EXPERIMENTAL AND NUMERICAL SIMULATION STUDY OF THE INFLUENCE OF CF_3CHFCF_3 ON CHARACTERISTIC OF HYDROGEN/METHANE/AIR EXPLOSION

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The effect of CF_3CHFCF_3 on the explosion of hydrogen/methane/air mixtures at low hydrogen doping ratios (X_{H_2}=10 %) has been investigated on a closed visualisation experimental platform. Different equivalence ratios (Φ = 0.8, 1 and 1.2) and CF_3CHFCF_3 concentrations ($X_{CF_3CHFCF_3}$= 0 % - 5 %) were considered. The results showed that the suppression effect of CF_3CHFCF_3 on the mixture was good under the conditions of different equivalence ratios. After the addition of CF_3CHFCF_3, both of the maximum explosion pressure and the maximum pressure rise rate decrease, which shows CF_3CHFCF_3 has an inhibitory effect on the explosion. However, pressure peak occurs earlier indicates that CF_3CHFCF_3 accelerated the progression of the explosion and facilitates its occurrence. The simulation results indicate that CF_3CHFCF_3 changes the mole fractions of the major species and increases the consumption of the O, H, and OH radicals. Besides, the results of sensitivity analyses show that CF_3CHFCF_3 not only play an inhibitory role but also enhances the laminar flame speed of the explosion flame. Meanwhile, the effect of CF_3CHFCF_3 on the reaction H + CH_3 (+M) <=> CH_4 (+M) is different under different equivalence ratios. This study can provide theoretical support for the safe use of hydrogen/methane/air mixtures.

Key words: *hydrogen/methane/air, CF_3CHFCF_3, explosion suppression, explosion flame.*

1. Introduction

Hydrogen is a efficient, clean and renewable energy source that is carbon-neutral in its use[1-3]. Currently, hydrogen is commonly used by blending hydrogen into natural gas in certain proportions and transporting it by existing natural gas pipelines or pipeline networks, which is currently the best way to achieve large-scale use of hydrogen[4,5]. However, due to the addition of hydrogen, characteristics such as laminar flame speed, explosion limit and flame temperature significantly increase during the transport and use of natural gas, making the process more dangerous[6-8]. In the event of an explosion, the damage to the surrounding environment would be enormous. Therefore, mastering how to control or attenuate the explosive properties of hydrogen / methane / air mixture is an important prerequisite for the safe use of hydrogen energy.

Some scholars for the control and attenuation of hydrogen / methane / air mixture explosion method to carry out research. Luo et al. [9] studied the effect of CO_2 on hydrogen / methane / air gas mixture explosion. The results of the study showed that CO_2 can significantly reduce the flame propagation velocity and lag the brightest moments of flame during the progress of explosion. At the same time, the addition of CO_2 reduces the maximum explosion pressure and the maximum pressure rise rate. Luo et al. [10] selected CO_2 and ultrafine $KHCO_3$ powder as explosion suppression materials. The results showed that the co-existence of CO_2 and modified $KHCO_3$ powder produced a synergistic effect on the suppression of H_2 / CH_4 explosion. When CO_2 was added at 5 %, 7.5 %, and 10 %, with the existence of 30 g/m^3 ultrafine $KHCO_3$ powder, the explosions of 9.5 % CH_4 and H_2 / CH_4 mixtures at hydrogen addition ratios of 20 % and 40 % could be inhibited, respectively. Xu et al. [11] studied the inhibitory effect of $NaHCO_3$ on stoichiometric hydrogen/methane/air explosions (hydrogen fraction ranging from 0 to 0.8) under different initial pressures (0.8 atm, 1.0 atm, 1.4 atm) in a 36 L spherical vessel. The study showed that increasing the initial pressure of the mixture or increasing the hydrogen concentration makes it more difficult to suppress the explosion. Wen et al. [12] studied the effect of ultrafine water mist on the hydrogen / methane / air mixture, found that under the conditions of the existence of ultrafine water mist flame speed and explosion overpressure have decreased significantly. And by the proportion of hydrogen increasing from 0 % to 60 %, the effect of explosion suppression has decreased.

Research about the inhibition of hydrogen / methane / air mixture explosions has mainly focused on inert gases, powders and fine water mist, relatively few studies on halogenated extinguishing agents. CF_3CHFCF_3 as a halogenated extinguishing agent, has attracted attention in the gas suppression research because of its high efficiency and fast extinguishing speed[13-16]. Andersson and Blomqvist [17] found that adding CF_3CHFCF_3 extinguishing agent to propane flames will produce HF and COF_2 compounds. Yang et al. [18] studied the comprehensive effects of different slit obstacles and CF_3CHFCF_3 on the characteristics of methane/air explosions. The results shows that low concentration of CF_3CHFCF_3 showed a promoting effect on flame propagation and pressure. After adding obstacles, the effect of 1 % CF_3CHFCF_3 on the flame propagation and pressure rise rate changes from promotion to suppression. Ji et al. [19] studied the inhibition effect of modified ABC powder driven by CF_3CHFCF_3 on methane explosion. The results showed that under the influence of CF_3CHFCF_3, the modified ABC powder will produce a kind of aerosol mist substance, the explosion suppression effect is improved. Dong et al. [20] found that CF_3CHFCF_3 inhibit the explosion of methane through the dilution of methane and oxygen concentration, absorption of heat and consumption of active radicals and other pathways. In addition, when the spray range of CF_3CHFCF_3 inhibition of 9.5 % methane / air premixed gas explosion propagation is 1.12, 1.72 and 2.32 m, the minimum spray volume is 360, 300 and 300 mL, respectively. Fan et al. [21] studied the effect of CF_3CHFCF_3 on the explosion of hydrogen / air, and found that CF_3CHFCF_3 can enhance the explosion at lean-fuel, but it shows an inhibitory effect at rich-fuel. Yang et al. [22] studied the coupling effects of CF_3CHFCF_3 and various obstacles on methane-air explosions. The results showed that increased the number of impediments increases the inhibitory effect of CF_3CHFCF_3. Obstructions that were staggered or symmetrical coupled to CF_3CHFCF_3 better than ipsilateral obstructions, and the explosion flame spread more slowly under staggered obstacle conditions than under symmetrical obstacle settings. Mi et al. [23] studied the effect of CF_3CHFCF_3 on the hydrogen-methane deflagration with 20 % H_2 addition at the equivalence ratios of 0.8, 1.0, and 1.2. The results showed that when CF_3CHFCF_3 was added to the hydrogen-methane-air mixture, the chain transfer reactions R333 (C_3F_7H=> CF_3 + CF_3CHF) and R343 (C_3F_7+O_2=>$C_3F_7O_2$) had a significant effect on inhibiting hydrogen-methane-air deflagration.

