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Citation: [AIP Conference Proceedings](#) **1628**, 1261 (2014); doi: 10.1063/1.4902736

View online: <http://dx.doi.org/10.1063/1.4902736>

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Investigation of Spontaneous Combustion of Hydrogen-Oxygen Mixture using DSMC Simulation

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Abstract. Combustion has been widely studied in the literature, but very little work was focused on the microscopic level. In this paper, the DSMC method is applied to simulate the microscopic behavior of the spontaneous combustion of hydrogen oxygen mixture. It is found that the ignition delay time of the mixture depends on many factors, such as the physical size, temperature, pressure, and dilution. Comparison between DSMC and CFD results shows that more atomic hydrogen is consumed through reaction $\text{HO}_2 + \text{H} \rightarrow \text{H}_2 + \text{O}_2$ at temperature close to the extended second explosion limit due to localized distribution of reactants, which may indicate the importance of microscopic behavior on low temperature combustion.

Keywords: spontaneous combustion, hydrogen oxygen mixture, DSMC method, ignition delay time.

PACS: 82.33.Vx, 47.45.-n

INTRODUCTION

One of the current challenges in combustion research is to advance fundamental understanding of combustion chemistry from molecule scales to engine scale [1]. While there are a lot of combustion studies at the macroscopic level, few are focused at the molecular level. At the molecular level, there are free transport of molecules and randomness of reactions, which is different from the macro-scale combustion where the combustor physical length scale is much larger than the molecular mean free path [2]. Since combustion is by nature at the molecular level, it is very beneficial to study the combustion phenomena at this level.

The hydrogen oxygen reaction is one of the simplest combustion processes and also the basis of hydrocarbon combustion. Many detailed chemical reaction mechanisms have been developed, and reasonable agreements have been observed between experiments and theoretical calculations over a wide range of temperature and pressure. Therefore, hydrogen-oxygen combustion is a good problem to examine combustion process at the molecule level. In literature, Bondar et al. [3] studied $\text{H}_2\text{-O}_2$ detonation using the direct simulation Monte Carlo (DSMC) method and Bird [4] illustrated the capability of the DSMC method to simulate the spontaneous combustion using a QK chemical reaction model. These preliminary studies show that particle simulation is very promising to illustrate the microscopic behavior of combustion.

In this study, we will investigate the combustion process of $\text{H}_2\text{-O}_2$ mixture in details using the DSMC method. We will first address the physical problem and simulation setup. Then we will discuss some factors affecting the ignition delay time. Later we will analysis the difference between CFD and DSMC results and end the discussion with some concluding remarks.

PHYSICAL PROBLEM AND SIMULATION SETUP

A homogenous mixture of hydrogen and oxygen is investigated in a physical space at a temperature above the auto ignition temperature. The physical space is limited to a cube with a length of L and the surface is treated as reflected boundary. The mixture may be diluted by adding argon. Because the mixture is above the auto ignition temperature, it will experience chemical reactions and cause combustion.

When the temperature is above the extended second explosion limit [5], the mixture is at the strong ignition region. Then a reaction mechanism consisting of 7 species can describe the $\text{H}_2\text{-O}_2$ combustion process well. Table 1 shows the 26 reactions used in this study. The corresponding reaction cross section (also the reaction rate) is determined using the QK reaction model of Bird [6]. In this mechanism, the production of atomic hydrogen is very important during the ignition process. In the initial mixture of H_2 and O_2 , the chain initiating reaction #11 will produce the first atomic hydrogen. Next the chain branching reaction #13, together with two other chain reactions

TABLE 1. The hydrogen and oxygen reaction mechanism.

