Full Length Article

Effects of water vapor dilution on the minimum ignition energy of methane, *n*-butane and *n*-decane at normal and reduced pressures

Weikuo Zhang [a,b], Xiaolong Gou [a], Zheng Chen [b,*]

[a] *Key Laboratory of Low-grade Energy Utilization Technologies and Systems, School of Power Engineering, Chongqing University, Chongqing 400044, China*
[b] *SKLTCS, Department of Mechanics and Engineering Science, College of Engineering, Peking University, Beijing 100871, China*

HIGHLIGHTS

- Ignition of methane, *n*-butane and *n*-decane were studied numerically.
- Effects of water vapor dilution on ignition were examined.
- The minimum ignition energy increases greatly with the water vapor dilution.
- The minimum ignition energy changes inversely with the pressure.

ARTICLE INFO

ABSTRACT

Water vapor dilution has great impact on fundamental combustion processes such as ignition, flame propagation and extinction. In the literature, there are many studies on how water vapor addition affects flame propagation and extinction limit. However, the influence of water vapor addition on ignition receives little attention. In this study, numerical simulations considering detailed chemical mechanisms are conducted for the ignition of methane, *n*-butane and *n*-decane/air/water vapor mixtures. The emphasis is spent on examining the effects of water vapor dilution on the ignition of these fuels at normal and reduced pressures. The minimum ignition energies (MIE) at different dilution ratios and initial pressures are obtained. It is found that at normal and reduced pressures, the MIE is proportional to the inverse of pressure and it increases exponentially with water vapor dilution ratio. A general correlation among the MIE, pressure and dilution ratio is proposed for each fuel. Furthermore, for stoichiometric methane/air/water vapor mixtures, the chemical and radiation effects of water vapor dilution are isolated and quantified. It is found that the three-body recombination reaction greatly increases the MIE and reduces the dilution limit.

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1. Introduction

Reliable relight at high altitude is crucial in jet-engine design. With the increase of altitude, the ambient pressure and temperature both decrease while the humidity increases. Therefore, relight at high-altitude becomes difficult and the ignition failure might occur. To understand the ignition process at such severe conditions, we need study the ignition process for fuel/air mixture with water vapor dilution at reduced pressures.

In the literatures, there are many studies [1–16] investigating the effects of humidity on fundamental combustion processes. For examples, previous studies in [1–8] examined the effects of water vapor dilution on flame propagation. Mazas et al. [1]

assessed the effects of water vapor addition on the laminar speed of $CH_4/O_2/N_2/H_2O$ mixtures and observed that the laminar flame speed decreases linearly with steam molar fraction. Das et al. [2] measured the laminar flame speeds of moist syngas mixtures and found the laminar flame speed varies non-monotonically with addition of water for fuel-rich mixtures. Xie et al. [3] studied the thermal and chemical effects of water addition on laminar flame speed of syngas and they found that water addition promotes the reaction process for the high CO/H_2 ratios. Yoshida et al. [4,5] found that the flame speed is reduced by water mist. Santner et al. [6] assessed the effects of water vapor addition on the burning rates of hydrogen, syngas, and ethylene flames at elevated pressures and they found the three-body effect of water vapor play an important role. Wang et al. [7] examined the cellular instability of syngas spherical propagation flames with water addition at elevated pressure and different CO/H_2 ratios. Galmiche et al. [8] assessed the

effects of water vapor dilution on the laminar flame speed of methane/air mixtures and they proposed an explicit correlation between the heat capacity of the diluent and the laminar flame speed. All these studies [1–8] indicated that water vapor dilution can effectively reduce the laminar flame speed. Besides, several studies [9–11] investigated the effects of water vapor dilution on flame extinction. Thomas et al. [9] and Yang et al. [10] examined the effects of water mist on the extinction of methane/air flames. Sakurai et al. [11] studied the extinguishment of propane/air co-flowing diffusion flames by fine water droplets and they found that the co-flowing air steam velocity is the crucial factor for flame stability.

Most of the previous studies were focused on examining how water vapor addition affects flame propagation and extinction limit. However, the influence of water vapor addition on ignition receives little attention.

