



Numerical study of the effect of water addition on gas explosion

Yuntao Liang^a, Wen Zeng^{b,*}

^a State Key Laboratory of Coal Mine Safety Technology, Shenyang Branch of China Coal Research Institute, Liaoning, Shenyang 110016, PR China

^b State Key Laboratory of Engines, Tianjin University, Tianjin 300072, PR China

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ABSTRACT

Through amending the SENKIN code of CHEMKIN III chemical kinetics package, a computational model of gas explosion in a constant volume bomb was built, and the detailed reaction mechanism (GRI-Mech 3.0) was adopted. The mole fraction profiles of reactants, some selected free radicals and catastrophic gases in the process of gas explosion were analyzed by this model. Furthermore, through the sensitivity analysis of the reaction mechanism of gas explosion, the dominant reactions that affect gas explosion and the formation of catastrophic gases were found out. At the same time, the inhibition mechanisms of water on gas explosion and the formation of catastrophic gases were analyzed. The results show that the induced explosion time is prolonged, and the mole fractions of reactant species such as CH₄, O₂ and catastrophic gases such as CO, CO₂ and NO are decreased as water is added to the mixed gas. With the water fraction in the mixed gas increasing, the sensitivities of the dominant reactions contributing to CH₄, CO₂ are decreased and the sensitivity coefficients of CH₄, CO and NO mole fractions are also decreased. The inhibition of gas explosion with water addition can be ascribed to the significant decrease of H, O and OH in the process of gas explosion due to the water presence.

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1. Introduction

In general, gas explosion is a rapid chemical reaction induced by fire sources. The reactants are the exposable mixed gas including combustible gases such as the mixture of methane and air [1,2]. This reaction will be automatically accelerated through the radical centers accumulated and the main factors that influence the methane branch-explosion are the concentrations of reactants and radical centers [3,4]. After gas explosion, a detonation wave may be formed in the roadway of the mine, which will damage the roadway and equipments, and injure miners. Furthermore, gas explosion will produce a large amount of catastrophic gases, which is the main factor for a large number of miners' casualties [5,6].

In the recent years, the reaction kinetics of gas explosion has become the focus of gas explosion research [7,8]. Oh et al. [9] studied the variation of the gas explosion characteristics caused by the built-in obstacles in enclosed/vented gas explosion vessels. In their study, the explosion characteristics and the flame behavior of vented explosions and constant-volume explosions were investigated. Shebeko et al. [10] measured the burning velocities and flammability limits of gaseous mixtures of combustible gas (hydrogen and methane), oxidizer (oxygen and air), and diluent (nitrogen, argon, helium, carbon dioxide, steam, water aerosol formed by

evaporation of superheated water) at elevated temperatures (up to 250 °C) and pressures (up to 4.0 MPa). Bielert and Sichel [11] used a front tracking method to describe the development of a turbulent flame zone due to convection and propagation/burning in a closed tube. The kinematic description of the flame propagation process made it possible to eliminate the details of the chemical reactions involved. Maremonti et al. [5] investigated the ability of the CFD code AutoReaGas to simulate a gas explosion in two linked vessels. A fair agreement was observed between the computed results and experimental data taken from literature. Moreover, the computed values of the turbulence intensity at varying diameters of the connecting pipe demonstrated that turbulence induced in both vessels represented a major factor affecting the explosion violence.

However, the reaction mechanisms in the studies of kinetics of gas explosion in the literatures were very simple which cannot reflect the detailed reaction kinetics of gas explosion process. At the same time, few studies were reported on the measurement of intermediate radicals in gas explosion and the technologies reported in the literatures can only measure the limited intermediate radicals and their mole fraction profiles. The effects of intermediate species or free radicals on the process of gas explosion were also scarcely reported. Moreover, the chemical kinetics effect of water addition on the process of gas explosion has not been well understood. Since the chemical kinetics mechanism of methane is reasonably well understood [12], and the chemical kinetics simulation can give comprehensive information on the chemical reaction

* Corresponding author. Tel.: +86 24 89724899.

E-mail address: zengwen928@sohu.com (W. Zeng).

process, the combination of methane and water may demonstrate different behavior. The objective of this study is to analyze the chemical kinetics effect of water addition on the process of gas explosion through the chemical kinetics simulation with detailed chemical reaction mechanism. The potential of catastrophic gases reduction of gas explosion with water addition will also be discussed.

