Study of the Suppression Mechanisms of Heptafluoropropane and Carbon Dioxide Mixtures on Hydrogen-air Explosions

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1 Introduction

Hydrogen energy is widely regarded as a promising clean and renewable energy source, while it presents a higher explosive hazard than conventional hydrocarbons due to its low ignition energy, wide flammability range, and high combustion rate. Currently, the focus of explosion suppression for hydrogen mixtures is on inert gases, fine water mist and powder. There is a growing interest in researching more economical, efficient, and environmentally friendly hydrogen explosion suppressants.

Heptafluoropropane (CF3CHFCF3) as a new environmentally friendly halon substitute with low ozone depletion potential, low global warming potential, low toxicity and good dispersibility, is widely used in the field of hydrocarbon fuel flare suppression [1]. The increase in the lower flammability limit of hydrogen combustion with C3F7H is significantly higher than with N2 and CO2. However, the critical inhibition concentration under lean conditions was found to be N2>CO2>C3F7H. The study on the inhibitory effects of CF3CHFCF3 on hydrogen explosions at different equivalence ratios showed that low concentrations of CF3CHFCF3 enhanced the explosion of lean hydrogen-air mixtures (Φ =0.8 and 1.0) but inhibited the explosion of rich mixtures (Φ =1.3 and 1.6).

Previous research has shown that CF3CHFCF3 has excellent suppression performance but also pointed out the potential risk of increased explosion overpressure and pressure rise rate due to its exothermic reaction process [5–7]. Some studies have shown that mixing CF3CHFCF3 with inert gases can enhance the inhibition on methane-air mixture, effectively reducing the explosion reaction rate and improving suppression effects. However, the study on the impact of CF3CHFCF3 and inert gas mixtures on hydrogen explosions is very limited. This study investigates the suppression effects of various concentration combinations of CF3CHFCF3 (0 - 6%) and CO2 (0 - 20%) on the stoichiometric hydrogen-air mixture through experiments and simulations. The analysis of the hydrogen combustion and explosion process consider both flame propagation characteristics and explosion intensity. Theoretical studies based on CHEMKIN-PRO are conducted to understand the impact of using CF3CHFCF3 and CO2 mixture suppressants on flame structure and laminar burning velocity of

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premixed gas flames.

2 Experimental setup

Figure 1 shows the schematic of the experimental setup. The experiment utilized a stainless-steel rectangular duct measuring 140x140x1000mm. The duct featured three evenly distributed circular observation windows, each with a diameter of 110mm, located on the side of the duct. The distance between the windows was 360mm. The ignition electrode is positioned at the center window on the left-hand side. The electrodes were triggered using an ignition control module (HY180). Ignition was initiated by a 50ms duration electric spark between the platinum electrodes. The flame propagation process was captured on a monochrome high-speed camera (Revealer X213) equipped with a Zeiss 35mm/F2.0 prime lens. The camera was set to record at a rate of 8000 frames per second (fps). The exposure was kept constant throughout the experiments for flame brightness analysis. The pressure-time curve was obtained by a high frequency pressure sensor located in the center of the rectangular pipe (ZXP660, range: 0 - 2MPa). The sampling rate of the pressure transducer was 5kHz.

All experiments in this work were carried out at ambient temperature and pressure. The Dalton partial pressure method was used to configure the gas mixture. Before conducting each experiment, the vacuum pump was used to evacuate the explosion duct. Specified volume fractions of H2 (stoichiometric H2/air ratio), CF3CHFCF3 (0 - 6%) and CO2 (0 - 20%) suppressants were sequentially added using fine-adjustable valves, followed by filling air to the ambient pressure (Fig. 1).