Currently, the mechanism of ignition with water vapor dilution is not well understood and deserves further study. Furthermore, there is little work on the ignition process at reduced pressures, which needs further exploration. In this study, numerical simulations considering detailed chemical mechanisms are conducted for the ignition of methane, *n*-butane and *n*-decane/air/water vapor mixtures. The objectives are to examine the effects of water vapor dilution on the ignition of these fuels at normal and reduced pressures.

2. Numerical methods and specifications

The in-house code A-SURF (Adaptive Simulation of Unsteady Reactive Flow) is used to simulate the transient one-dimensional ignition and spherical flame propagation processes. A-SURF has been validated and used in a series of studies on spherical flame initiation and propagation [17–19]. It was used in our previous studies [20,21] on the ignition of hydrogen/air and methane/air mixtures with different types of diluents (He, Ar, N_2 and CO_2). In A-SURF, the finite volume method is used to solve the conservation equations (including the unsteady Navier–Stokes equations as well as the energy and species conservation equations) for multicomponent reactive flow. The second-order-accurate Strang splitting fractional-step procedure is employed to separate the time evolution of the stiff reaction term from that of the convection and diffusion terms. Detailed chemistry is considered in A-SURF. A multi-level, dynamically adaptive mesh refinement algorithm is employed in A-SURF to maintain adequate numerical resolution of the moving flame front. A-SURF was successfully in our previous studies on ignition and flame propagation [28–30]. The details on the governing equations, numerical methods, and code validation were presented in [17,19] and thereby are not repeated here.

In all simulations, the computational domain is $0 \leqslant r \leqslant 50$ cm. Zero flow velocity and zero gradients of temperature and mass fractions are enforced at both boundaries at $r = 0$ and 50 cm. Initially, the homogeneous mixture is static and the initial temperature and pressure are uniformly distributed. Similar to our previous studies [20,21], flame ignition is achieved by spatial dependent energy deposition within a given time and the following source term is included in the energy equation:

$$q_{ig}(r,t) = \begin{cases} \frac{E_{ig}}{\pi^{1.5} r_{ig}^3 \tau_{ig}} \exp\left[-\left(\frac{r}{r_{ig}}\right)^2\right] & if \quad t < \tau_{ig} \\ 0 & if \quad t \geqslant \tau_{ig} \end{cases} \quad (1)$$

where E_{ig} is the total ignition energy, τ_{ig}, the duration of the ignition energy, and r_{ig}, the radius of the ignition energy deposition region. The minimum ignition energies (MIE) is calculated by the method of trial-and-error with relative error below to 2% [17,18]. It is noted that both τ_{ig} and r_{ig} affect the MIE [22]. In this study, since the

emphasis is focused on the change of the MIE with water vapor dilution, we fix the values of τ_{ig} and r_{ig}. Large values of $\tau_{ig} = 250$ μs and $r_{ig} = 250$ μm are used in this study so that in the simulation the temperature at the center is not too high after ignition energy deposition. It is noted that the main results and conclusions of this study are found to be independent of the ignition kernel sizes and times.

The composition of the initial stoichiometric fuel/air/water vapor mixture is specified according to the molar ratio given by the following expression

$$(1-a)\frac{C_nH_{2n+2} + (1.5n+0.5)(O_2 + 3.76N_2)}{1 + 4.76(1.5n+0.5)} + aH_2O \quad (2)$$

where a is the dilution ratio of water vapor and n is the carbon number of the hydrocarbon fuel. In this study, we consider three types of fuels: methane (CH_4), *n*-butane (nC_4H_{10}) and *n*-decane ($nC_{10}H_{22}$). The following detailed chemical mechanisms are considered in simulations: GRI-Mech. 3.0 [23] for CH_4, the mechanism of Sung et al. [24] for nC_4H_{10}, and the mechanism of Chaos et al. [25] for $nC_{10}H_{22}$.