At present, some scholars have studied CF_3CHFCF_3 inhibition of single component gas explosion, but the CF_3CHFCF_3 inhibition of multi-component gas explosion research is rarely involved, which cannot guide practice. Our team has previously conducted experimental studies and kinetic simulations on explosion of hydrogen/methane/air mixtures with a hydrogen doping concentration of 20 %[23]. However, hydrogen concentration has a significantly different effect on the premixed explosion characteristics and the inhibitory effect[13,24-25]. Therefore, to further reveal the influence and mechanisms of CF_3CHFCF_3 on explosion, this paper analyses and discusses the effect of CF_3CHFCF_3 on the explosion of hydrogen/methane/air mixtures in the case of a hydrogen doping ratio (X_{H_2}=10 %), and demonstrates the effect of CF_3CHFCF_3 on the flame structure, flame propagation speed and explosion pressure. Numerical simulations were used to theoretically investigate the laminar flame speed, temperature and explosion products of the explosion of hydrogen/methane/air mixtures with the addition of CF_3CHFCF_3. This study is going to provide new ideas and methods for suppressing the explosion of gas mixtures, and a basis for proposing economical and efficient precautions against pipeline explosions.

2. Experimental and numerical methods

2.1.Experimental apparatus and procedures

Figure 1 shows the rectangular closed visualization experimental platform of CF_3CHFCF_3 in hydrogen / methane / air mixture explosion. The platform mainly consists of five subsystems: (1) the explosion experiment shock tube; (2) the gas distribution system; (3) the high-frequency pulse ignition system; (4) the high-speed camera acquisition system; (5) the high-frequency pressure acquisition system. The pipe material is acrylic, with high transparency, the length of the pipe is 1000 mm, the cross-sectional area of 100 mm × 100 mm. The gas distribution system consists of hydrogen cylinders, methane cylinders, CF_3CHFCF_3 cylinders, air compressors, gas mass flowmeter. Gas quality flowmeter is the American ALICAT 20 series standard mass flowmeter. The purity of the experimental gas was 99.99 %. The high-frequency pulse ignition system used a high-voltage electric spark to trigger the premixed gas explosion. The electric spark generator consisted of copper wire electrodes and a pulse DC generator. The diameter of the copper wire electrode was 0.1 mm, the distance between the electrodes was 2 mm, with a voltage of 6 V and an ignition energy of 490.87 mJ. The high-speed camera acquisition system was composed of a Phantom VEO 710L high-speed video camera and PCC 3.1 software on the PC, with an acquisition frequency of 4000 fps. The high-frequency pressure acquisition system consisted of a high-frequency pressure sensor and a pressure collector. The high-frequency pressure sensor is High frequencyICP ® pressure sensor, model 113B28, produced by PCB Piezotronics, USA. And the pressure collector is a Blast-PRO type impact tester manufactured by Chengdu Tytest Technology Co., Ltd. The pressure sensor is located at 87.5 cm from the ignition point and is fixed to the pipe wall and 1 mm below the plane of the inner wall surface to protect the sensor. The vent is located 94 cm to the left of the pipe and is covered with PVC film.