2. Reaction mechanism and computational method

2.1. Reaction mechanism

A detailed gas reaction mechanism of methane combustion (GRI-Mech) is adopted. GRI-Mech is an optimized detailed chemical reaction mechanism for the calculation of natural gas chemical reaction process and the latest version is GRI 3.0 [13], which consists of 325 elementary chemical reactions with associated rate coefficient expressions and thermo-chemical parameters for 53 species. The applicable ranges of GRI 3.0 are 1000–2500 K in temperature, 10 Torr–10 atm in pressure and 0.1–5 in equivalence ratio. The GRI 3.0 mechanism has been validated by a large amount of experimental data for methane, ethane, carbon monoxide and hydrogen [14,15].

2.2. Computational method

The processes of gas explosion in the constant volume bomb were calculated by using SENKIN code [16] of CHEMKIN III program [17] with GRI-Mech 3.0 mechanism. The basic equations for gas explosion in the constant volume bomb which is an adiabatic system are as follows:

Conservation of species

$$\frac{dY_i}{dt} = \nu \dot{w}_i W_i \quad i = 1, \dots, K \quad (1)$$

Conservation of energy

$$c_v \frac{dT}{dt} + \nu \sum_{i=1}^K e_i \dot{w}_i W_i = 0 \quad (2)$$

Reaction rate

$$\dot{w}_i = \sum_{k=1}^{N_g} \nu_{ik} k_{fk} \prod_{j=1}^K [X_j]^{v'_{jk}} \quad i = 1, \dots, K \quad (3)$$

The forward rate coefficient of reaction k is the modified Arrhenius form

$$k_{fk} = A_k T^{b_k} \exp \left[\frac{-E_{ak}}{RT} \right] \quad k = 1, \dots, N_g \quad (4)$$

where $\nu_{ik} = \nu'_{ik} - \nu''_{ik}$, ν'_{ik} and ν''_{ik} are the forward and reverse stoichiometric coefficients of species i and reactions k respectively, t is reaction time, \dot{w}_i , W_i , Y_i , e_i are the gas reaction rate, molecular weight, mass fraction and internal energy of species i respectively, ν , R , c_v are the specific volume, gas constant, and the constant volume specific heat respectively, p , T are the pressure and gas temperature respectively, K , N_g are the total number of species and elementary reactions respectively, $[X_j]$ is mole concentration of species j , A_k , b_k , E_{ak} are the pre-exponential factor, the temperature exponent, and the activation energy of the elementary reaction k .

The system of these ordinary differential equations is generally stiff, and, thus, is most efficiently solved by implicit techniques. In this paper, we used a software package called DASAC (differential

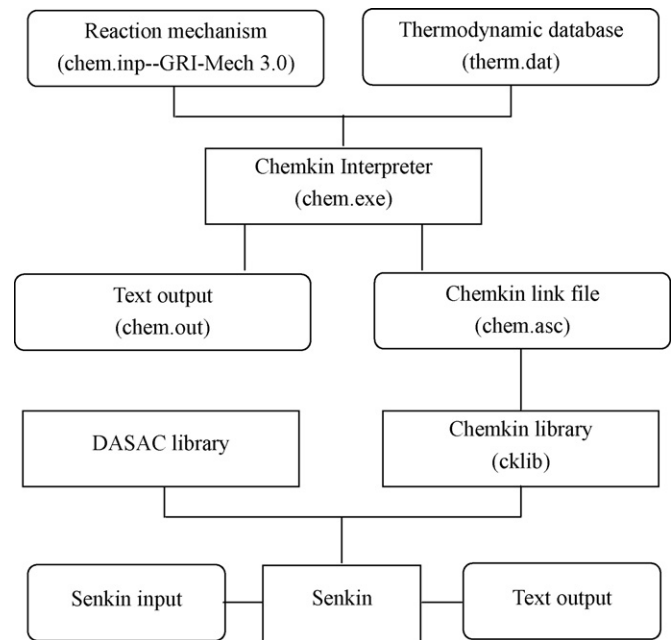


Fig. 1. Computational process of coupling the SENKIN code with GRI-Mech 3.0.

algebraic sensitivity analysis code) to perform time integration. The DASAC package is based on the differential/algebraic system solver DASL, which performs the time integration using a backward differentiation formula (BDF). These BDF methods are in regular use for solving a wide range of stiff problems, including chemical kinetics ones. The notions of stiffness and implicit numerical methods are described elsewhere [18]. The details of the numerical methods in DASL are described by Petzold [19].

Sensitivity analysis is a powerful and systematic way to determine quantitatively the relationship between the solution to a model and the various parameters that appear in the model's definition [20]. The system of ordinary differential equations that describe a physical problem is of the general form

$$\frac{dZ}{dt} = F(Z, t, a) \quad (5)$$

where in our case, $Z = (T, Y_1, Y_2, \dots, Y_K)^T$ is the vector of temperature and mass fractions. The parameter vector a represents the pre-exponential constants A_k for each of the elementary reactions, as shown in Eq. (4).

