Explosion Limit of Hydrogen/Oxygen Mixture with Water Vapor Addition

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1   Introduction

In recent years, hydrogen as a fuel has drawn lots of attention due to its zero-carbon nature. However, explosion hazards may occur during the production, transportation, storage, and application of hydrogen. Water mist is an effective fire and explosion suppressant. The role of water mist in suppressing explosion hazards includes heat absorption due to droplet evaporation and the various effects of the water vapor, including composition dilution [1], heat transfer modulation [2], and even participation as a reactant [3]. In this study, we will focus on the effects of water vapor addition on the hydrogen explosion limits.

In the previous studies, experimental results show that addition of water vapor had a suppressive effect on hydrogen combustion characteristics, such as auto-ignition temperature [4], ignition delay time [5] and laminar flame propagation speed [6]. Moreover, the numerical results indicate that the third body reactions related to H_2O should be responsible for the suppressive effect on combustion characteristics caused by water vapor addition [4, 7, 8]. Explosion limits are the pressure–temperature boundaries for a specific fuel–oxidizer mixture ratio that separates the regions of slow and fast reaction, indicating whether the reacting system experience chemical runaway [9]. Furthermore, when hydrogen is mixed with other fuels, such as carbon monoxide [10], methane [11], and ammonia [12], it fundamentally changes the explosion limits of blending fuels from monotonic to "Z" shape.

However, the effect of water vapor on the explosion limit of hydrogen, as well as the effect of water vapor addition on the dominant reactions in each limit pressure range, need to be explained in detail. Furthermore, the understanding regarding the relative significance of the composition dilution, heat transfer modulation and chemical effects caused by water vapor is still lacking.

2   Computation Specification

The CHEMKIN-PRO software is used to calculate the homogeneous ignition process of $H_2/O_2/H_2O$ mixtures. The initial pressure is from 10^1 to 10^8 Pa, whilst the temperature is from 650 to 1,000 K. The Hanson-2011 [13] mechanism is adopted due to its good accuracy under different pressure ranges [14]. To describe the wall destruction of radicals, the wall termination reactions for H, O, OH, HO_2, and H_2O_2 radicals are added to Hanson-2011. The wall termination reactions can be written as [15]:

$$R \xrightarrow{\ k\ } \text{Wall destruction} \tag{1}$$

where R denotes the H, O, OH, HO_2, and H_2O_2. The rate coefficients of the wall destruction reactions are

$$k = \frac{1}{4} \varepsilon \bar{v} \frac{S}{V} \tag{2}$$

where ε is the sticking coefficient, which is typically 10^{-5} to 10^{-2} for glass and quartz [16], and here it is 10^{-3} [10, 11]. S and V are the surface area and volume of the reactor, and the radius of a spherical chamber is fixed as $r = 37\,mm$ in our study following the previous studies [10, 11, 17]. Moreover, $\bar{v}$ is the average thermal velocity

$$\bar{v} = \sqrt{8k_B T / \pi m} \tag{3}$$

where k_B is the Boltzmann constant, T is the temperature, and m is the mass of a single particle. In this study, following Liang et al.[10, 11, 15], explosive and non-explosive conditions are based on whether the temperature rise exceeds 50 K in 10 s in the constant volume, adiabatic reactor.
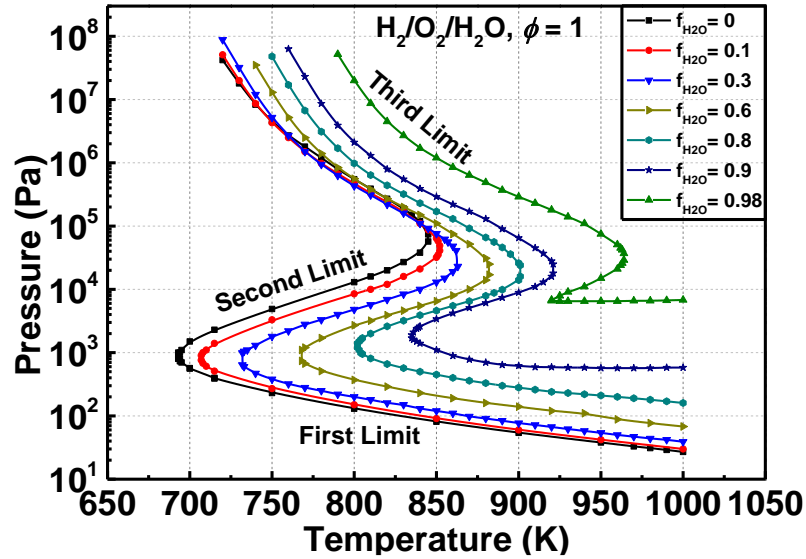

Figure 1: Explosion limits of $H_2/O_2/H_2O$ mixtures with different water vapor mole fractions.

