simulation of methane-oxygen-argon in a stoichiometric mixture at temperatures from of 2500K to 3000K.

Previously in our methane decomposition study we found that CH_3 is the most prominent immediate species generated after methane decomposition. In this study we observed that CH_3 decomposition at 3000K and 3500K is somewhat lower in case of argon than in mixtures with only fuel and oxidizer even though methane decomposition seems to be slightly higher in the former case. This indicates the possibility of CH_3 radicals either consumed by the production of C_2H_6 shown in (Figures 10-11) which can be seen in or $\text{CH}_2/\text{CH}_3\text{OH}$ species which requires further study.

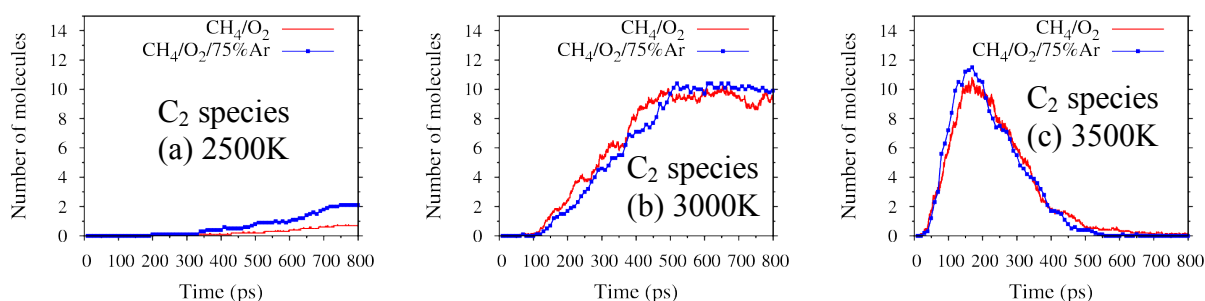


Figure 11: Time evolution of C_2 species observed during ReaxFF-MD simulations of methane-oxygen-argon in a stoichiometric mixture of density 0.2 kg/dm^3 at a temperature range of 2500K-4000K.

3.7 Checking Berendsen Thermostat bias on Ar-dilution results.

We checked the settings of Berendsen Thermostat used in our ReaxFF-MD simulations to investigate whether there is a thermostat bias for unusual temperature zone within argon atoms. To do this, we considered methane/oxygen and 75% argon mixture, generated and equilibrated as in the previous section. We divided the simulation box into two temperature zones. It is to be noted here that the simulation was carried out as before, the zones only represented temperature output for each time step. The first zone contained only methane and oxygen molecules and the second zone contained argon molecules. For both zones, the temperature was set to 3000K and the run time was 700ps. Zone 1 had a temperature damping constant of 100fs and zone 2 had that of 10000fs essentially becoming an NVE ensemble. We compared the temperatures of the two zones during the entire simulation and there was no significant difference in Figure 12. We observed some fluctuations in argon temperature than that of methane-oxygen system but this could be attributed to the higher number of argon atoms presence in the system. Overall it can be concluded that there is not presence of thermostat bias for argon atoms in the system.

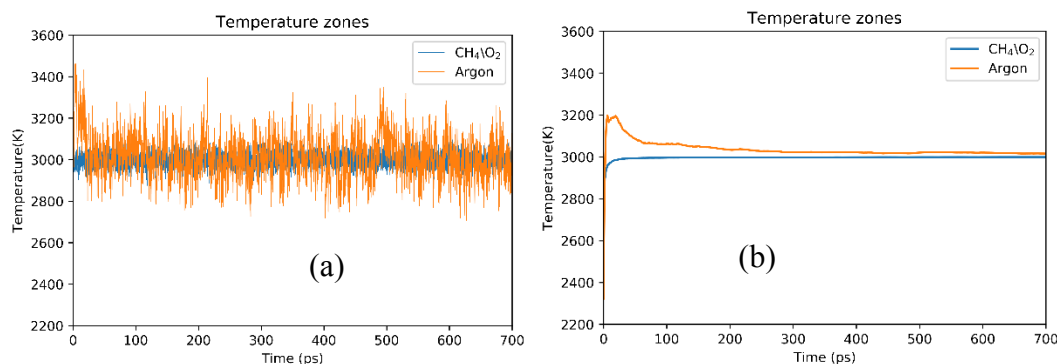
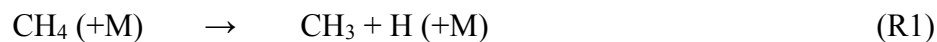


Figure 12: Variation of (a) temperatures and (b) average temperatures for zone 1 and 2 observed during ReaxFF-MD simulation of methane-oxygen-argon in a stoichiometric mixture at temperatures of 3000K.