The first-order sensitivity coefficient matrix is defined as

$$w_{l,i} = \frac{\partial Z_l}{\partial a_i} \quad (6)$$

where the indices l and i refer to the dependent variables and reactions, respectively. Differentiating Eq. (5) with respect to the parameters a_i yields

$$\frac{dw_{l,i}}{dt} = \frac{\partial F_l}{\partial Z} \cdot w_{l,i} + \frac{\partial F_l}{\partial a_i} \quad (7)$$

Note that this equation for the sensitivity coefficients is linear, even though the model problem may be nonlinear. Of course, when coupled with a nonlinear model problem, the whole system is still nonlinear. Nevertheless, when solved via the same BDF method as the model problem, the sensitivity solution is efficient because of the linearity. The Newton iteration for the corrector step converges in one iteration. The computational process of coupling SENKIN code with the GRI-Mech 3.0 is shown in Fig. 1.

In the following computations the mole fraction of water in the mixed gas is 0%, 5%, 10%, 20%, respectively. The initial tem-

Table 1
Reactant mole fractions of the calculated mixed gas.

Cases	Methane	Oxygen	Nitrogen	Water
1	0.07	0.22	0.71	0.0
2	0.063	0.198	0.639	0.1
3	0.0595	0.187	0.6035	0.15
4	0.056	0.176	0.568	0.2

perature and pressure are 1300 K and 1.0 atm, respectively. The induced explosion time is too short as the initial temperature and pressure are too high. If the initial temperature is too low (lower than 1000 K), the mixed gas will not explode. The reactant mole fractions of the calculated mixed gas are given in Table 1.

3. Results and discussion

The profiles of temperature and pressure, mole fraction can be derived from the calculation results. Some representative species including the reactant species such as CH_4 and O_2 , the free radicals such as H, O, and OH, the catastrophic gases such as CO, CO_2 , and NO are selected to analyze the effect of water addition on the process of gas explosion in the constant volume bomb.

3.1. Temperature and pressure

The temperature and pressure profiles of the gas explosion process in the constant volume bomb are given in Fig. 2.

Since the reaction rate coefficient in Arrhenius form has strong temperature dependence, the temperature must have a great effect on the chemical reaction process. Fig. 2(a) shows that water addition has great influence on temperature. The temperature after gas explosion is 2700 K without water fraction, however, is decreased to 2600 K with 10% water fraction in the mixed gas. Furthermore, compared with the case with 10% water fraction, the temperature is decreased by about 220 K with 20% water fraction in the mixed gas. Fig. 2(b) shows the effect of water addition on pressure. The pressure is 2.15 atm after gas explosion without water fraction and is decreased with the increasing of water addition in the mixed gas. Compared with the case that no water fraction in the mixed gas, the pressure is decreased by 0.15 atm with 10% water fraction in the mixed gas and another 0.1 atm decrease is found when water fraction is changed from 10% to 20%.

3.2. Reactant species

The mole fraction profiles of CH_4 and O_2 in the process of gas explosion are shown in Fig. 3. The mole fraction of reactant

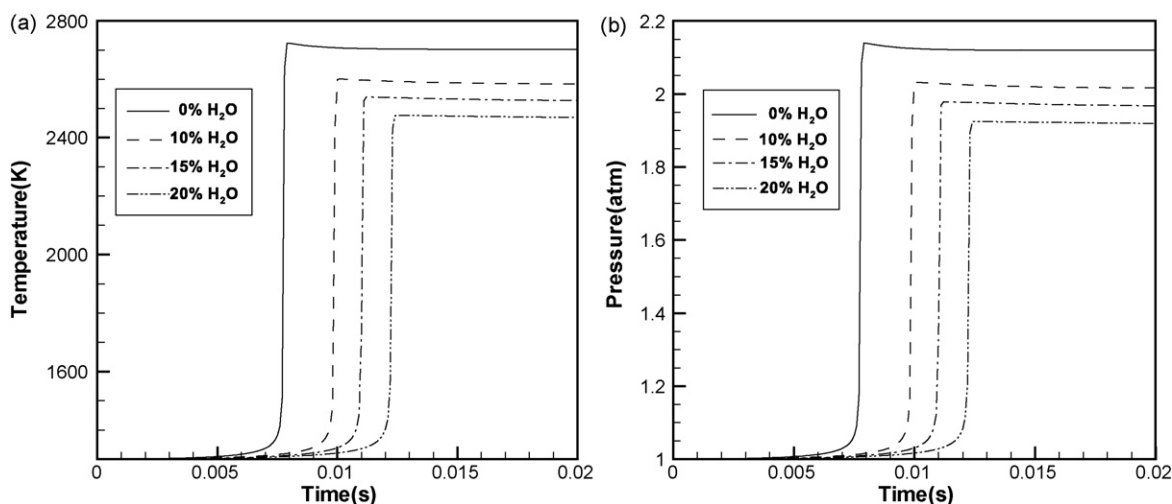


Fig. 2. Temperature and pressure profiles in the process of gas explosion.