3   Results and discussion

3.1 Explosion limits of hydrogen/oxygen with water addition

The explosion limit curves of the $H_2/O_2/H_2O$ mixture are shown in Figure 1. Here the equivalence ratio is unity, and the H_2O mole fractions are varied from 0 to 0.98, which is defined as $f_{H2O} = C_{H2O} / (C_{H2} + C_{H2O} + C_{O2})$, C_i is the mole fraction of i-th species. It can be seen from Figure 1 that with H_2O addition, both the first and second limits move toward the high-temperature range. For

instance, when the water mole fraction increases from 0 to 0.6, the first limit at 100 Pa moves from 824 K to 947 K. Moreover, the third limit moves towards the low temperature range first, and towards the high temperature range after the H_2O mole fraction is greater than 0.3.

3.1.1 First explosion limit

The effects of water vapor addition on the first explosion limit will be discussed in this section. To identify the controlling reactions, the temperature sensitivity analysis has been performed with different H_2O additions at P = 300 Pa, and the temperature is chosen on the limit of the explosive conditions. The most sensitive reactions are shown in Figure 2. It is found that with H_2O addition, R1: $H+O_2 = O+OH$ and the wall destruction reaction of H radicals (R32) still control the combustion process, same as those when $f_{H2O} = 0$. Moreover, the reaction R5: $H+O_2(+M) = HO_2(+M)$, where M=H_2O, which consumes H radicals to produce relatively inactive HO_2, becomes important. The importance of H/O wall termination reactions (R32/R33) on the temperature change is slightly increased with increased f_{H2O}. In conclusion, H_2O addition has a positive effect on the wall destruction reactions of H and OH, which make contributions to the shift of the first limit to the higher temperature range.
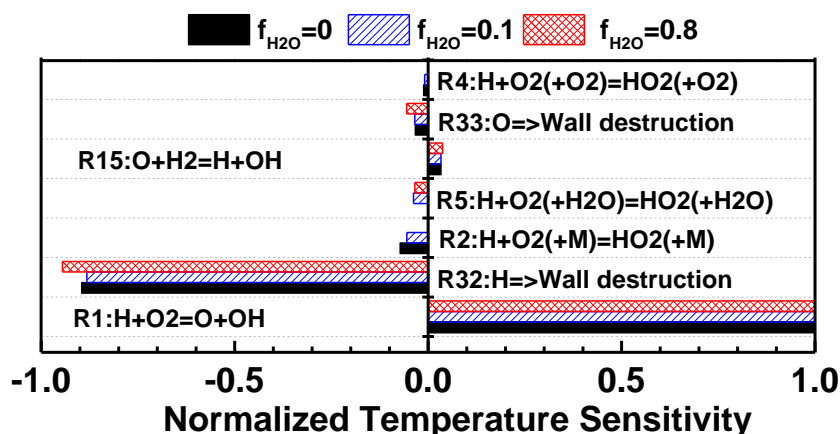

Figure 2: Temperature sensitivity of the first explosion limit to individual reaction rates normalized by the largest value at each case at P = 300 Pa.

3.1.2 Second explosion limit

The temperature sensitivity analysis with different H_2O mole fractions as the pressure increases to 1×10^4 Pa (i.e., around the second limit range), is shown in Figure 3. With H_2O addition, R1: $H+O_2=O+OH$ is still the most important related to the temperature increase. Also, R5: $H+O_2(+M) = HO_2(+M)$, where M=H_2O, becomes important. The temperature sensitivity of the reaction R22: $H_2O_2 + H = HO_2 + H_2$ that contributes to the temperature increase also increases with the addition of H_2O but consumes the reactive radical H to form HO_2, causing the system to become less active. Besides, the HO_2 wall termination reaction (R35) also becomes important. When f_{H2O} increases to 0.8, some reactions associated with H_2O_2 start to become important, including the H_2O_2 wall termination reaction (R36), R6:$H_2O_2(+M) = 2OH(+M)$, and R7/R8: $OH+H_2O_2 = HO_2+H_2O$.