Endothermic	Reaction	Exothermic
01	$\text{H}_2 + \text{M} \leftrightarrow \text{H} + \text{H} + \text{M}$	02
03	$\text{O}_2 + \text{M} \leftrightarrow \text{O} + \text{O} + \text{M}$	04
05	$\text{OH} + \text{M} \leftrightarrow \text{H} + \text{O} + \text{M}$	06
07	$\text{H}_2\text{O} + \text{M} \leftrightarrow \text{H}_2 + \text{O} + \text{M}$	08
09	$\text{HO}_2 + \text{M} \leftrightarrow \text{H} + \text{O}_2 + \text{M}$	10
11	$\text{H}_2 + \text{O}_2 \leftrightarrow \text{HO}_2 + \text{H}$	12
13	$\text{O}_2 + \text{H} \leftrightarrow \text{OH} + \text{O}$	14
15	$\text{H}_2 + \text{O} \leftrightarrow \text{OH} + \text{H}$	16
17	$\text{H}_2\text{O} + \text{H} \leftrightarrow \text{OH} + \text{H}_2$	18
19	$\text{H}_2\text{O} + \text{O} \leftrightarrow \text{OH} + \text{OH}$	20
21	$\text{OH} + \text{OH} \leftrightarrow \text{HO}_2 + \text{H}$	22
23	$\text{H}_2\text{O} + \text{O} \leftrightarrow \text{HO}_2 + \text{H}$	24
25	$\text{OH} + \text{O}_2 \leftrightarrow \text{HO}_2 + \text{O}$	26

#15 and #18, will become the main source to produce atomic hydrogen. Typically, a long period of H accumulation (called induction time) will exist with little variation of temperature and pressure until a strong reaction stage appears with significant heat release. It should be noted that the pathway of reactions (#13,#15,#18) produces atomic hydrogen randomly in the space where the total collision energy of a pair is enough for reactions.

When the initial temperature is close to the extended second explosion limit, a large part of H will be consumed by two reactions #10 and #12, which leads to a much longer induction time. This phenomenon becomes apparent when pressure increases because recombination reaction #10 is more sensitive to pressure.

The previous physical problem is simulated using the DSMC method. The DSMC method is widely used in rarefied gas dynamics and can deal with chemical reactions at the molecular level, which can give microscopic information of physical processes. The earlier work of Bird [6] demonstrated the DSMC simulation of the hydrogen oxygen combustion using a one-dimensional code. We made two modifications to the 1D code for this study. The code is first extended to three-dimensional so that the microscopic behavior of spontaneous combustion can be better simulated. In addition the reverse reaction rate of reaction #10 is adjusted to match the equilibrium constant in the JANAF database. Specifically the recombination rate parameters (a,b) in the QK model for reaction #9 and #10 are adjusted from (0.00002, -1.7) to (0.01858,-0.3532), which makes the equilibrium constant in the QK model much closer to the JANAF equilibrium constant as shown in Fig. 1.

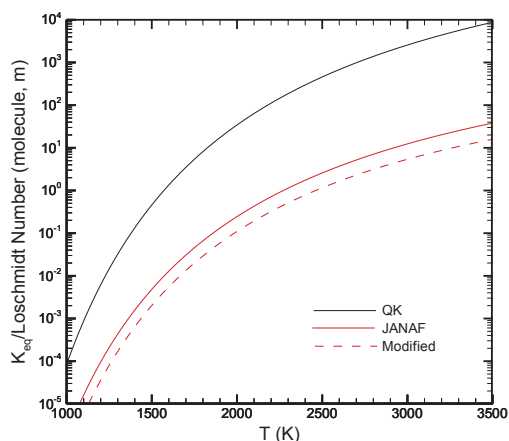


FIGURE 1. Comparison of the equilibrium constant for reactions #9 and #10 used in the QK model and JANAF database.

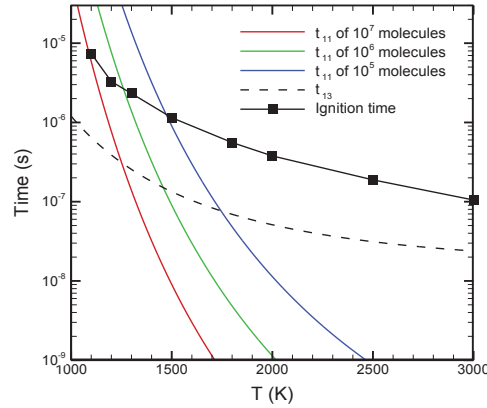


FIGURE 2. The time for the first reaction of reaction #11 and #13 under different temperature (67% H₂, 33% O₂, p = 1 atm). Colored curves are the times of reaction #11; dashed curve is the time of reaction #13; solid black curve is the predicted macroscopic ignition time.

The simulation runs on a single PC and each collision cell has about 15 simulated particles. As in reference [6], the VHS molecular model and QK chemical model is employed to simulate the collisions and reactions.

RESULTS AND ANALYSIS

At the microscopic level, there are many factors affecting the combustion processes, such as molecule number, number density and temperature. We will start the analysis by varying the physical size of the combustion region.