3.8 Ar-dilution effects on formation mechanism and reaction pathways of CH₃ radicals

ReaxFF-MD simulations carried out for methane-oxygen mixtures at different revealed that the initial formation of methyl radical (CH₃) consists of four major pathways:



During this study we have added another reaction pathway due to its importance regarding the presence of argon:



Figure shows the total number occurrences for each type of reaction at a temperature of 4000K for two cases of methane oxidation with and without argon dilution. The detection of chemical reactions is carried out with an interval of 0.05ps. In order to eliminate reversible reactions, the numbers reported in Figure 13 are calculated by subtracting the number of backward reactions from the number of forward reactions. The reaction R1 is the chain initiating step where hydrogen dissociation from CH₄ molecule leads to the formation of CH₃ and it seems the number of this reaction decreased about 16% with the presence of argon. Other initiation mechanisms for the conversion of methane to methyl radical due to the attack of O₂, and H remains mostly unchanged. However, the decrease in the number of R1 is largely offset by the increase in the number of reactions R3 and R5 where CH₄ molecule reacts with OH and O radicals. This requires further investigation into the production of active radicals with the presence of argon.

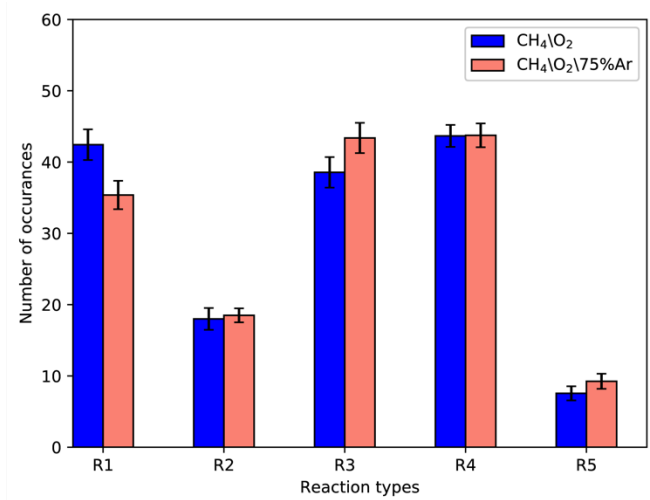


Figure 13: Number of occurrences of methyl producing reactions observed during ReaxFF-MD simulation of methane-oxygen in a stoichiometric mixture of density 0.2 kg/dm³ at temperatures of 2500K and 4000K.

4. Conclusion

In the present study, NVT-MD simulations with ReaxFF reactive force field are carried out at a moderately high to very high temperature range (2500K-4000K) to study the combustion of stoichiometric methane-oxygen mixture and to investigate the overall process of fuel conversion to final products. The initial decomposition mechanism of CH₄ molecules to produce CH₃ radicals and the radical/intermediate species production have also been studied. Two different pathways for CH₃ radical to CO₂ conversion involving CH₃OH and CH₂ production has been observed depending on the temperature. We have also applied an acceleration method named CVHD to perform low temperature ReaxFF-MD simulations (1200K-1800K). The decomposition of fuel molecules revealed another pathway of fuel oxidation through the formation of CH₃O₂ radicals.

In addition, NVT-MD simulations with ReaxFF reactive force field were carried out at a moderately high to very high temperature range (2500K-4000K) to study the combustion of stoichiometric methane-oxygen-argon mixture and to investigate the effect of argon dilution on the pyrolysis and oxidation of methane. The initial decomposition mechanism of CH₄ molecules shows that with argon increase have minor effects on increasing the number of decompositions, specially at comparatively lower temperatures. The amount of CH₃ radicals shows that in some cases the CH₃ production is lower and corresponding increase in C₂ species production with higher amount of argon in the system. The distribution of initial reaction pathways also showed a variation in the types of reaction we observed where CH₄ converts in to CH₃ radicals.

Overall, ReaxFF-MD simulations showed good capability to capture the intricacies of methane oxidation and Ar-dilution as observed in experiments providing, at the same time, detailed atomistic level information.

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