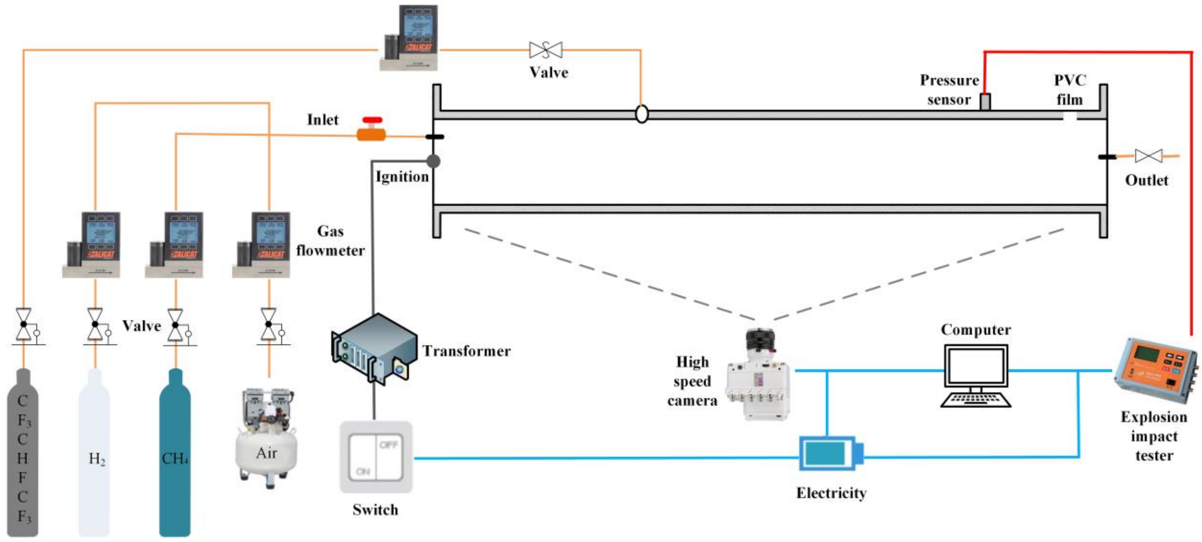


Fig 1. Schematic of the experimental apparatus

The effect of CF_3CHFCF_3 on hydrogen/methane/air mixtures with different equivalence ratios (Φ=0.8, 1 and 1.2) was experimentally investigated by selecting six volume fractions of CF_3CHFCF_3 ($X_{CF_3CHFCF_3}$): 0 %, 1 %, 2 %, 3 %, 4 % and 5 %, with a fixed fraction of 10 % for hydrogen. The equivalence ratio, Φ, is defined by equation (1), hydrogen fraction, X_{H_2}, is defined by equation (2), as follows[26]:

$$\Phi = \frac{(F/A)}{(F/A)_{stoichiometric}} \tag{1}$$

$$X_{H_2} = \frac{V_{H_2}}{V_{H_2}+V_{CH_4}} \tag{2}$$

where F/A is the volume ratio of fuel to air, $V_{H_2}$and V_{CH_4} are the volume fractions of H_2 and CH_4 in the fuel mixture. Similarly, $X_{CF_3CHFCF_3}$ is the volume fraction of CF_3CHFCF_3 in the fuel mixture.

To ensure that the residual gas in the pipe was expelled, the pipe was filled with four times the volume of the pipe with about 8 minutes for filling. When the filling was complete, CF_3CHFCF_3 was added to the pipe using a mass flow controller and the gas in the pipe was left to stand for 15 s to ensure the repeatability of the explosion experiment. The ignition device was then triggered to ignite the gas mixture. Each set of experiments was repeated at least three times to ensure the accuracy of the experimental results.

2.2. Numerical methods

Chemkin Pro was used to calculate the sensitivity coefficients of laminar flame speed and the mole fractions of the main substances. For the simulation, the initial temperature was set to 298 K, the initial atmospheric pressure was set to 1.0 atm, and the solution gradient and solution curvature were determined to be 0.01 [27]. The full chemical kinetic model used to simulate the concentration distribution in a CF_3CHFCF_3-doped hydrogen / methane / air explosion consists of 409 reactions and 104 substances. It consists of two sub-mechanisms: the GRI-Mech 3.0 for hydrogen and methane oxidation and the HFC mechanism [28,29,30].

3. Results and discussions

3.1. Explosion pressure

The pressure histories of hydrogen / methane / air mixture explosions (Φ = 1) under different CF_3CHFCF_3 concentrations (0 %, 1 %, 2 %, 3 %, and 4 %) are shown in Figure 2. Complete suppression is achieved at a CF_3CHFCF_3 concentration of 5 % (Φ = 1). According to Figure 2, the pressure history plots of premixed gases with and without CF_3CHFCF_3 show three pressure peaks. When the premixed gas is ignited without CF_3CHFCF_3, the combustion products expand rapidly and the explosion relief film is broken. Since the rate of explosion pressure rise at this point is greater than the rate of pressure relief, the explosion pressure continues to rise and reaches the first pressure peak. Combustion products and unreacted gas mixture from the explosion discharge from vent, the pressure in the pipeline dropped sharply. Because of the sudden change in pressure near the vent, fresh air is sucked into the pipeline again to promote the explosive reaction, and the pressure rose to the second peak. At this point, the flame rushed out of the pipe, and the pressure dropped sharply. It can be found that the pressure drop is more drastic at this point compared to the first pressure drop, which is due to the fact that the fuel in the pipe is consumed and more air and combustion products in the pipe are shucked as the flame rushes out of the pipe. The pressure wave generated by the previous explosion formed reflective wave after reaching the right side of the pipeline, and at the same time, due to the rapid exclusion of gas inside the pipe, resulting in repeated oscillations of the pressure wave with the formation of negative pressure zone in the pipeline, the pressure rises to the third peak. It can be seen that the third peak pressure is larger than the second peak pressure, which is presumed to be the interaction between the pressure wave and the inner wall of the pipe, resulting in more complex propagation characteristics of the shock wave.

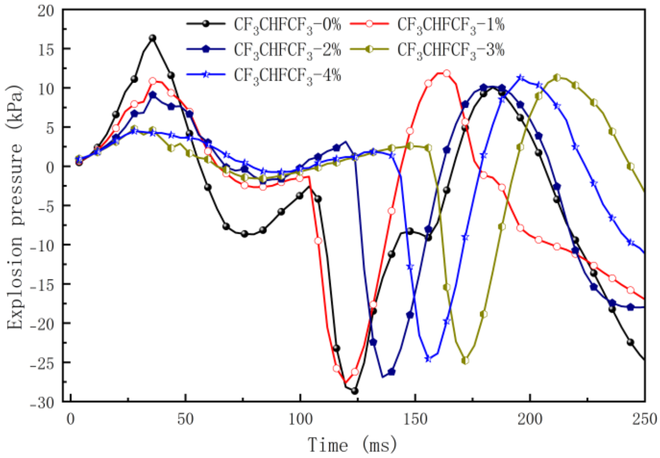


Fig 2. Pressure history of hydrogen/methane/air mixture explosion (Φ = 1) under different CF_3CHFCF_3 concentrations (0 %, 1 %, 2 %, 3 %, and 4 %)

