Chemical Effect of Hydrogen Peroxide Addition on Characteristics of Methane-Air Combustion

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Abstract

The effects of hydrogen peroxide addition on the reaction pathway of premixed methane/air flames are numerically investigated using the PREMIX code with the GRI-Mech 3.0 chemical kinetic mechanisms and detailed transport properties. Hydrogen peroxide is used as the oxidizer substituent of air. Results show that the laminar burning velocity and adiabatic flame temperature of premixed methane-air flame are significantly increased with H_2O_2 addition. The addition of hydrogen peroxide increases not only all the reaction rates of intermediate species, but also the concentrations of intermediate species. The traditional reaction pathways of CH_4 /air flame are altered by the addition of hydrogen peroxide, due to the enhanced production of OH and HO_2 . The enhanced OH radicals promote HO_2 productions through reaction (R85). The increased HO_2 accelerates the progressive reaction of CH_3 to form CH_3O and then CH_2O .

Keywords: Hydrogen peroxide, chemical pathway, laminar burning velocity, adiabatic flame temperature, numerical simulation.

1. Introduction

Plenty of flame-stabilized strategies have been investigated and applied in macro- and micro-scale combustion systems for decades [1]. For example, swirler and bluff body are extensively utilized in combustion systems to increase flow residence time as well as fuel-air mixing, and hence to improve flame stability by means of flow structures modification [2]. Nevertheless, these approaches result in extra expenses for assembling additional mechanical auxiliaries in combustion system and retrofitting the mechanical design of combustor configuration. Besides, the operational procedure of the retrofitted combustion system and the optimum operating range of the combustor are also needed to be re-modified.

In order to minimize the modification of combustion system, an attractive alternative is to employ active fuels [3] or adding strong oxidants [4-6] to fuels to enhance combustion. Accordingly, the addition of hydrogen [3], hydrogen peroxide [4, 5] or nitrous oxide [6] in hydrocarbon fuels has received increasing attention recently. Among these energetic additives, hydrogen peroxide (H_2O_2) is particularly an environmentally friendly oxidant with strong oxidability and it appears as liquid state in normal temperature with benefits of easy-to-store and recharging.

Golovitchev et al. [7] found that the improvement of methane auto-ignition with hydrogen peroxide addition is much stronger than that with hydrogen. Kim et al. [8] discovered that the present of hydrogen peroxide can evidently reduce the concentration of unburnt hydrocarbons, CO and NO_x. Furthermore, Ting and Reader [4] as well as Chen et al. [5] numerically investigate the effects of hydrogen peroxide on the premixed methane-air flame under various concentrations of H_2O_2 additions. They found that the adiabatic temperature and laminar burning velocity of the premixed methane-air flames are increased due to the increase of OH, H, and O radical concentration. It is conjectured that the existence of hydrogen peroxide leads to the shift of chemical Chen, G.-B.

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reaction pathways, and to further produce chemical radicals. In order to further understand the flame structure of methane-air flame with hydrogen peroxide addition and the roles of hydrogen peroxide on methane reactions, the reaction pathways under the condition of partial replacement of air with hydrogen peroxide are investigated.

2. Numerical method and chemical mechanism

In this study, the adiabatic, unstrained, free propagation velocities of the laminar premixed $CH_4/air/H_2O_2$ flames are calculated by the PREMIX code of CHEMKIN Collection. The PREMX code solves the equations governing steady, isobaric, quasi-one-dimensional flame propagation. For a freely propagation flame, the mass flow rate is an eigenvalue and must be determined as part of the solution. An additional constraint is required and a flame-fixed coordinate system is established by fixing the temperature of 500 K. Temperature and species gradients at the boundaries should be avoided to obtain the accurate flame speed. It means that the boundaries should be sufficiently far from the flame. In this work, the adiabatic flame temperature is calculated by the EQUIL code of CHEMKIN Collection. An initial reactant mixture is specified with the constraints of constant enthalpy and constant pressure. To obtain accurate adiabatic flame temperature, besides reactants and products, all radical species that might occur in the flame are also included.

The GRI-Mech 3.0 mechanism composing of 53 chemical species and 325 reaction steps is used for the $CH_4/air/H_2O_2$ flame calculations. Detailed thermal and transport properties are also included. This mechanism has been used satisfactorily to simulate non-catalytic H_2O_2 decomposition [9]. The chemical kinetics with CHEMKIN format is used in the code. Details of the chemical reaction rate formulation and CHEMKIN format can be found in the user's manual [10].