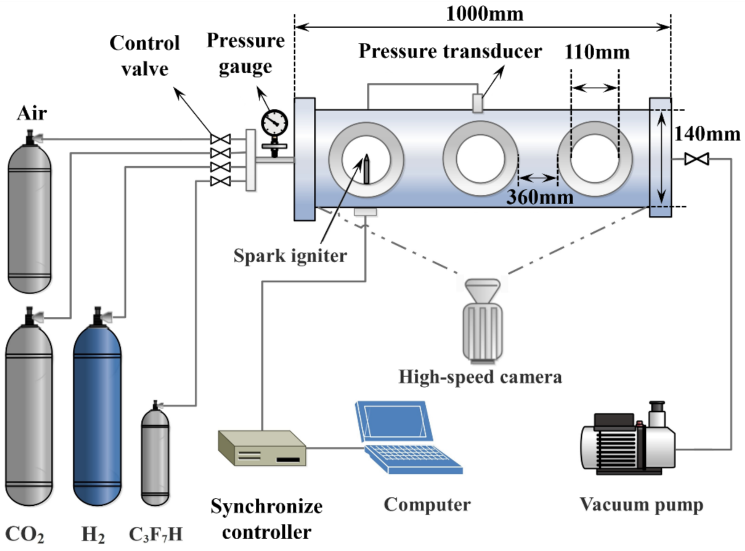

Fig. 1. *Schematic of the experimental setup.*

3 Results and discussion

3.1 Flame structure

Figure 2 shows the flame evolution of the H2-air premixed flame propagating through the three observation windows (Fig. 1) under different concentrations of suppressant mixtures. In all cases, the first two observation windows are observed in the flame structure from "spherical" to "finger-shaped" process, which matches with works by (Xiao et al., 2012). Increasing the concentration of suppressants slows down the spherical and finger-shaped flames, reducing their brightness. The time for the flame to reach the center of the observation window was 7.3ms for the baseline, and that was extended to 33.1, 13.1 and 98.8ms by using 4% CF3CHFCF3, 10% CO2 and 4% CF3CHFCF3-10% CO2 mixtures respectively.

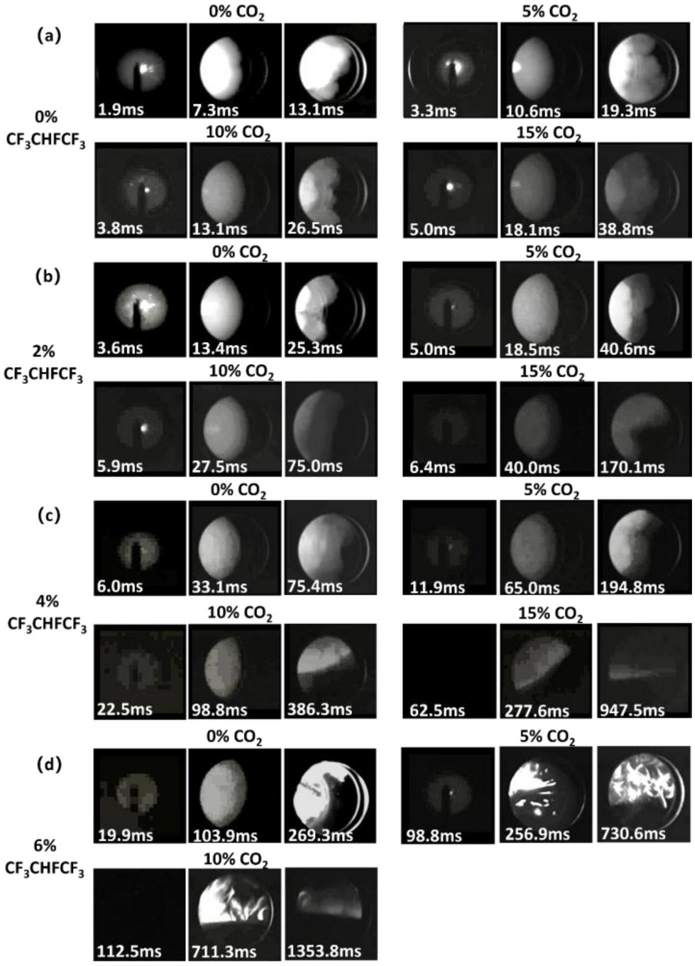

Fig. 2. Flame Snapshots in three observation windows with CF3CHFCF3 and CO2 concentrations varying from 0-6% and 0-15%. (a) 0% CF3CHFCF3. (b) 2% CF3CHFCF3. (c) 4% CF3CHFCF3. (d) 6% CF3CHFCF3.