After the addition of CF_3CHFCF_3, the premixed gas is ignited, the explosion pressure rises to the first peak, and the explosion pressure is significantly lower than the situation when the CF_3CHFCF_3 was not added. As the flame continues to develop into the suppression zone, the explosion pressure decreases. The disturbance of the gas flow in the unignited zone by the settling of CF_3CHFCF_3, and the generation of fuel-like substances by thermal decomposition of CF_3CHFCF_3, the explosion pressure rises to the second peak. As the flame propagates to the explosion vent, it carries the products of combustion and the unreacted gas mixture out of the pipeline, resulting in a rapid decrease in explosion pressure. The flame propagation velocity near the upper wall of the pipe gradually increases due to the influence of the vent. The result is velocity differences at the flame front, leading to Kelvin-Helmholtz instability and turbulence. The high-temperature, low-density combustion products and the low-temperature, high-density CF_3CHFCF_3 inside the pipe are affected by the fresh air flow involved from the vent, which strengthens the Rayleigh-Taylor instability and creates a vortex in the middle of the pipe. At this time, the vortex in the pipe intensified combustion, causing a rapid pressure rise to the third peak.

In order to evaluate the inhibition effect of CF_3CHFCF_3 on the explosion of hydrogen/methane/air mixtures ($\Phi = 1$), the maximum explosion pressure P_{max}, the pressure peak occurrence time t_{max}, and the maximum pressure rise rate $(dP/dt)_{max}$ were selected as the measures. Figure 3 shows the changes of P_{max}, t_{max} and $(dP/dt)_{max}$ with the increase of CF_3CHFCF_3 concentration. It can be seen that P_{max} shows a decreasing trend with increasing CF_3CHFCF_3 concentration. When the concentration of CF_3CHFCF_3 was 4 %, the P_{max} decreased the most compared to the unadded one, by 73.3 %. This is because the addition of CF_3CHFCF_3 has a diluting and heat-absorbing effect on the mixture[31,32]. On the other hand, when hydrogen/methane/air mixtures explode, CF_3CHFCF_3 thermally decomposes to produce fluorine-containing radicals such as CF_3 and CF_2. Fluorine-containing radicals consume a large number of key radicals in the chain reaction related to the explosion of the mixture (H-, O- and OH-, etc.). By consuming radicals, the explosion reaction chain is interrupted, so that the effect of effective explosion suppression is achieved[18,19]. t_{max} with the increase in the concentration of CF_3CHFCF_3 shows a decreasing trend. This indicates that the addition of CF_3CHFCF_3 has not only an inhibitory effect on the burning of the gas mixture, but also a facilitation effect. Because CF_3CHFCF_3 in the pyrolysis process will produce fuel-like substances and cyclic compounds, and thus promote the explosion of hydrogen / methane / air mixture[33]. When the concentration of CF_3CHFCF_3 is 1 %, $(dP/dt)_{max}$ decreases by 33.5 %. And with the increase of CF_3CHFCF_3 concentration, $(dP/dt)_{max}$ showed the same decreasing trend with P_{max}. $(dP/dt)_{max}$ and P_{max} are used as an important parameter for evaluating the explosion intensity, which means that the explosion hazard of the gas mixture decreases. In addition, the gas mixture did not ignite at a concentration of 5 % CF_3CHFCF_3, indicating the existence of a complete inhibition threshold for CF_3CHFCF_3.

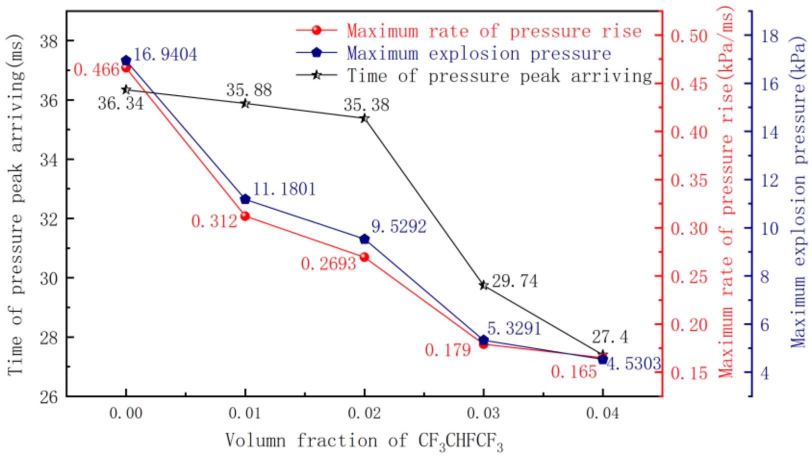


Fig 3. P_{max}、t_{max} and $(dP/dt)_{max}$ of hydrogen/methane/air mixture explosion (Φ = 1) under different CF_3CHFCF_3 concentrations (0 %, 1 %, 2 %, 3 %, and 4 %)

Table 1 shows the variation of P_{max}, t_{max}, and $(dP/dt)_{max}$ for hydrogen/methane/air mixture explosions (Φ = 0.8, 1, and 1.2) with the increase of CF_3CHFCF_3 concentration. It can be seen that both P_{max} and $(dP/dt)_{max}$ decreased significantly with the addition of CF_3CHFCF_3. This suggests that CF_3CHFCF_3 showed inhibition of hydrogen/methane/air mixture explosion at lean-fuel, equivalence ratio and rich-fuel. Meanwhile, it is known that the decrease of maximum pressure is 59.61 %, 73.26 % and 56.68 % when the equivalence ratios is 0.8, 1 and 1.2, respectively. This indicates that CF_3CHFCF_3 is more effective in suppressing the explosion of mixtures with an equivalence ratios of 1. Interestingly, the trend of t_{max} increases and then decreases with the increase of CF_3CHFCF_3 concentration (Φ = 0.8, 1.2), and it is speculated that with the increase of CF_3CHFCF_3 concentration, the production of fuel-like substances and cyclic compounds increases as well, thus showing a certain contribution. In addition, when the CF_3CHFCF_3 concentration was 3 % and 5 %, the hydrogen/methane/air mixtures with equivalence ratios of 1.2 and 1.0, respectively, could not be ignited, and the explosions were completely suppressed.