3. Results and discussion

3.1. The MIE of different fuel/air mixtures with water vapor dilution

We first study the ignition of stoichiometric methane/air mixture with different amounts of water vapor dilution at the initial temperature of $T_u = 353$ K. Different pressures of $P = 0.5$, 0.6, 0.8 and 1.0 atm are considered. The results are shown in Fig. 1. Fig. 1(a) shows that at a given initial pressure, the minimum ignition energy, E_{min}, increases monotonically with the dilution ratio, a. At high dilution ratio, E_{min} is shown to increase exponentially with a. Water vapor dilution eventually results in an infinite value of the MIE, indicating that there is a critical dilution limit and the mixture cannot be successfully ignited once the dilution limit is reached [17,18]. The increase of the MIE with water vapor addition is mainly caused by three factors: (1) thermal/dilution effects due to the reduction of flame temperature by water vapor dilution; (2) chemical effects due to the change of reaction rates by water vapor dilution; and (3) radiation effects due to the radiative heat loss caused by water vapor dilution. This will be discussed in Section 3.2.

Fig. 1(b) shows that the minimum ignition energy, E_{min}, decreases monotonically as the pressure, P, increases. Moreover, it is observed E_{min} is more sensitive to pressure change at lower pressure. The decrease of E_{min} with P is mainly due to the fact that the flame thickness becomes smaller at higher pressure and so does the critical ignition kernel size. Therefore, successful ignition is more difficult to be achieved at lower pressure.

Fig. 2 plots the MIE multiplied by the pressure for different water vapor dilutions and pressures. It is observed that the results at different pressures fall on the same curve descried by the following expression

$$E_{min} = f(a)/P \quad \text{with } f(a) = \exp(32.155a^2 + 1.755a - 1.618) \quad (3)$$

Therefore, at normal and reduced pressures, the MIE is inversely proportional to the pressure. The change of E_{min} with P can be explained with the help of the following estimation of MIE

$$E_{min} \sim \delta^3 \rho_u c_P(T_{ad} - T_u) \sim \frac{\lambda^3}{S_L^3 \rho_u^2 c_p^2}(T_{ad} - T_u) \quad (4)$$

in which the laminar flame speed S_L changes with pressure according to $S_L \sim P^{0.5n-1}$, where n is the overall reaction order. Since the density is proportional to pressure, Eq. (4) indicates the relationship between the MIE and pressure is $E_{min} \sim P^{(1-1.5n)}$. Usually the overall reaction order is within the range of $1 < n < 2$ and it is around 1.5.
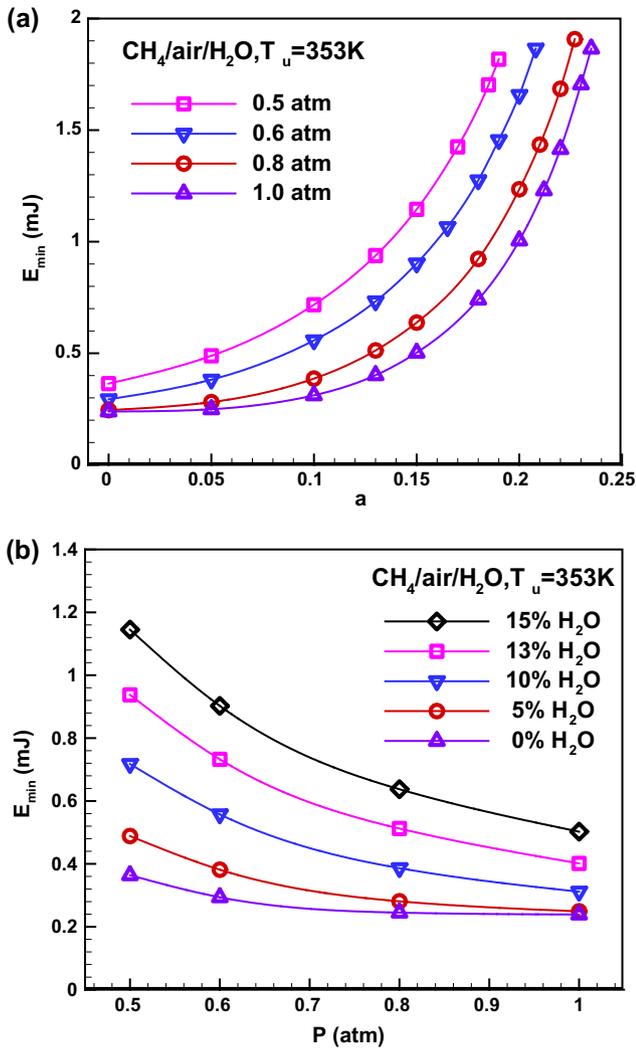
Fig. 1. Change of the MIE with (a) water vapor dilution ratio and (b) pressure for stoichiometric CH_4/air/H_2O mixture at T_u = 353 K and different pressures.
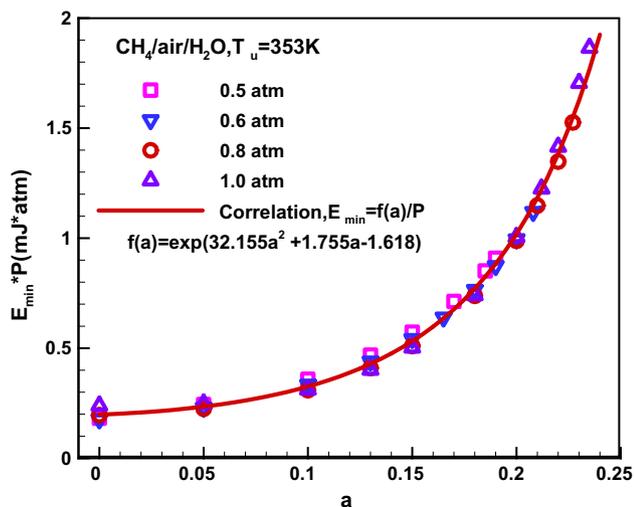
Fig. 2. Change of $E_{min}*P$ with water vapor dilution ratio for stoichiometric CH_4/air/H_2O mixture at T_u = 353 K and different pressures.