Physical Size Dependence

DSMC simulations are rather expensive numerically if a large number of particles are simulated. If one simulated particle represents some number of real molecules, the simulation cannot produce the collision process under the molecule size of this number, which may affect the early stage of the ignition process. Thus we let one simulated particle to represent one real molecule. Then the number of simulated particles determines the physical size of the combustion region if the initial number density is specified.

It can be analyzed that the number of physical molecules will affect the combustion process. For instance, the average time having the first reaction for the initiating reaction #11 is inversely proportional to the total molecule number, whereas the average time having the first reaction for reaction #13 doesn't depend on the molecule number, which can be clearly identified from Eqs. (1) and (2),

$$\bar{t}_{11} = \frac{1}{\alpha_{O_2} \alpha_{H_2} k_{11} n_0 N}, \quad (1)$$

$$\bar{t}_{13} = \frac{1}{\alpha_{O_2} k_{13} n_0}, \quad (2)$$

where k is the reaction rate, α is the mole fraction of a species, n is number density and N is total molecule number. Figure 2 shows a comparison of several times related to the H₂-O₂ combustion, where the ignition time is the predicted macroscopic ignition time that will be explained later. As can be seen, t_{13} is relatively small compared to the ignition time under the given temperature. Both the ignition time and t_{11} increase as the temperature decreases, but the dependence of t_{11} on temperature is much stronger. Then t_{11} can be larger than the ignition time at low temperature with limited molecules. Actually t_{11} for a realistic volume of 1 dm³ is less than 10⁻²⁰ s for a mixture at 1100 K. This indicates that the ignition process strongly depends on the size of the physical domain under certain conditions.

Another concern with limited physical space is the statistical fluctuation. Figure 3a shows the fluctuation of the predicted ignition time using the DSMC method with different number of simulated particles. Each test is a separated and statistically independent DSMC simulation. When only 10⁵ particles are simulated, there is a fluctuation on the ignition time about 1 μs. When the number of simulated particles is increased to 10⁶, the

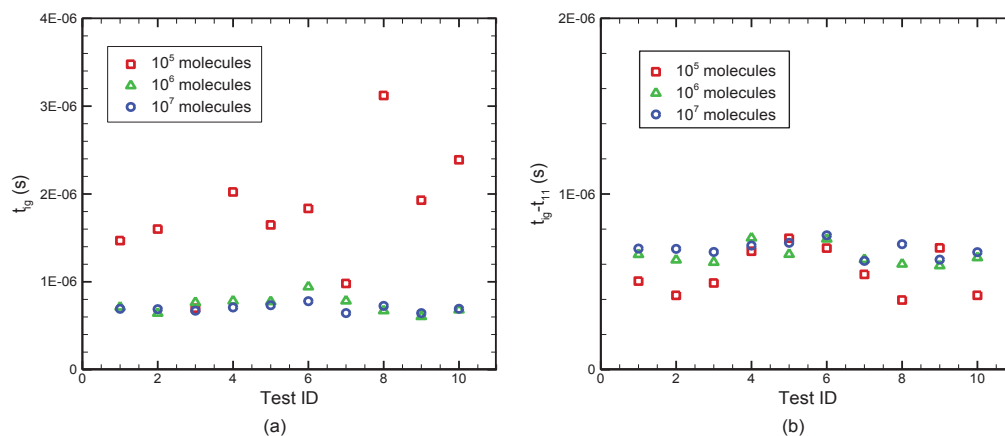


FIGURE 3. Ignition time predicted using DSMC with different number of molecules (67% H₂, 33% O₂, $p = 1$ atm, $T = 1500$ K). (a) predicted ignition time; (b) modified ignition time, $t_{ig} - t_{11}$.

fluctuation is reduced to about $0.2 \mu\text{s}$. It will be further reduced if more particles are simulated. Figure 3a also shows that the ignition time predicted using 10^5 particles is larger than the time predicted when 10^6 particles are simulated, which is consistent with the analysis regarding \bar{t}_{11} . It seems that the predicted ignition time will approach to a constant about $0.7 \mu\text{s}$ if enough particles are simulated (say 10^7 in this case), which can be regarded as the macroscopic ignition time.