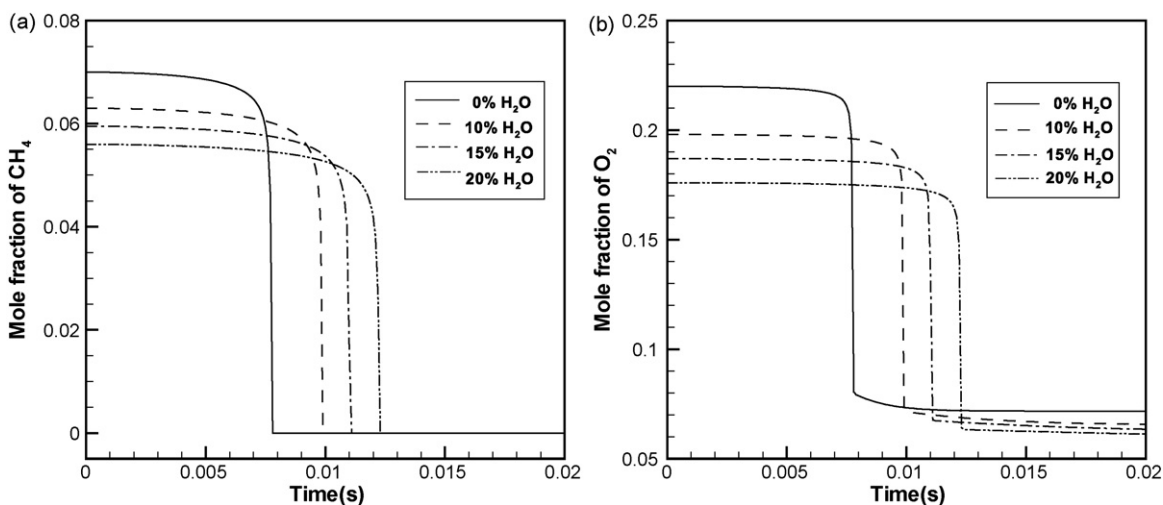


Fig. 3. Mole fraction profiles of CH_4 and O_2 in the process of gas explosion.

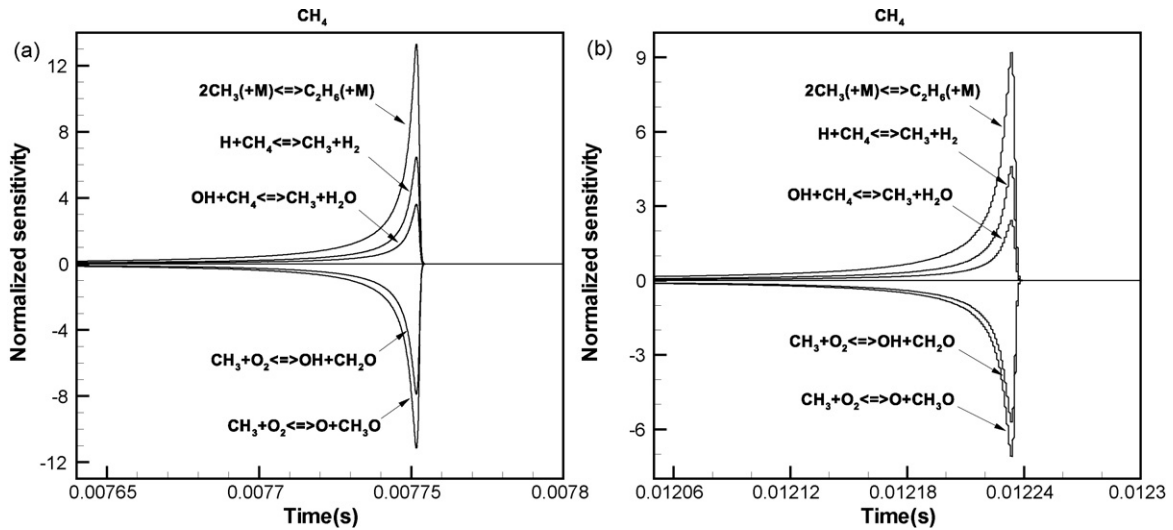


Fig. 4. Sensitivity analysis of CH₄ in the process of gas explosion (a: CH₄/O₂/N₂ = 0.07/0.22/0.71, b: CH₄/O₂/N₂/H₂O = 0.056/0.176/0.568/0.2).