When the overall reaction order is around n = 4/3, we have $E_{min} \sim P^{-1}$. Therefore, it is reasonable that the MIE changes inversely with the pressure. Since the adiabatic flame temperature changes nearly linearly with the dilution ratio [20] and laminar flame speed changes exponentially with the flame temperature, it is reasonable that the MIE changes exponentially with the water vapor dilution ratio.

Besides methane, the ignition of *n*-butane and *n*-decane with different amounts of water vapor dilution at normal and reduced pressures is also studied. Fig. 3 shows the results for stoichiometric nC_4H_{10}/air/H_2O mixtures at T_u = 353 K and $nC_{10}H_{22}$/air/H_2O mixtures at T_u = 453 K. Similar trend to that of methane is observed. At normal and reduced pressures, E_{min} increases monotonically with the dilution ratio *a*. With the increase of pressure, E_{min} is shown to decrease monotonically. Besides, the water vapor dilution limit is shown to become smaller at lower pressure, indicating that the successful ignition is more difficult to be achieved at lower pressure.

Fig. 4 shows the MIE multiplied by the pressure for nC_4H_{10}/air/H_2O and $nC_{10}H_{22}$/air/H_2O mixtures at different amounts of water vapor dilution. The results are similar to that of methane. The MIE is shown to be inversely proportional to the pressure and the following two correlations work for *n*-butane and *n*-decane, respectively:
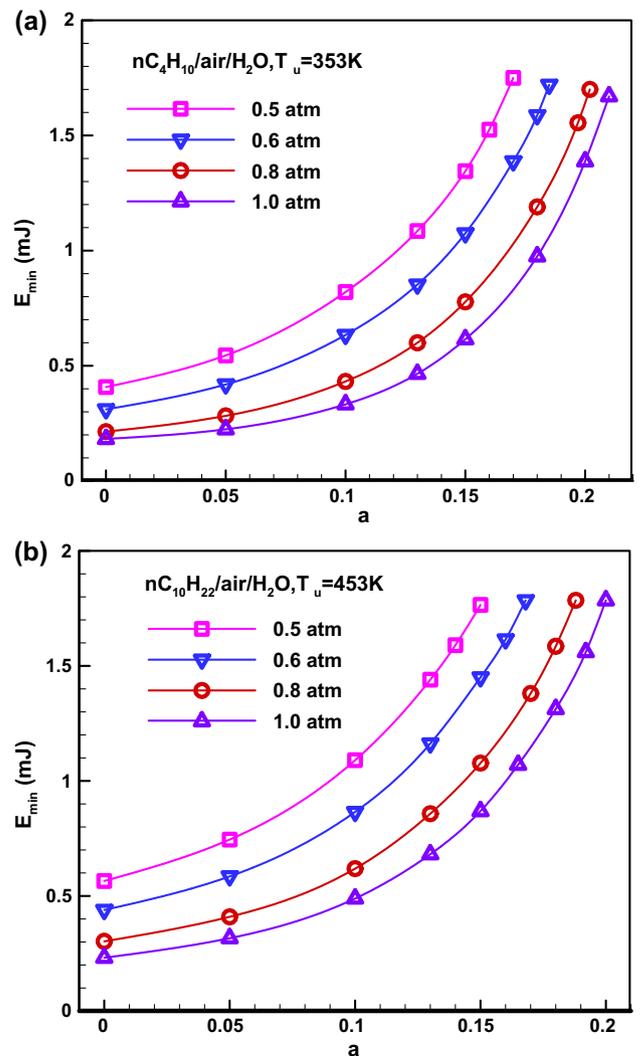
Fig. 3. Change of the MIE with water vapor dilution ratio for stoichiometric (a) nC_4H_{10}/air/H_2O and (b) $nC_{10}H_{22}$/air/H_2O mixtures.