It is interesting to know whether we can predict the macroscopic ignition time from the ignition time predicted with a limited number of molecules. Considering that \bar{t}_{11} is very small at the macroscopic level and \bar{t}_{13} does not depend on the particle number, the effect of particle number on the ignition time could be reduced by extracting \bar{t}_{11} from the predicted ignition time as shown in Fig. 3b. Another change from Fig. 3b is that the new time decreases when the particle number decreases. This is reasonable because the new time is for a slightly different initial condition where one HO₂ particle and one H particle have been included. The concentration of the pair of HO₂ and H is larger when fewer particles are simulated.

In order to minimize the effect of the physical space, we will use the predicted ignition time subtracted \bar{t}_{11} as the derived ignition time. For this purpose, one pair of H and HO₂ is placed in the center of the cube before calculation in our following simulations. In this way, \bar{t}_{11} is not included in the ignition time and the calculation cost can also be reduced.

Temperature Dependence

Temperature is an important parameter for combustion, which determines the reaction rates and final equilibrium state. Figure 4 shows a comparison on the ignition time (multiplied by the initial mole concentration of oxygen) for the DSMC results (10^7 simulated particles) and data of shock tube experiments [7]. The ignition time in DSMC is the time when the mole fraction of OH reaches 10^{-4} in the mixture, which is in accordance with the experimental data.

It seems that the ignition time falls on a straight line on Fig. 4. The DSMC results are almost one order smaller than the experimental data. This is mainly because the reaction rates of reaction #11 and #13 given by the QK model are smaller than the Arrhenius rates, which makes a slower production of atomic hydrogen. This study, however, does not focus on the evaluation of chemical reaction rates. The qualitative agreement between DSMC and experiments indicates that DSMC is able to predict the combustion process.

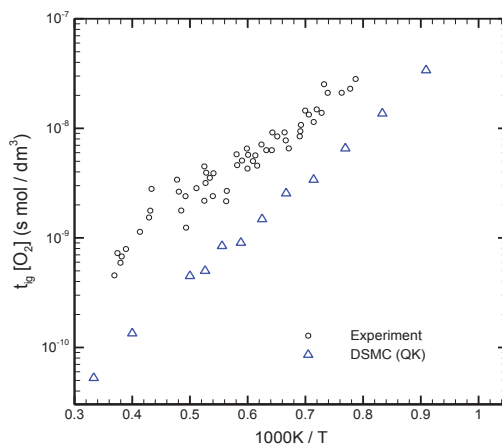


FIGURE 4. Comparison of the ignition time between DSMC results and experimental data of Schott & Kinsey [7] (4% H₂, 2% O₂, 94% Ar, p = 1 atm).

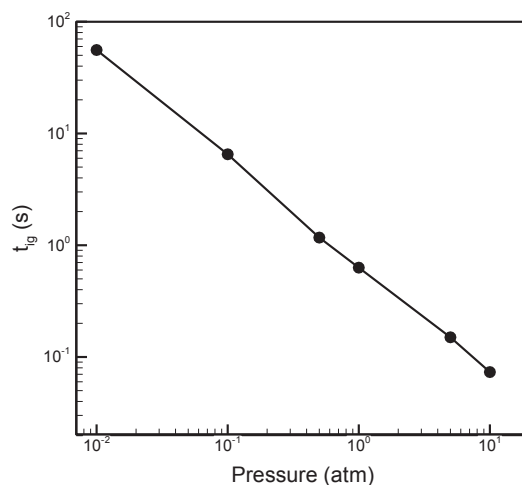


FIGURE 5. Ignition time at different pressure (67% H₂, 33% O₂, T = 1500 K).

Pressure Dependence

For two-body reactions, the reaction rate is proportional to the pressure and the equilibrium constant is pressure independent. However, the reaction rate of three-body reactions is more sensitive to the pressure. For instance, the reaction rates will both increase for reactions #9 and #10 when the pressure increases, but it will consume more H because the recombination reaction #10 involves three species. Figure 5 shows the ignition time as the pressure changes. It seems that the data falls on a straight line considering the statistical error in the data, which may indicate that the recombination reactions play a minor role in the ignition process at the temperature of 1500 K.

Dilution Dependence

In many situations, a non reactive species exists in combustion, such as nitrogen in low temperature hydrogen air combustion. In this study, we consider argon as a dilution species. Figure 6 shows the influence of dilution on the ignition time. As the mole fraction of Ar increases, the concentration of H₂ and O₂ decreases and the production rate of H drops. In addition, Ar atoms absorb the released heat from reactions, which makes it difficult to raise temperature and slows the ignition process.