3.2 Pressure

Figure 3 shows the pressure curves of the suppression of CF3CHFCF3 and the mixture of CF3CHFCF3-CO2. A pressure curve with three steps was observed as the concentration of CF3CHFCF3 increased. The first was a steep pressure rise due to the H2 reaction, followed by a decrease in pressure rise, and then acceleration again. This phenomenon is caused by the reaction of the fluorinated suppressants and their intermediates, which can decrease the overall chemical reaction rate and the laminar burning velocity [10]. Furthermore, during the thermal decomposition of CF3CHFCF3, which produces hydrofluorocarbon intermediates, as well as CO, CO2, HF, and H2O, there is a volume expansion that can lead to the maximum explosion overpressure being reached [11]. Meanwhile, as the hydrogen flame propagates to the end of the enclosed duct, the interaction of the flame with the compression and shock waves caused the pressure rise, when the flame propagation shows a periodic acceleration and deceleration propagation phenomenon in the later stages [12].

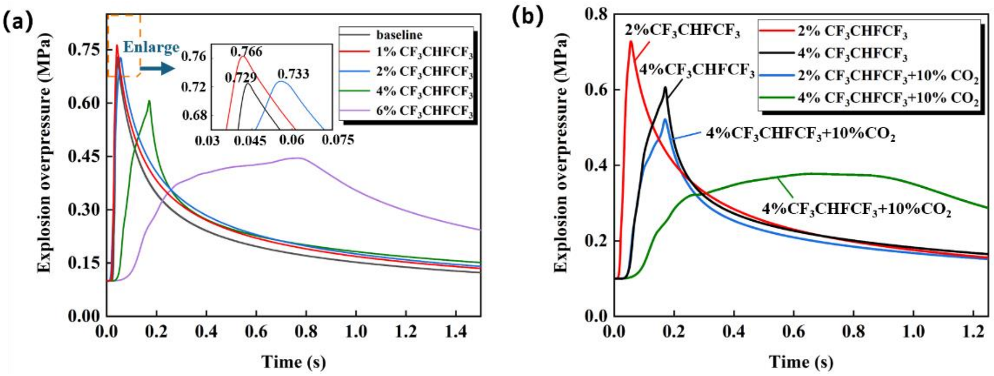

Fig. 3. Pressure comparisons of CF3CHFCF3 and the mixture of CF3CHFCF3-CO2. (a) Baseline case with 1, 2, 4, and 6% CF3CHFCF3. (b) 2, 4% CF3CHFCF3 with 10% CO2.

3.3 Burning velocity and suppression mechanisms

The spherical flame propagation method is used to calculate the experimental laminar burning velocity for flames in the pre-pressure stage of combustion [13]. The laminar burning velocity is approximated by the following expression,

$$\boldsymbol{S_L = \frac{\rho_b dR}{\rho_u dt},} \tag{1}$$

Figure 5 shows the effects of CF3CHFCF3 and CO2 on the laminar burning velocity. For 0% CF3CHFCF3 cases, the laminar burning velocity decreased linearly with the CO2 concentration. For CF3CHFCF3-CO2 cases, the decrease in laminar burning velocity decreases with increasing CO2 concentration when the CF3CHFCF3 concentration is fixed, and this trend becomes more evident at higher CF3CHFCF3 concentrations. Great agreements were achieved between the results predicted by this model and the experimental measurements with $\boldsymbol{R^2}$ of 0.98 (Fig. 5).

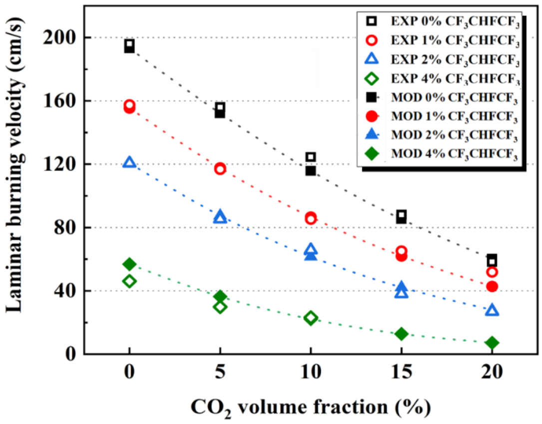

Fig. 5. *Effects of CF$_3$CHFCF$_3$ and CO$_2$ on the laminar burning velocity*

Figure 6 shows the sensitivity coefficients of the primary elementary reactions for the laminar burning velocity with a mixture of 10% CO2 and 0, 2, 4, 6% CF3CHFCF3. Positive and negative coefficients represent enhancement and inhibition of the laminar burning velocity. When 2% CF3CHFCF3 is used, the chemical conversion of CO2 is increased thereby facilitating the reaction. In CF3CHFCF3-CO2 mixture cases, the sensitivity coefficient becomes ineligible, which means the unwanted reaction enhancement by CF3CHFCF3 ¬is effectively seized by the addition of CO2. On the other hand, CO2 absorbs the heat released by the combustion thus reducing the system temperature and performs as a dilutant that reduces the collision probability of the reactant molecules. Moreover, CO2 undergoes ternary collision reactions (e.g. R9, R12) with high energy radicals such as H, OH, turning active radicals into stabilized molecules, by which the reaction rate decreases.