(a)

(b)
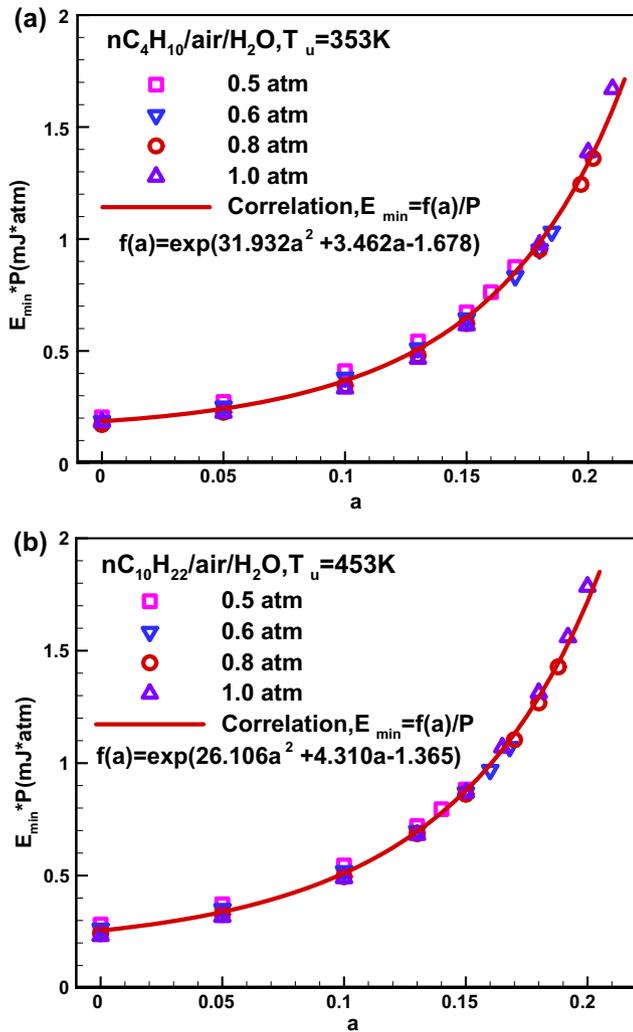
Fig. 4. Change of $E_{min}*P$ with water vapor dilution ratio for stoichiometric (a) $nC_4H_{10}/air/H_2O$ and (b) $nC_{10}H_{22}/air/H_2O$ mixtures.

$$E_{min} = f(a)/P \quad \text{with } f(a) = \exp(31.932a^2 + 3.462a - 1.678)$$
$$\text{for } nC_4H_{10} \tag{5}$$

$$E_{min} = f(a)/P \quad \text{with } f(a) = \exp(26.106a^2 + 4.310a - 1.365)$$
$$\text{for } nC_{10}H_{22} \tag{6}$$

Therefore, the above results indicate that water vapor dilution can greatly affect the MIE of different hydrocarbon fuels and that the influence becomes stronger at lower pressure.