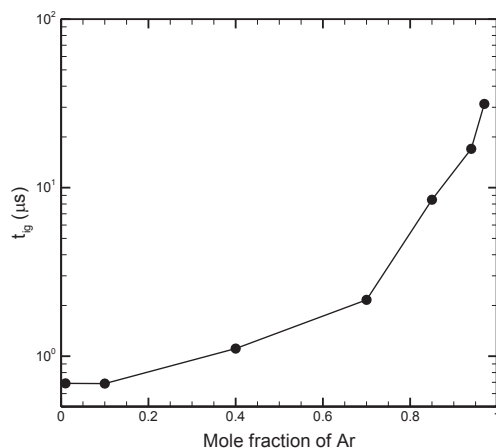


FIGURE 6. Ignition time at different mole fraction of Ar ($\text{H}_2:\text{O}_2 = 2:1$, $T = 1500$ K, $p = 1$ atm; 10^6 molecules are used).

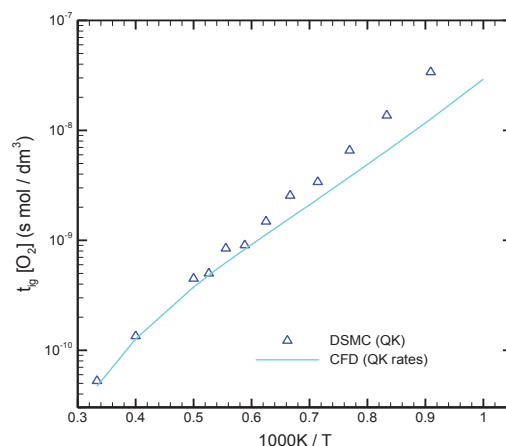


FIGURE 7. Comparison of ignition time obtained from DSMC and CFD (4% H_2 , 2% O_2 , $p = 1$ atm; 10^6 molecules are simulated). The initial mole fraction in CFD calculation is set to be the same as in DSMC, $10^{-5}\%$ H and $10^{-5}\%$ HO_2 .

H Consumption at Low Temperature

Figure 7 compares the ignition time obtained from DSMC simulation and homogeneous CFD calculation, where the same reaction rates of QK model are used both in DSMC and CFD. It is found that the two approaches predict very close results at high temperature, but DSMC results become larger than the CFD data as the temperature decreases and approaches to the extended second explosion limit. This is because only reaction #10 is important for H consumption in CFD, but in DSMC both reactions #10 and #12 are key pathways for the H consumption.

With a homogeneous assumption in CFD studies, the effect of reaction #12 is negligible. The reactants of reaction #12, H and HO_2 , are scattered uniformly in the whole region, making the collisions between H and HO_2 hard to happen. For the DSMC simulation, H and HO_2 are produced at the same time in the domain, but their number is very few. So the inverse reaction is seldom encountered because of molecular motion. However, when the concentration of H reaches to a certain value through the chain reactions, the HO_2 particles will have reactions with H although the average concentration of HO_2 is still low. This is the localized effect that makes reaction #12 occurs more frequently.

It should mention that the consumption of H is a critical factor for combustion at a temperature near the extended second explosion limit (low temperature and high pressure). Many previous studies investigated low temperature combustion (e.g., Lee and Hochgreb [5] and Alamo et al. [8]) and the homogeneous assumption is always employed, which may not be appropriate as indicated from this study.

CONCLUDING REMARKS

The spontaneous combustion of a hydrogen oxygen mixture is investigated using the DSMC method. We have shown that the ignition depends on many factors including the physical size, temperature, pressure and dilution.

This study also shows that DSMC simulations have advantages over CFD calculation. For instance, reaction events are the results of collisions where localized distribution of species affects the macroscopic behavior of low temperature combustion. Of course there is still challenge for DSMC to simulate combustion. For instance, the physical size or the number of simulated particles should be increased. At the microscopic level, particle motion and collisions reflect the molecular nature of combustion, but some physical processes such as diffusion would require a large simulation domain so that important phenomena including minimum ignition energy could be investigated. Further studies will be focused on increasing the simulation capability of DSMC for combustion simulation.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China through grants 11372325 and 91116013. The second author would like to acknowledge the discussion with Prof. Graeme Bird and the kind accommodation from Prof. Kun Xu during his visit in Hong Kong University of Science and Technology in 2013. That discussion initiated the present study.

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