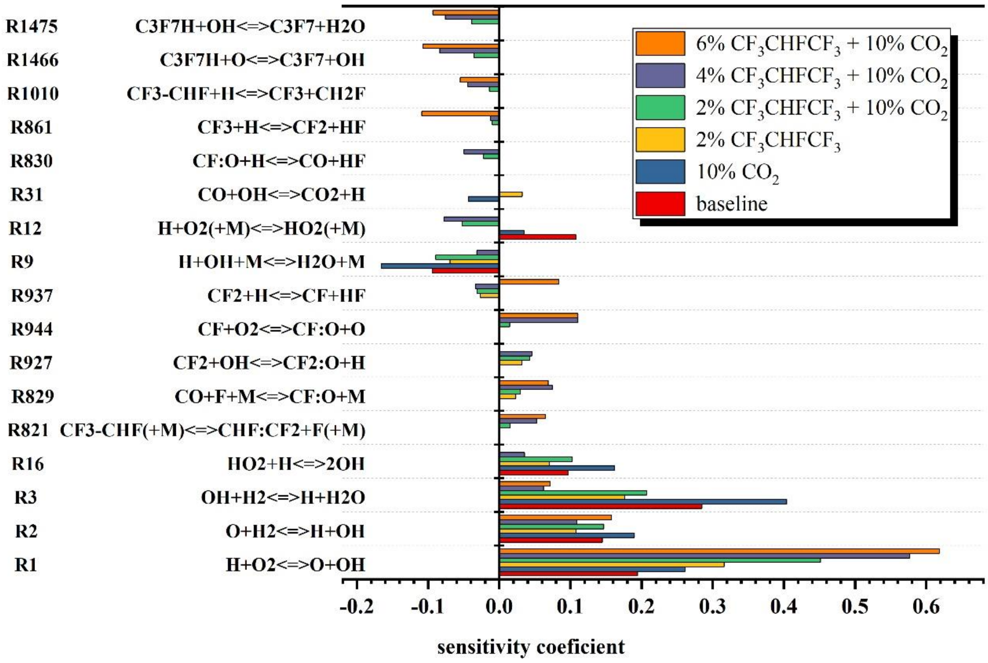

Fig. 6. *Effects of CF_3CHFCF_3 and CO_2 on sensitivity coefficient of hydrogen-air mixtures.*

Conclusion

This paper studies the effects of CF3CHFCF3 and CO2 mixtures in varying concentrations on the H2-air explosion at the equivalence ratio and investigates the relating chemical kinetic mechanisms. The gas mixture presents noticeable suppression performance reducing the explosion pressure and the flame propagation speed. The additional CO2 mixed with low concentration CF3CHFCF3 ($< 4\%$) counteracted the exotherm reaction of CF3CHFCF3, achieving the decrease of P_{max} and $(dP/dt)_{max}$ up to 48.4% and 93.72% respectively compared to the baseline. A mixture of 6% CF3CHFCF3-15% CO2 reached the quench limit of premixed gases at stoichiometric ratio. Furthermore, CF3CHFCF3-CO2 mixture was found to present both physical and chemical suppression effects on H2-air explosion, mainly because of CF3CHFCF3 consuming reactive radicals, cutting off the hydrogen-oxygen chain reactions. The concentration of CF3CHFCF3 has a significant effect on the reaction rate when combined suppressants are used. Dehydrogenation of CF3CHFCF3 (R1466, R1475) and defluorination of CF3 become more important to reduce the combustion rate at higher CF3CHFCF3 concentrations. In low CF3CHFCF3 concentrations, the mixing of CO2 effectively reduces the sensitivity coefficient of R31. In addition, it enhances the heat absorption and dilution effects, and acts as a third body in the chain reaction (R9, R12), suppressing the reaction rate and thus reducing the explosion intensity.

Acknowledgements

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