CH₄ is decreased rapidly (named induced explosion time) at about 0.0075 s and completely consumed at the same time in the case that no water fraction in the mixed gas. Furthermore, the induced explosion time is prolonged with the increasing water content. The induced explosion time is 0.01, 0.011, and 0.0125 s when water fraction in the mixed gas is 10%, 15%, and 20%, respectively. This would be due to the decrease of reactant CH₄ mole fraction and the inhibition of chemical reaction as water is added (reaction temperature is decreased as shown in Fig. 2). The study shows that gas explosion is inhibited significantly as water is added.

The dominant reactions contributing to CH₄ in the process of gas explosion can be identified from sensitivity analysis as shown in Fig. 4. Furthermore, the effects of water addition on the sensitivity coefficients of CH₄ mole fraction are given in Fig. 5 with the factors lower than -4 and larger than 4 were plotted for gas explosion with different water fractions. CH₄ mole fraction has the highest sensitivity to reactions such as

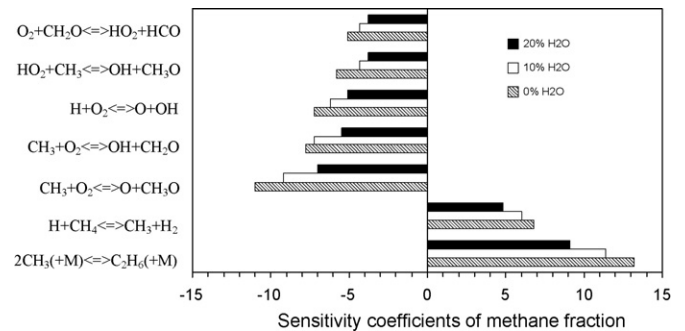
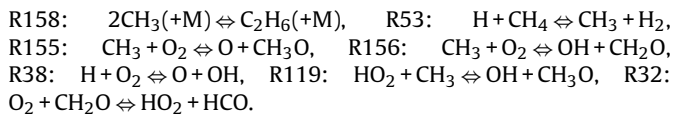


Fig. 5. The effects of water addition on the sensitivity coefficients of CH₄ mole fraction.

The main consumption reactions of CH₄ in the process of gas explosion are the abstraction reactions attacked by H, O and OH such as R155, R156, R38, R119, and R32. As shown in Fig. 5, the sensitivity coefficients of CH₄ mole fraction in the process of gas explosion are decreased as water is added. Furthermore, with the water fraction in the mixed gas increasing more, the sensitivity coefficients of CH₄ mole fraction are decreased more. This suggests

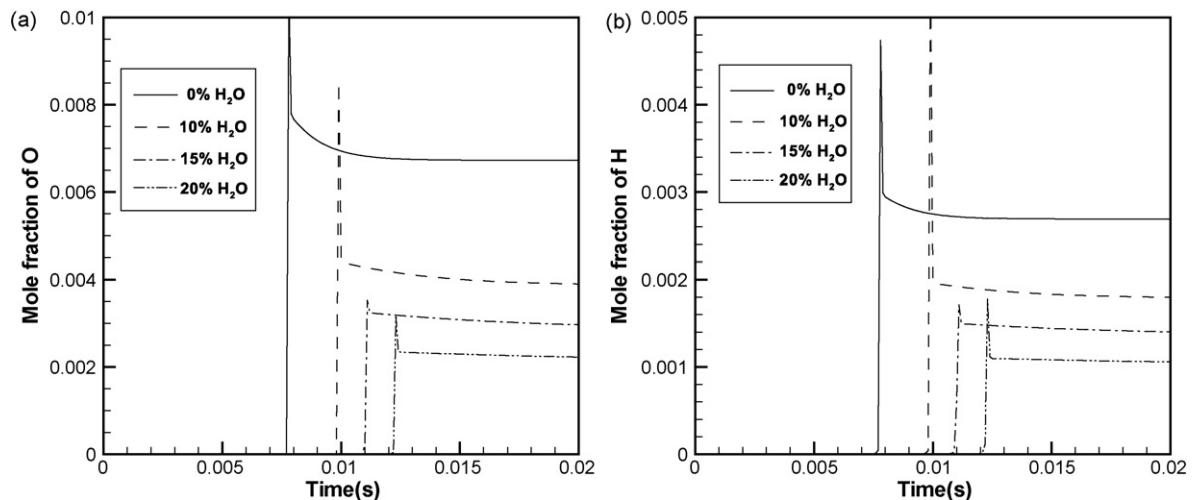


Fig. 6. Mole fraction profiles of O and H in the process of gas explosion.