Fig. 5 compares the results for these three alkane fuels. It is seen that at small value of water vapor dilution ratio, the results for $CH_4/air/H_2O$ and $nC_4H_{10}/air/H_2O$ mixtures are nearly the same. However, at high dilution ratio $E_{min}*P$ is shown to increase exponentially with a and the discrepancy between methane and n-butane increases with a. Fig. 5 indicates that at a given dilution ratio and pressure, the MIE is $nC_{10}H_{22}/air/H_2O$ is the highest while that of $nCH_4/air/H_2O$ is the smallest. It is noted that the initial temperature for $nC_{10}H_{22}/air/H_2O$ is $T_u = 453$ K, while that for $CH_4/air/H_2O$ and $nC_4H_{10}/air/H_2O$ is $T_u = 353$ K. Therefore, the MIE of normal-alkane/air/H_2O mixture increases with the carbon number n.

3.2. Different effects caused by water vapor dilution

Water vapor is chemically active: it reacts with different species (e.g., $OH + H_2 = H + H_2O$) and it can also act as a third body with
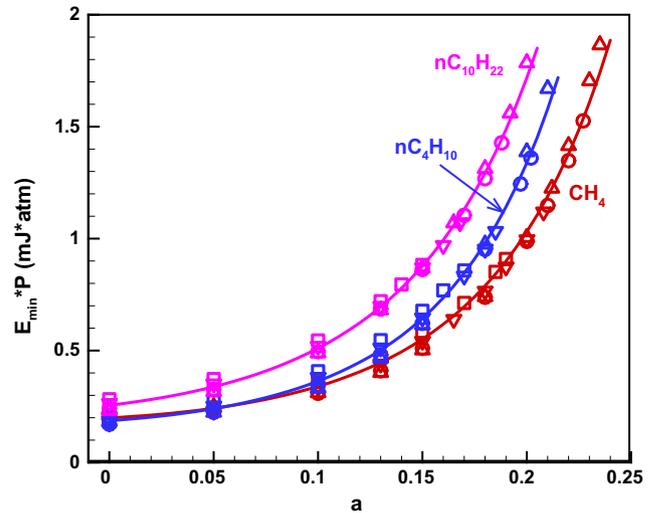
Fig. 5. Comparison among results for different fuels.

large value of collision coefficient (e.g., $H + O_2 + H_2O = HO_2 + H_2O$). In order to understand the kinetic effect of H_2O dilution on the ignition process, we conduct numerical analysis using the approach similar to the work of Liu et al. [26]. An artificial species, named as inert H_2O (FH_2O), is introduced. The artificial species FH_2O has the same thermal and transport properties as the real H_2O but it does not participate in any chemical reaction (i.e. chemically inert). Since the three-body recombination reactions are very important for water vapor diluted mixtures, we consider another artificial inert H_2O named as TH_2O in the simulation: it acts as a three-body (the three-body coefficient of TH_2O is the same as that of H_2O). For the real water, to demonstrate the radiation effects caused by water vapor addition, we compare the results with and without considering radiative heat loss. The optically thin model [27] (OPTM) is used in the simulation to account for radiative heat loss.