In general, these reactions include three H consumption pathways. The first is the chain-branching reaction (R1:$H+O_2=O+OH$), which consumes H to obtain O and OH, leading to ignition. The second is the chain termination reaction represented by R5: $H+O_2(+M) = HO_2(+M)$ and R22: $H_2O_2 + H = HO_2 + H_2$), which consumes H radicals to obtain relatively inactive HO_2 radicals. The last one is the wall destruction reaction of H radical (R32). The addition of H_2O enhances the pathway of consuming H to obtain HO_2 and decreases the activity of the reaction system, which leads to the second limit moving toward the high temperature range.
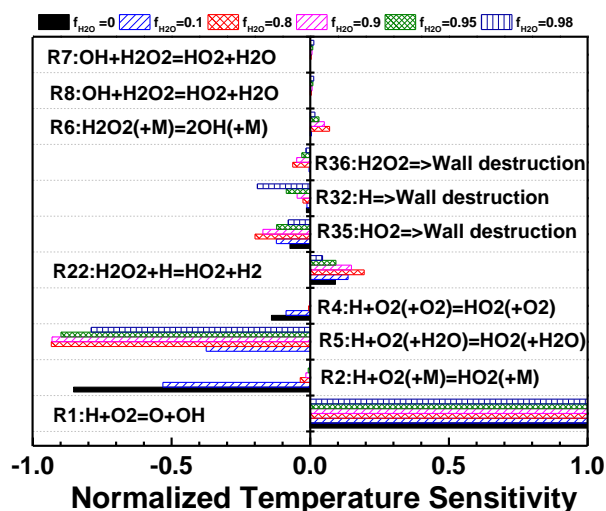
Figure 3: Temperature sensitivity of the second explosion limit to individual reaction rates normalized by the largest value at each case at $P = 1\times10^4$ Pa.

3.1.3 Third explosion limit

When the pressure is further increased to 1×10^7 Pa (i.e., around the third limit range), the reactions with high temperature sensitivity coefficients are shown in Figure 4. It can be seen that R22: $H_2O_2 + H = HO_2 + H_2$ is the most important reaction contributing to the temperature increase when the H_2O mole fraction is 0-0.95, while the reaction with the greatest temperature sensitivity is R6:$H_2O_2(+M) = 2OH(+M)$ when the H_2O mole fraction is 0.98. Besides, the temperature sensitivity of almost all other reactions increased with H_2O mole fraction. Hence, the chemical reactions are not the main reason for the third limit shifting to the high temperature range.

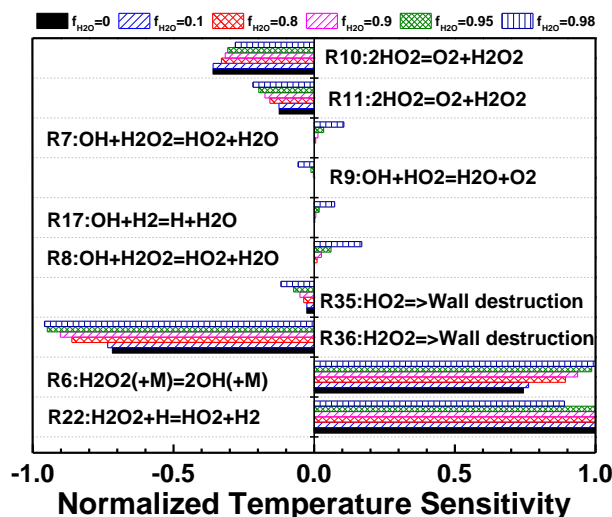
Figure 4: Temperature sensitivity of the third explosion limit to individual reaction rates normalized by the largest value at each case at $P = 1\times10^7$ Pa.

3.2 Different effects caused by water addition

Adding H_2O may result in both physical and chemical effects, and in this section we will analyze these effects through numerical experiments with artificial H_2O species. Firstly, inert water with the same thermodynamic parameters as H_2O is added to the mechanism to study the effect of the dilution effect

of H_2O and the thermal effect on the H_2/O_2 explosion limit. This inert water does not participate in any reactions. Secondly, an artificial species with the same thermodynamic parameters as H_2O but only involved in the third body reaction is added to the mechanism to study the role of the third body reaction associated with H_2O on the explosion limit.