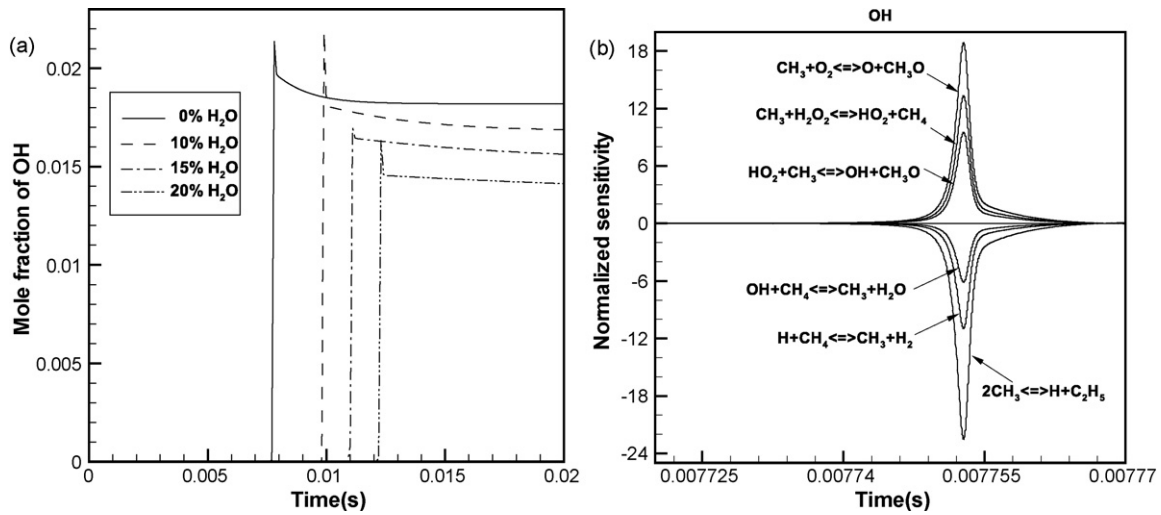


Fig. 7. Mole fraction profile of OH and sensitivity analysis of OH in the process of gas explosion (b: CH₄/O₂/N₂ = 0.07/0.22/0.71).

that the chemical reactions contributing to CH₄ are inhibited as water is added.

3.3. Free radicals

The mole fractions of O, H and OH are illustrated in Figs. 6 and 7(a). The free radicals such as H, O and OH are extremely active due to the presence of unpaired electrons and are short-lived during the combustion. The chain-branching and chain-propagating reactions initiated by the free radicals play the most important role in the chemical reaction. As shown in Figs. 6 and 7(a), the mole fractions of H, O and OH are increased rapidly as the mixed gas exploding and decreased to some constant values after gas explosion. After gas explosion, parts of these free radicals are extinguished, and so the concentrations of these free radicals are decreased. Furthermore, the mole fractions of H, O and OH are decreased as water is added.

The dominant reactions contributing to OH in the process of gas explosion can also be identified from the sensitivity analysis as shown in Fig. 7(b). Furthermore, the effects of water addition on the sensitivity coefficients of OH mole fraction are given in Fig. 8 with the factors lower than -7 and larger than 7 were plotted for gas explosion with different water fractions. The dominant reactions contributing to OH formation are

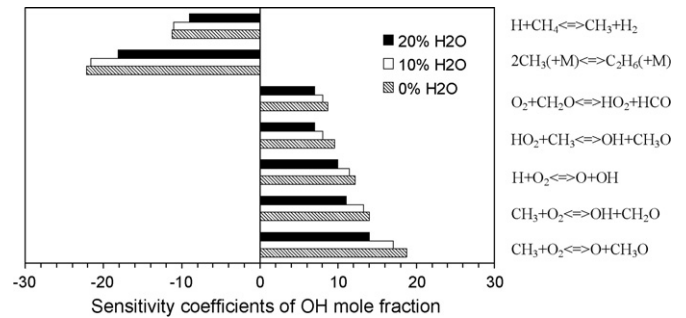
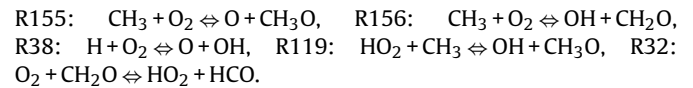


Fig. 8. The effects of water addition on the sensitivity coefficients of OH mole fraction.



At the same time, as shown in Fig. 8, the sensitivity coefficients of OH mole fraction in gas explosion are decreased as water is added. This indicates that the chemical reactions contributing to OH are inhibited as water is added.