Fig. 6 shows the results for stoichiometric CH_4/air at different amount of water vapor dilution at $T_u = 353$ K and $P = 1$ atm. Fig. 6 indicates that, for highly H_2O-diluted mixtures, the MIE only slightly decreases if H_2O does not react with other species but still acts as a three-body, and that the MIE can be greatly reduced if H_2O
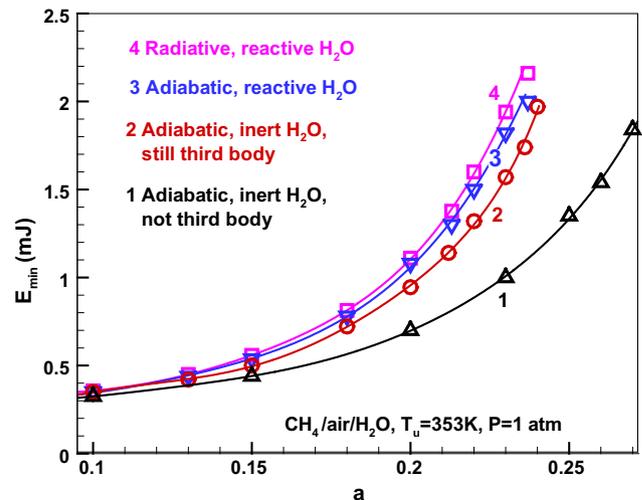
Fig. 6. Chemical and radiation effects of H_2O on the MIE of stoichiometric $CH_4/air/H_2O$ at $T_u = 353$ K and $P = 1$ atm.
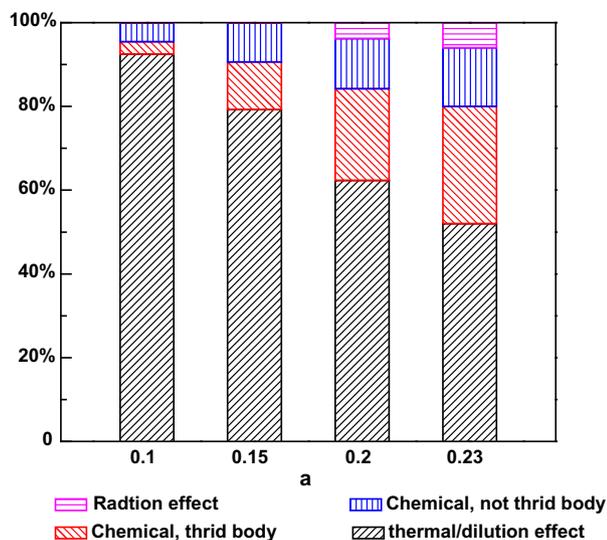
Fig. 7. The relative contributions of different effects caused by water vapor dilution for MIE of stoichiometric CH_4/air/H_2O at T_u = 353 K and P = 1 atm.

vapor dilution ratio and pressure is obtained. It is found that the MIE of normal-alkane/air/H_2O mixture increases with the carbon number. Moreover, for stoichiometric CH_4/air with water vapor dilution, the chemical and radiation effects of water vapor dilution are examined. These effects are found to increase significantly with the dilution ratio. The three-body recombination reaction effect is shown to be important for the near-limit mixtures. However, compared to other effects, the relative contribution of radiation effect is the smallest.

does not act as a three-body. The large difference between results for the two types of artificial inert H_2O (i.e., lines #1 and #2 in Fig. 6) demonstrates the importance of the three-body recombination reactions in highly H_2O diluted mixtures. The dilution limits, a_c, for these three cases, lines #3, #2 and #1 in Fig. 6 are 49.0%, 51.0%, and 54.7%, respectively. Therefore, in terms of the kinetic effect of H_2O dilution, the dilution limit is mainly reduced by H_2O involved in the three-body recombination reactions (e.g., $H + O_2 + H_2O = HO_2 + H_2O$). Besides, the result of comparison between lines #3 and #4 in Fig. 6 indicates that the radiation effects on the MIE and dilution limit is nearly negligible.

Fig. 7 shows the relative contributions of different effects caused by water vapor dilution. It is observed that the thermal/dilution (i.e., reduction in flame temperature caused by water vapor addition) dominates over other effects while its contribution decreases as the increase of the water vapor dilution ratio. The reduce of the thermal/dilution effects leads to the increase of chemical, radiation and three-body effects. However, it is seen from results in Fig. 7 that three-body effects and radiation effects both increase with the dilution ratio. Therefore the three-body recombination reaction is extremely important for the near-limit mixtures (i.e., at high dilution of a = 0.23). This demonstrates the higher the dilution ratio, the stronger effect of three-body recombination reaction. Compared to other effects, the relative contribution of radiation effect is the smallest for the stoichiometric mixture and it becomes discernable only when the dilution ratio is large enough. Therefore, the radiation effect only needs to be considered for stoichiometric mixtures near the dilution limit. Similar conclusion was drawn in our previous study on hydrogen ignition [20].

4. Conclusions

Numerical simulations are conducted to assess the effects of water vapor dilution on the ignition of methane, n-butane and n-decane at normal and reduced pressures. Detailed chemistry and variable thermodynamic properties are considered in simulation. The MIE at different dilution ratios and different pressures is obtained. It is found that the MIE changes inversely with the pressure and it changes exponentially with the water vapor dilution ratio. For each fuel, a general correlation among the MIE, water

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