At the inlet boundary, the unburned reactants are supplied at 423 K and 1 atm. This selected temperature is the boiling temperature of H_2O_2 and it is assumed that all reactants at this temperature are in gas phase. Hydrogen peroxide is used as the oxidizer substituent by partial replacement of air. One mole H_2O_2 can be decomposed to produce half mole O_2 and one mole H_2O . In the case of using H_2O_2 to replace partial air, the total amount of O_2 is maintained to keep the constant fuel/oxidizer ratio. Therefore, the reduced O_2 from air is supplied from the decomposed H_2O_2 . For the stoichiometric condition, the global reaction is defined as:

 $CH_4 + 4\beta H_2O_2 + (2 - 2\beta)(O_2 + 3.76N_2) \rightarrow CO_2 + (4\beta + 2)H_2O + 3.76(2 - 2\beta)N_2$ where β is the replacement percentage of air by H₂O₂. The reduction of air also leads to reduction of N₂ in the oxidizer stream.

3. Results and Discussion

3.1 Characteristics of CH₄/air/H₂O₂ flame

To examine the effects of H_2O_2 on premixed methane flames, the numerical results of premixed stoichiometric CH_4/air and $CH_4/50\%$ air + 50% H_2O_2 are compared for illustration. Figure 1 shows the resultant temperature and species concentration profiles. With 50% of air replaced by hydrogen peroxide, the adiabatic flame temperature increases approximately by 400 K due to the reduction of nitrogen dilution and heat release from thermal decomposition of hydrogen peroxide. For pure air case, the reactant CH_4 is completely consumed within 1.0 mm of the spatial coordinate but 0.78 mm for the 50% H_2O_2 replacement case. Hydrogen peroxide enhances methane consumption. In addition, the H_2O_2 decomposition results in an increase of H_2O production. Hydrogen peroxide significantly decreases CO_2 formation and increases CO formation in a reaction zone. Figure 1 also shows that the mole fraction of OH, H and O increases with increasing hydrogen peroxide addition. Especially, the increasing trends of HO_2 , HCO, CH_2O and CH_3O are more significant. These facts suggest that the dominant reactions of methane combustion are altered by H_2O_2 addition. Hydrogen peroxide decomposition increases the active radicals, enhances the reaction rate, and then accelerates the laminar burning velocity.

3.2 Burning velocity of CH₄/air/H₂O₂ flame

Figure 2 shows the effect of replacement of air with H_2O_2 on the laminar burning velocity and adiabatic flame temperature at the stoichiometric condition. It can be seen that the laminar burning velocity is increased with increasing the percentage of hydrogen peroxide addition. The laminar burning velocity is about 0.71 m/s for the stoichiometric CH_4 /air flame at an inlet temperature of 423 K and it is increased to about 2.1 m/s with 50% of air replaced by H_2O_2 . When air is completely replaced by H_2O_2 , the laminar burning velocity approaches 4.7 m/s. This significant increase is because that the oxidizer is completely provided from decomposition of hydrogen peroxide and hydrogen peroxide dominates the reaction rate of methane oxidation. Figure 2 also shows

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that the adiabatic flame temperature increases with increasing the percentage of H_2O_2 addition. The maximum temperature increase is up to 520 K when air is completely replaced by H_2O_2 . The increase of adiabatic temperature is primarily due to heat release from hydrogen peroxide decomposition. The maximum heat release rate is about 6.09×10^9 J/m³-s for stoichiometric CH₄/air flame. For the case of stoichiometric CH₄/50% air + 50% H₂O₂ flame, the maximum heat release rate is about 5.42×10^{10} J/m³-s which is almost 9 times higher than that of stoichiometric CH₄/air flame. When the air is completely replaced by H₂O₂, the maximum heat release rate can even reach to 4.49×10^{11} J/m³-s which is about two-order of magnitude higher than that for stoichiometric CH₄/air flame. It is apparent that the decomposition of H₂O₂ dominates the heat release and then increases the adiabatic flame temperature.

In order to understand the effect of chemical reaction on the flame speed of $CH_4/air/H_2O_2$ flames, the firstorder sensitivity analysis of laminar burning velocity is shown in Fig. 3 for different reactant compositions at stoichiometric condition. In the case of pure air, the dominant reactions for laminar burning velocity are,

$O_2 + H \leftrightarrow O + OH$	(R38)
$H + CH_3 + M \leftrightarrow CH_4 + M$	(R52)
$OH + CO \leftrightarrow H + CO_2$	(R99)

For the hydrogen peroxide replacement cases, the dominant reactions shift to the following reaction steps:

1 ,	
$O_2 + H \leftrightarrow O + OH$	(R38)
$2OH + M \leftrightarrow H_2O_2 + M$	(R85)
$OH + H_2O_2 \leftrightarrow HO_2 + H_2O$	(R89)
$OH + CH_4 \leftrightarrow CH_3 + H_2O$	(R98)

Among these reactions, (R85) and (R89) are the most important chemical reactions. Hydrogen peroxide promotes the production of OH radicals, modifies the reaction pathway, and enhances the reaction rate leading to the increase of flame speed.