3.2. Flame structures

Figure 4 shows the effect of different volume fractions of CF_3CHFCF_3 on the structure of the hydrogen/methane/air mixture explosion flame under the condition of Φ = 1. At uninhibited condition, the hydrogen / methane / air gas mixture explosion flame shows four typical stages: "spherical", "finger ", "flat", "Tulip" flame stage[34]. With the addition of CF_3CHFCF_3, the appearance of spherical and finger flames was significantly delayed. At the same time, the flame propagation process was destroyed, and the flat flame and tulip flame disappeared. When the concentration of CF_3CHFCF_3 is 2 %, compared with the flame without the addition of CF_3CHFCF_3, the emergence time of the spherical flame and finger flame increased by 23 ms and 27 ms, respectively. Due to the large molecular mass of CF_3CHFCF_3, it sprayed into the pipeline after the rapid settlement to the bottom, resulting in the emergence of the "horn-like" non-combustible zone with the flame passing through the suppression zone[23]. After passing the explosion suppression zone, the flame appeared obvious wrinkles, which is due to the influence of thermal diffusion instability, the flame front propagated against the upper wall of the tube. And the flame front is affected by the boundary layer stretching, the flame instability increases. When the flame spreads to the right end of the pipe, the pressure wave effect is amplified in the later stage of flame burning, which enhances the Rayleigh-Taylor instability[27]. It is noteworthy that a yellow patchy flame appeared in the flame. This is mainly due to the pyrolysis of CF_3CHFCF_3 to produce polymers, which generates a combustion reaction with the gas mixture to form a yellow flame[20]. When the concentration of CF_3CHFCF_3 increased to 4 %, the flame profile became blurred because the addition of CF_3CHFCF_3 diluted the oxygen volume fraction in the combustion zone and the reaction rate in the combustion zone decreased. At the same time, the time required for the flame to propagate to the same position was significantly longer, especially the time required for the flame to propagate to the right end of the pipe was extended by 92 ms. As the concentration of CF_3CHFCF_3 increased, the amount of polymer produced by pyrolysis increased, forming a large yellow flame. In particular, the addition of CF_3CHFCF_3 changed the flame color from blue to purple. It is possible that the addition of CF_3CHFCF_3 promotes the involvement of nitrogen in the explosion of hydrogen/methane/air mixtures, which in turn causes a change in flame color by the spectrum of CN radicals during the reaction[35].

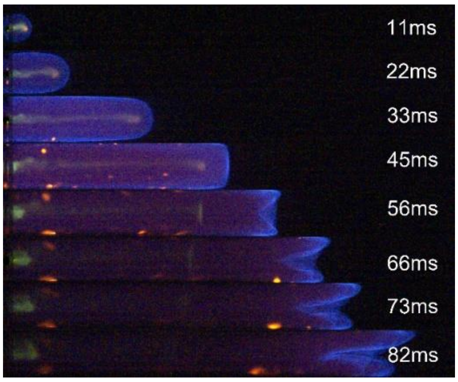
Table 1. P_{max}、t_{max} and $(dP/dt)_{max}$ of hydrogen/methane/air mixture explosion (Φ = 0.8, 1, and 1.2) under different CF_3CHFCF_3 volume concentrations (0 %, 1 %, 2 %, 3 %, 4 % and 5 %)

Φ=0.8	CF_3CHFCF_3 (%)	0	1	2	3	4	5
	P_{max} (kPa)	12.2837	8.4201	6.7921	5.5395	4.9615	7.1185
	t_{max} (ms)	43.64	45.42	44.14	39.18	37.3	41.72
	$(dP/dt)_{max}$	0.2815	0.1854	0.1539	0.1414	0.133	0.1706
Φ=1.0	CF_3CHFCF_3 (%)	0	1	2	3	4	
	P_{max} (kPa)	16.94	11.18	9.52	5.32	4.53	
	t_{max} (ms)	36.34	35.88	35.38	29.74	27.4	
	$(dP/dt)_{max}$	0.466	0.312	0.269	0.179	0.165	
Φ=1.2	CF_3CHFCF_3 (%)	0	1	2			
	P_{max} (kPa)	18.5217	13.3494	8.0229			
	t_{max} (ms)	38.9	39.64	34.7			
	$(dP/dt)_{max}$	0.4791	0.3368	0.2312			