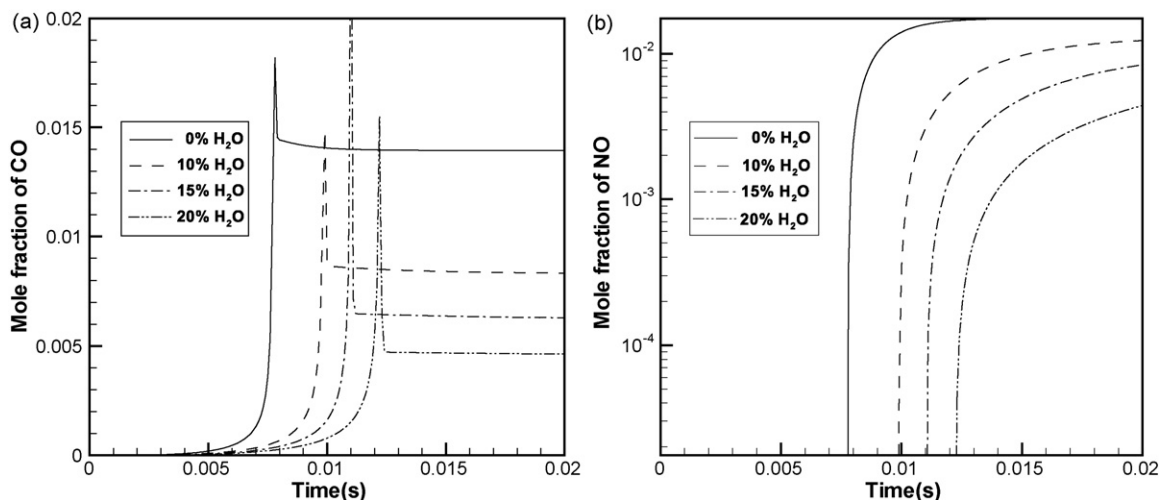


Fig. 9. Mole fraction profiles of CO and NO in the process of gas explosion.

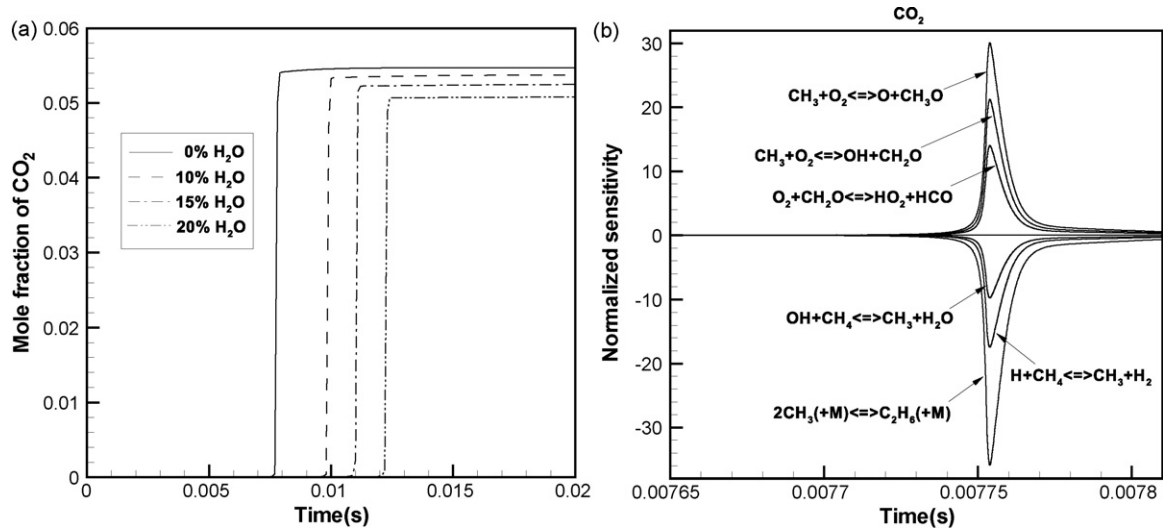


Fig. 10. Mole fraction profiles of CO₂ and sensitivity analysis of CO₂ in the process of gas explosion (b: CH₄/O₂/N₂ = 0.07/0.22/0.71).

3.4. Catastrophic gases

After gas explosion, some types of catastrophic gases would be produced, such as CO, CO₂, and NO. The mole fractions of CO, NO and CO₂ in the process of gas explosion are plotted in Figs. 9 and 10(a). With the increase of water fraction, the mole fractions of CO, NO and CO₂ are decreased. Among these three species, the mole fraction of CO is the most sensitive to the water fraction. As shown in Fig. 9(a), after gas explosion, the mole fraction of CO is about 0.015 without water fraction and is about 0.0085 with 10% water fraction in the mixed gas. At the same time, with the water fraction increasing from 10% to 20%, the mole fraction of CO is decreased from 0.0085 to about 0.005. Among these three species, as shown in Fig. 10(a), the mole fraction of CO₂ is the least sensitive to the water fraction. With the water fraction increasing from 0% to 20%, the mole fraction of CO₂ is slightly decreased from 0.054 to about 0.05.