3.3 Production rate of intermediate species

The effects of H_2O_2 on the major species and OH radical of the $CH_4/air/H_2O_2$ premixed flames have been discussed in our previous paper [5]. In the present study, the dominate reactions for the intermediate species (O, H, HO₂, HCO, CH₃O and CH₂O) in CH₄/air/H₂O₂ premixed flames are further analyzed. These species are crucial to clearly reveal the reaction pathway in CH₄/air/H₂O₂ flames.

Figure 4 left figure shows the production rate of H for CH_4/air and $CH_4/50\%$ air + 50% H_2O_2 flames at stoichiometric condition. With hydrogen peroxide addition, some of the main reactions are enhanced and shifted in axial position. Reactions (R46) and (R57) are evidently increased. The dominated reaction for H production is $OH + H_2 \leftrightarrow H + H_2O$ (R84)

Since OH is significantly increased by H_2O_2 , it then assists in yielding H from reaction (R84). However, the dominant reaction for H consumption is

$$O_2 + H \leftrightarrow O + OH$$
 (R38)

In Fig. 4 left figure it is obvious that all the main reactions are enhanced by hydrogen peroxide addition. Figure 4 right figure shows the production rate of O for two different flames at stoichiometric condition. With hydrogen peroxide addition, the main reactions of O are not altered. Nonetheless, the rates of dominate reaction steps are enhanced and the total production rate of O is also increased. The dominate reactions for O production is

$$O_2 + H \leftrightarrow O + OH$$
 (R38)

And the main O consumption reactions are

$$\begin{array}{ll} O+H_2 \leftrightarrow H+OH & (R3) \\ O+CH_3 \leftrightarrow H+CH_2O & (R10) \end{array}$$

The chain branching reaction (R38) is one of the most important reactions in combustion process.

Figure 5 left figure shows the HO₂ production rate for two different flames at stoichiometric condition. For the CH₄/air flames, the domination reactions for the production and consumption of HO₂ are (R168) and (R46), respectively.

$$O_2 + HCO \leftrightarrow HO_2 + CO$$
(R168)
$$U + HO_2 \leftrightarrow 2OU$$
(R46)

 $H + HO_2 \leftrightarrow 2OH$ (R46)

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(R89)

When 50% of air is replaced by hydrogen peroxide, all the major reactions and the total production rate are greatly increased. The dominant reaction for HO₂ production is shifted from (R168) to (R89).

$$OH + H_2O_2 \leftrightarrow HO_2 + H_2O$$

Hydrogen peroxide promotes the production of HO_2 . In addition to reaction (R46), the other dominant reaction for HO_2 consumption is reaction (R116).

$$2HO_2 \leftrightarrow O_2 + H_2O_2 \tag{R116}$$

Figure 5 right figure compares the CH_3O production rate for two different flames at stoichiometric condition. Similarly to the previous intermediate species, the existence of H_2O_2 promotes the main reactions and the total reaction rates substantially. The dominant reactions for CH_3O production and consumption are (R119) and (R57), respectively,

$$\begin{array}{ll} HO_2 + CH_3 \leftrightarrow OH + CH_3O & (R119) \\ CH_3O + M \leftrightarrow CH_2O + H + M & (R57) \end{array}$$

Reaction (R57) is also the dominate reaction for CH_2O production when hydrogen peroxide is used to replace air (see Fig. 6 left figure).

Figure 6 left figure shows the CH_2O production rate for two different flames at stoichiometric condition. For the CH_4 /air flame, the dominate reactions of CH_2O consumption and production are (R58) and (R10), respectively,

$$H + CH_2O \leftrightarrow H_2 + HCO$$
 (R58)

$$O + CH_3 \leftrightarrow H + CH_2O \tag{R10}$$

Reaction (R10) is the most important step for CH₃ oxidation to form CH₂O, which belongs to progressive dehydrogenation of CH₄ to CH₃ and then CH₃O, CH₂O, HCO, CO and finally to CO₂. For the CH₄/50% air + 50% H₂O₂ flame, hydrogen peroxide enhances reactions (R10) and (R57), but the enhancement of reaction (R57) is more significant than that of reaction (R10). Therefore, the reaction pathway of CH₃ to CH₂O is changed. The primary path is from CH₃ to CH₃O and then to CH₂O. With 50% of H₂O₂ replacement, the reactions (R10), (R15), (R57), (R58), and (R101) are all enhanced. In addition to reaction (R58), the reaction (R101) is enhanced to become the second important reaction for CH₂O consumption.