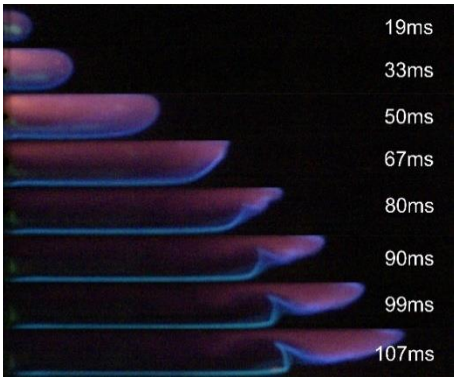
3.3. Flame propagation velocity

Figure 5 shows the effect of CF_3CHFCF_3 concentration on flame propagation velocity (Φ = 1). No addition of CF_3CHFCF_3, the early stage of the explosion flame propagation speed increases rapidly, after reaching the maximum flame propagation velocity (V_{max} = 19.74 m / s) the flame propagation velocity decreases. When the flame reaches the explosion vent, due to the traction of the gas flow at explosion vent and the involvement of fresh air to trigger the second explosion, the flame propagation speed increased. When the flame passes through the explosion vent, the flame propagation velocity decreases sharply. When the CF_3CHFCF_3 concentration is 1 %, 2 %, 3 %, V_{max} is 11.99, 11.4, 9.53 m / s, respectively, which shows the values are lower than the case of no added CF_3CHFCF_3, and V_{max} and CF_3CHFCF_3 concentration is negatively correlated. When the concentration of CF_3CHFCF_3

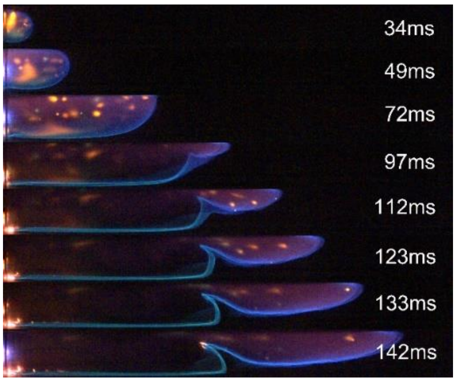
is 4 %, V_{max} is 14.81 m/s, and have risen compared with other concentrations, but still lower than that of V_{max} without adding CF_3CHFCF_3. At this time, the flame in the yellow bright spot is more obvious, and the fuel-like substances generated from CF_3CHFCF_3 pyrolysis promote the flame combustion, so that the flame propagation velocity can not be further reduced. When Φ = 0.8, 1.2, similar observations were made about the effect on the explosion. These results indicate that CF_3CHFCF_3 can reduce the flame propagation velocity. This finding also suggests that CF_3CHFCF_3 can effectively slow down the reaction rate of hydrogen/methane/air mixture explosion.



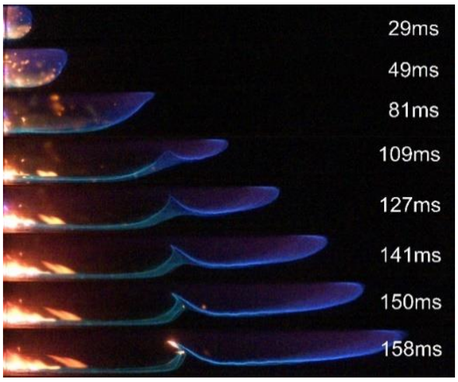
(a) 0 % CF_3CHFCF_3



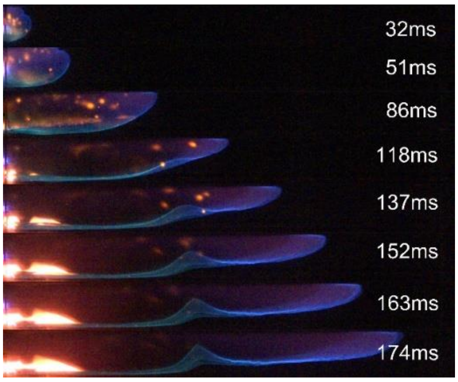
(b) 1 % CF_3CHFCF_3



(c) 2 % CF_3CHFCF_3



(d) 3 % CF_3CHFCF_3



(e) 4 % CF_3CHFCF_3

Fig 4. Flame structures of hydrogen/methane/air mixture explosion (Φ = 1) under different CF3CHFCF3 concentrations (0 %, 1 %, 2 %, 3 %, and 4 %)

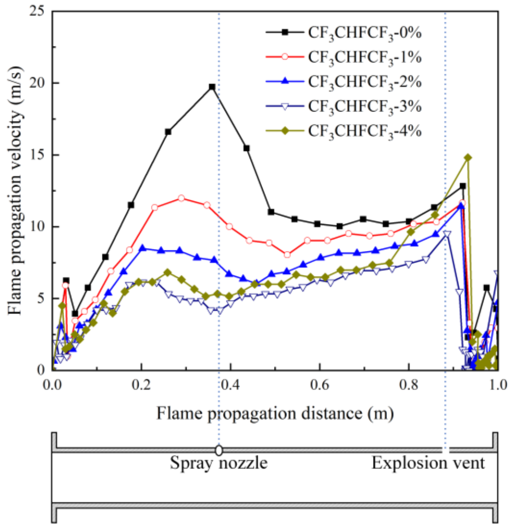
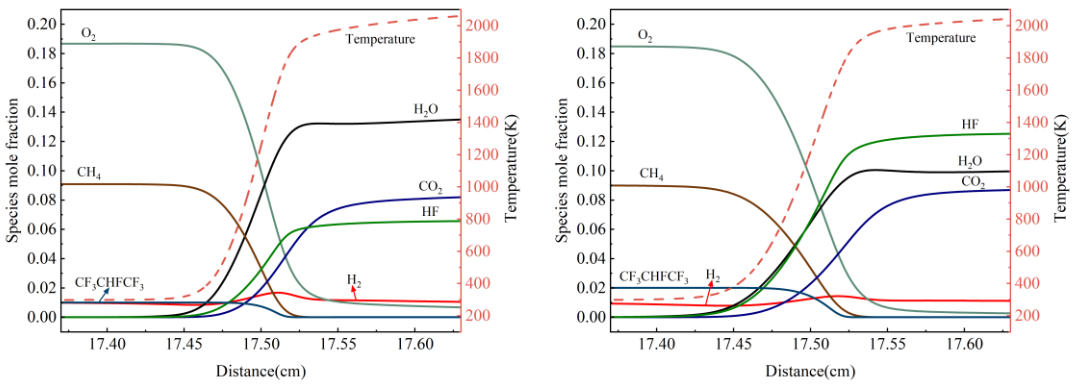