A comparison of the effect of H_2O and inert H_2O on the explosion limit of H_2/O_2 under the same mole fraction conditions is shown in Figure 5(a). It can be seen that the chemical effects caused by H_2O result in a significant shift of the second limit to the high temperature range and the third limit to the low temperature range. In other words, the chemical reactions involving H_2O lead to a more explosive mixture under high pressure conditions. It can be seen from Figure 5(b) that under the same mole fraction, original H_2O and H_2O acting as third body have almost the same impact on the explosion limit of H_2/O_2, which means that the chemical reactions involving H_2O as a reactant have limited effects on the explosion limit.
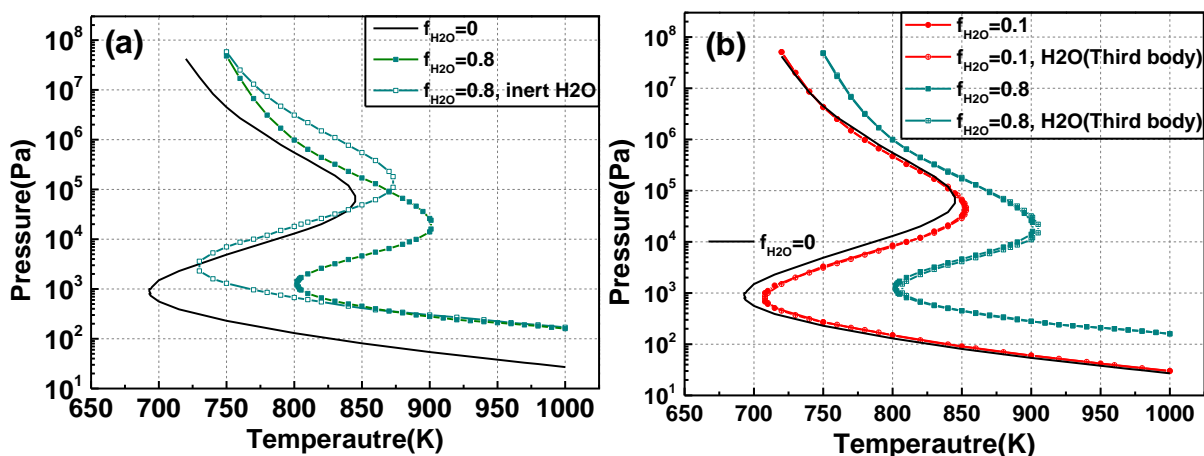

Figure 5: Comparison of the effects of (a) H_2O and inert H_2O, (b) H_2O and H_2O acting as third body on the explosive limit of H_2/O_2 mixtures at equivalence ratio.

4 Conclusions

The explosion limits of $H_2/O_2/H_2O$ mixture are investigated in this study. It is shown that both the first and second limits move toward the high temperature range with H_2O addition, which is caused by enhancement of H wall destruction reaction and the pathway from H to HO_2, respectively. The third limit moves toward the low temperature range first and starts to move toward the high temperature range after the mole fraction of H_2O is greater than 0.3. With H_2O addition, the dominant reactions in first limit range are still R1: $H+O_2 = O+OH$ and the wall destruction reaction of H radicals (R32), same as those when without H_2O. For the second limit, R1 is still the most important reaction related to the temperature increase. With the increased H_2O mole fraction, R5: $H+O_2(+M) = HO_2(+M)$, where $M=H_2O$ and the wall destruction reaction of HO_2 (R35) tend to be more important. For the third limit, reactions related to H_2O_2 are quite important, including the wall destruction reactions of H_2O_2 (R36), the formation of H_2O_2 (R22/R10/R11) and the formation of OH from H_2O_2 (R6).

Numerical experiments are carried out to identify the physical and chemical effects caused by water vapor. The results indicate that the chemical effects make the mixture more explosive in the third limit range, while the physical effects make the mixture less explosive. The combined effect of the two causes the third limit to move first to the low temperature range and then to the high temperature range. Among the chemical effects, the third body reactions related to H_2O play a major role.

Acknowledgment

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