$$OH + CH_2O \leftrightarrow HCO + H_2O$$
 (R101)

The HCO production rate is shown in Fig. 6 right figure. For the CH_4 /air flames, the domination reactions for HCO production and consumption are

$H + CH_2O \leftrightarrow H_2 + HCO$	(R58)
$OH + CH_2O \leftrightarrow HCO + H_2O$	(R101)
$CH + O_2 \leftrightarrow O + HCO$	(R125)
$HCO + H_2O \leftrightarrow H + CO + H_2O$	(R166)
$HCO + M \leftrightarrow H + CO + M$	(R167)
$O_2 + HCO \leftrightarrow HO_2 + CO$	(R168)

When air is partially replaced by hydrogen peroxide, all the main reactions and the total production rate are increased. Reactions (R166), (R167), and (R168) are also the dominate reactions for CO production. The produced CO is then reacted with OH to form CO_2 .

Finally, the effect of hydrogen peroxide addition on reaction pathways is shown in Fig. 7. The black arrows indicate the traditional dominant CH_4/air combustion pathways. The red arrows represent the enhanced reaction steps by H_2O_2 addition and the black dashed lines represent the increased radicals to enhance the dominant reaction steps. It has been shown that the addition of hydrogen peroxide increases the productions of OH and HO_2 in CH_4/air flames. The increased OH radicals promote progressive dehydrogenations of CH_4 to CH_3 and of CH_2O to HCO, and finally oxidation of CO to CO_2 . In traditional CH_4/air combustion, CH_2O is primarily produced from oxidation of CH_3 through reaction (R10). However, with the addition of H_2O_2 , CH_2O is primarily produced from CH_3O through reaction (R57). In addition, the increased HO_2 also accelerates CH_3O production through reaction (R119).

4. Conclusions

In the present study, the effects of hydrogen peroxide addition on premixed methane/air flames are numerically investigated with GRI-Mech 3.0 chemical kinetic mechanisms and detailed transport properties. Hydrogen peroxide is used as an oxidizer to replace partial air. The characteristics of laminar burning velocity,

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adiabatic flame temperature, and production rate of intermediate species (O, H, HO₂, HCO, CH₂O and CH₃O) are studied. The following findings are obtained from this study.

1. The laminar burning velocity and adiabatic temperature of premixed CH_4/air flames are obviously increased with the addition of H_2O_2 . The dominant reactions for laminar burning velocity are shifted from (R38), (R52), and (R99) to (R38), (R85), (R89), and (R98). In addition, the decomposition of H_2O_2 dominates the net heat release rate and then affects the adiabatic flame temperature.

2. Hydrogen peroxide increases not only the reaction rates, but also the concentrations of intermediate species. The increase of intermediate species then alters the reaction pathway of methane flames.

In CH₄/air flame, CH₂O is primarily produced by the oxidation of CH₃ with O. With the addition of H₂O₂, the primary reaction pathway is shifted from the progressive reaction of CH₃ to CH₃O and then to CH₂O. This difference is primarily due to the substantial increase of HO₂.

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Figure 1. Profiles of temperature and species concentration of stoichiometric $CH_4/air/H_2O_2$ flames. (a) $CH_4/100\%$ air (b) $CH_4/50\%$ air+50% H_2O_2 .



Figure 2. Computed laminar burning velocity and adiabatic flame temperature of methane/air flames with different percentages of air replaced by H_2O_2 .



Figure 3. Sensitivity analysis of laminar burning velocity for stoichiometric $CH_4/air/H_2O_2$ flames.



Figure 4. Effect of H_2O_2 on different H production rate for CH_4/air and $CH_4/50\%$ air + 50% H_2O_2 flames at

stoichiometric condition. Left: H production rate. Right: O production rate.



Figure 5. Effect of H_2O_2 on different production rate for CH_4/air and $CH_4/50\%$ air + 50% H_2O_2 flames at stoichiometric condition. Left: HO_2 production rate. Right: CH_3O production rate.



Figure 6. Effect of H_2O_2 on different CH_2O production rate for CH_4/air and $CH_4/50\%$ air + 50% H_2O_2 flames at stoichiometric condition. Left: CH_2O production rate. Right: HCO production rate.



Figure 7. Effect of H_2O_2 addition on reaction pathways.