It is well known that NO can be formed through the thermal, the N₂O intermediate and the prompt routes. It seems that there exists an explicit relation between the NO mole fraction and the flame temperature profile (as shown in Fig. 2(a)). With the water fraction in the mixed gas increasing, the temperature of the gas explosion is decreased, and the mole fraction of NO is also decreased.

The dominant reactions contributing to CO₂ in the process of gas explosion can be identified from sensitivity analysis as shown in Fig. 10(b).

The dominant reactions contributing to CO₂ formation are

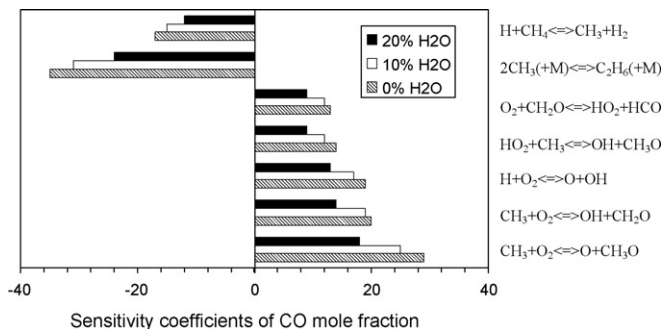


Fig. 11. The effects of water addition on the sensitivity coefficients of CO mole fraction.

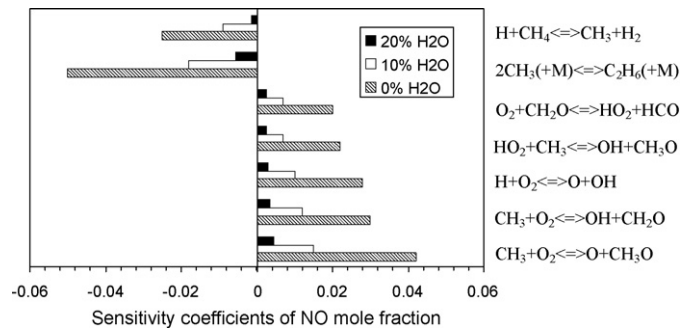


Fig. 12. The effects of water addition on the sensitivity coefficients of NO mole fraction.

R155: CH₃ + O₂ ⇌ O + CH₃O, R156: CH₃ + O₂ ⇌ OH + CH₂O, R38: H + O₂ ⇌ O + OH, R119: HO₂ + CH₃ ⇌ OH + CH₃O, R32: O₂ + CH₂O ⇌ HO₂ + HCO. The main CO₂ consumption reaction pathways are R158: 2CH₃(+M) ⇌ C₂H₆(+M), R53: H + CH₄ ⇌ CH₃ + H₂, R98: OH + CH₄ ⇌ CH₃ + H₂O.

The effects of water addition on the sensitivity coefficients of CO and NO mole fractions are given in Figs. 11 and 12 with the factors lower than -10 and larger than 10 for CO and with the factors lower than -0.02 and larger than 0.02 for NO were plotted for gas explosion with different water fractions. The dominant reactions contributing to CO and NO formation and consumption are the same reaction pathways to CO₂ formation and consumption. At the same time, with the water fraction increasing from 0% to 20%, the sensitivity coefficients of CO and NO mole fractions are decreased.

4. Conclusions

The process of gas explosion in the constant volume bomb was calculated by using SENKIN code of CHEMKIN III program with GRI-Mech 3.0 mechanism. The effect of water addition on the process of gas explosion was evaluated by sensitivity analysis of the selected species. The potential of catastrophic gases reduction with addition of water to the mixed gas was analyzed. The main results are summarized as follows:

- (1) The temperature and pressure are 2700 K and 2.15 atm after gas explosion respectively without water fraction, and are decreased to 2600 K and 0.15 atm respectively with 10% water fraction in the mixed gas. Furthermore, compared with the case with 10% water fraction, the temperature and pressure are decreased by about 220 K and 0.1 atm respectively with 20% water fraction in the mixed gas.
- (2) The induced explosion time is prolonged with increasing water addition. The induced explosion time is 0.0075, 0.01, 0.011, and 0.0125 s respectively when water fraction in the mixed gas is 0%, 10%, 15%, and 20% respectively.
- (3) With the water fraction in the mixed gas increasing, the sensitivities of the dominant reactions contributing to CH₄, CO₂ are decreased and the sensitivity coefficients of CH₄, CO and NO mole fractions are also decreased. The inhibition of chemical reaction with water addition is due to the decrease of H, O and OH mole fractions in the process of gas explosion as water is added.

Acknowledgments

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