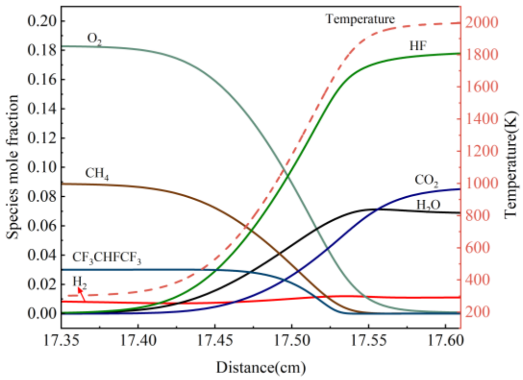
Fig 5. Flame propagation velocity of hydrogen/methane/air mixture explosion (Φ = 1) under different CF_3CHFCF_3 concentrations (0 %, 1 %, 2 %, 3 %, and 4 %).

3.4. Calculated mole fractions of the major species

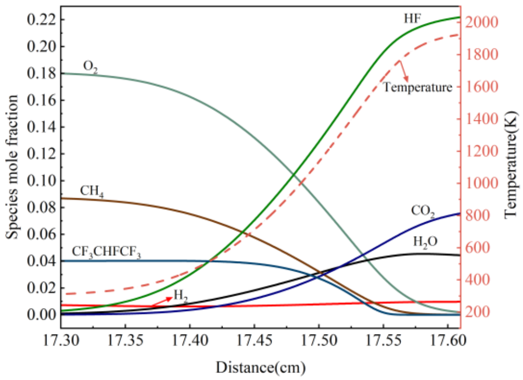
Figure 6 presents the calculated mole fractions of the major species as a function of distance at Φ=1.0 in flames with 1 % to 4 % concentration of CF_3CHFCF_3. In the flame with inhibitor added, CF_3CHFCF_3 decreases rapidly in the reaction zone and is eventually consumed. The mole fractions of oxygen and methane decrease rapidly as they pass through the reaction zone, and the mole fractions of the products H_2O, HF, and CO_2 increase rapidly, while the mole fraction of H_2 peaks during the course of the reaction and ends up larger than the initial value. With the increase of CF_3CHFCF_3 concentration, the equilibrium mole fraction of product H_2O decreased, the equilibrium mole fractions of HF and CF_2O increased, while the equilibrium mole fraction of CO_2 showed a trend of increasing and then decreasing. Although the increase in CF_3CHFCF_3 concentration resulted in a decreasing trend in temperature, the effect was small. This indicates that the inhibition effect of CF_3CHFCF_3 on the explosion is mainly reflected in the chemical kinetics.



(a) 1 % CF_3CHFCF_3 (b) 2 % CF_3CHFCF_3



(c) 3 % CF_3CHFCF_3



(d) 4 % CF_3CHFCF_3

Fig 6. The calculated mole fractions of the major species of hydrogen/methane/air mixture explosion (Φ = 1) under different CF_3CHFCF_3 concentrations (1 %, 2 %, 3 %, and 4 %)

3.5. Sensitivity analysis

To better analyze the effect of CF_3CHFCF_3 on the explosion flame, the sensitivity coefficients of the significant reactions that have a major effect on the laminar flame speed were obtained. The promotive or suppressive effect of a reaction is expressed through a positive or negative coefficient. As shown in Figure 7, the reaction H + O_2 <=> O + OH is the most sensitive to the laminar flame speed with a positively sensitive coefficient. This sensitivity coefficient decreases with the increase of CF_3CHFCF_3 concentration. When the equivalence ratio was 0.8, the addition of a certain concentration of CF_3CHFCF_3, the reaction CF_3CHF + O <=> CF_3 + CHFO, CF_2O + H <=> CFO + HF and CF_3 + H <=> CH_2 + HF presents inhibition on the explosion, reducing the laminar flame speed of the explosion flame. Meanwhile, the reaction H + HO_2 <=> O_2 + H_2 with negatively sensitive coefficients disappeared directly after the addition of CF_3CHFCF_3. The equivalence ratio was 0.8 and 1, the reaction H + CH_3 (+M) <=> CH_4 (+M) showed a decreasing inhibition of the laminar flame speed as the concentration of CF_3CHFCF_3 increased. However, when the equivalence ratio was 1.2, the addition of CF_3CHFCF_3 increased the negatively sensitive coefficients of the reaction H + CH_3 (+M) <=> CH_4 (+M), which enhanced the inhibition of laminar flame speed. The reaction CH_3+CF_3 <=> CH_2CF_2+HF plays an important role in suppressing explosions with equivalence ratios of 0.8 and 1 at CF_3CHFCF_3 concentrations greater than 3 %. When the equivalence ratios is 0.8, 1 and 1.2, the sensitivity coefficients of the positively sensitive reactions O + CH_3 => H + H_2 + CO and HCO + H_2O <=> H + CO + H_2O were decreased after the addition of CF_3CHFCF_3. It is noteworthy that some fluorination reactions show positively sensitive coefficients, which enhance the laminar flame speed, such as the reaction CF + O_2 <=> CFO + O.

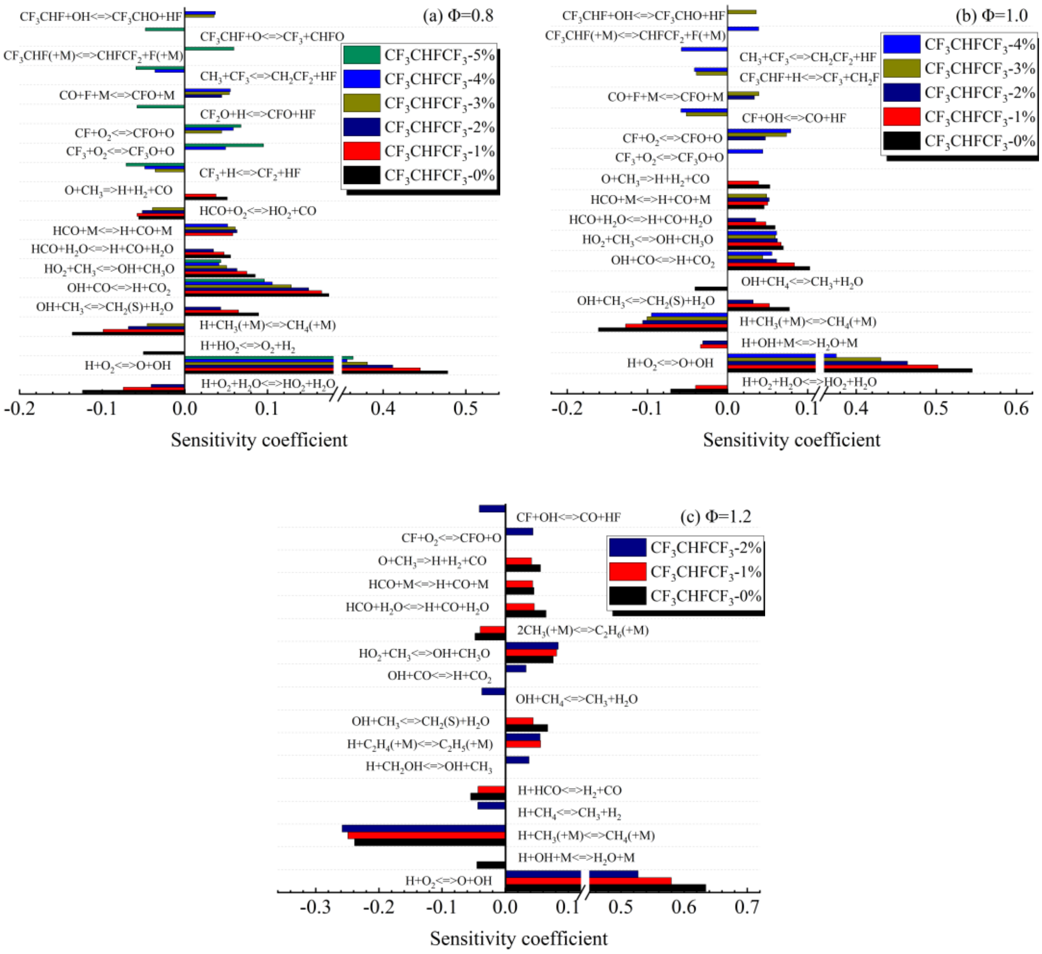


Fig 7. Sensitivity coefficients of significant reactions on laminar flame speed of hydrogen / methane / air gas mixture explosion (Φ = 0.8, 1, 1.2) under different CF_3CHFCF_3 concentrations (0 %, 1 %, 2 %, 3 %, and 4 %)

4. Conclusions

In this study, the effect of CF_3CHFCF_3 on the explosion of hydrogen/methane/air mixtures (Φ=0.8, 1, 1.2 and X_{H_2}=10 %) was investigated using experiments and simulations, and the main conclusions are as follows:

By comparing the explosion pressures before and after the addition of CF_3CHFCF_3, it can be found that the CF_3CHFCF_3 significantly suppressed the mixture explosion. With the increase of CF_3CHFCF_3 concentration, $(dP/dt)_{max}$ and P_{max} showed the same decreasing trend, which further weakened the explosion reaction. The effect of CF_3CHFCF_3 on t_{max} changed from suppression to increase when the CF_3CHFCF_3 concentration was 2 % (Φ = 1.2), and the same change was observed when the CF_3CHFCF_3 concentration was 3 % (Φ = 0.8). The explosion is suppressed completely for hydrogen/methane/air mixture (Φ = 1) at CF_3CHFCF_3 concentrations above 4 % and for hydrogen/methane/air mixture (Φ = 1.2) at CF_3CHFCF_3 concentrations above 2 %.

Under Φ = 1, CF_3CHFCF_3 showed significant suppression of flame propagation structure and flame propagation velocity. Spherical and finger-shaped flames appeared time was delayed, and flat and tulip flames disappeared. Due to the addition of CF_3CHFCF_3, the flame propagation became unstable and “horn-like” non-combustible zones appeared. The maximum flame propagation velocity all decreased when add the CF_3CHFCF_3. In the case of CF_3CHFCF_3 concentration of 3 %, the maximum flame propagation speed of the explosion of hydrogen/methane/air mixture (Φ = 1) decreased by 51.7 %.

The addition of CF_3CHFCF_3 caused the decreasing of temperature, but the effect was small. This indicates that chemical kinetics play a dominant role in the suppression of the explosion. Under different equivalence ratios, CF_3CHFCF_3 showed opposite effects on the reaction H + CH_3 (+M) <=> CH_4(+M). And the fluorine-containing substances have not only suppression effects on the laminar flame speed, but also increase effects. The sensitivity coefficients of the reactions such as CF_3CHF+OH <=> CF_3CHO+HF are positive at specific concentrations, which enhances the laminar flame speed.

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