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Study on the Synergistic Effect of Multicomponent Gas Mixture on the Dynamic Characteristics of Gas Explosion

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With the development of industry and technology, multi-element gases coexist in many places. The study of the influence of appropriate concentration of flammable gas on the chemical kinetic characteristics of methane-air explosion is great significance for preventing and controlling gas explosions. An experimental system was set up to carry out different concentrations of $C_3H_8/H_2/CH_4$/air premixed gas explosion. The effects of multiple gases on the methane explosion characteristic parameters were studied. It is shown that the pressure peak firstly increases and then decreases with the increase of propane concentration when the C_3H_8/CH_4/air mixture gas explosion experiment is carried out. The explosion of propane/methane/air mixture is most significant when the propane concentration is 0.4%. The experiment of H_2/CH_4/air mixed gas explosion was carried out. With the increase of H_2 concentration, the pressure peak increased gradually. In the experiment of $C_3H_8/H_2/CH_4$/air mixed gas explosion, the peak pressure firstly increases and then decreases with the increase of propane concentration. $C_3H_8/H_2/CH_4$/air mixture gas explosion is most significant when the concentration of C_3H_8 is 0.2% and the concentration of H_2 is 1%. The elementary reactions process were numerical simulated by CHEMKIN-PRO software. The micro-mechanism of multi-element gas explosions based on key radicals, sensitivity and reactions paths. Reaction step R38: $H+O_2$<=>O+OH and R53: $H+CH_4$<=>CH_3+H_2 to affect the explosion process. 0.1%C_3H_8+1%H_2 and 0.2%C_3H_8+1%H_2 will accelerate the CH_4/air premixed gas explosion reaction rate, 0.3%C_3H_8+1%H_2 will inhibit the methane/air premixed gas explosion reaction rate. It is mainly because R312 elementary reaction at this concentration: $CH_3+C_2H_5$(+M)<=>C_3H_8(+M) dominates the explosion, inhibiting R38 elementary reaction: $H+O_2$<=>O+OH, reducing OH the amount of production, thereby inhibiting the explosion process. The research results have important practical value for preventing and controlling multi-element gas explosion accidents and reducing accident losses.

1. Introduction

With the rapid development of science and technology, complex multi-element gases are widely present in industries such as coal mines, petrochemicals, metallurgy and pharmaceuticals, underground spaces and laboratories. The multi-element gas in coal mines and underground spaces is mainly methane, and contains other elements. Studying the influence of the appropriate concentration of combustible gas on the chemical kinetic characteristics of methane-air explosion and analyzing the laws of multi-element gas explosion are of great significance to the prevention and control of gas explosions. Scholars' research on multi-systems is mainly divided into three aspects: the mixture of methane and dust, methane and combustible gas, and methane and inert gas. (Pinaeva et al., 2020) proved that in the hybrid systems studied, coal combustion competes with methane combustion, but methane is chemically more active than coal. Methane, rather than coal carbon has a decisive influence on the parameters of combustion and detonation waves. (Li et al., 2012) found with appropriate hydrogen and methane ratio, the lower explosion limits of the mixtures are even smaller than that of each component gases. (Wang et al., 2021) reported montmorillonite powders inhibitors generated NH_4, ·NCO, and ·OH which can interrupt explosion chain reactions to suppress methane explosion. (Wang et al., 2020) studied CO may increase the collision frequency and make the chain initiation reaction of $CH_4/CO/C_2H_6/H_2$/air mixtures easier than CH_4/air mixtures. (Liang et al., 2019) analysed the nonlinear effect shows that HO_2 recombination is important at high H_2 conditions, while the interaction of HO_2 and CH_3

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dominates when the H_2 concentration in the fuel mixture is relatively low. (Luo et al., 2019) proposed the key radicals OH and CH_2O show a high degree of correlation, with CH_2O being more susceptible to oxygen content than OH during the reaction process. (Tan et al., 2020) the addition of $CH_4/CO_2/O_2$ significantly decreased the minimum ignition temperature of dust, and the minimum ignition temperature of hybrid mixture was inversely proportional to the increase of gas mole fraction. (Chang et al., 2020) measured the effect of CO_2 dilution dominating the explosion behavior becomes more apparent than N_2 dilution. (Zhao et al., 2020) pointed out the inhibition effect of CO_2 was found to be stronger than N_2 due to its higher specific heat, but the addition of 1.14% CH_4 can offset the inhibition effect of CO_2 somehow. (Wang et al., 2020) discovered the extrema of these explosion parameters are found to be at$\leqslant \varphi$1.0.

2. Experimental apparatus, methods and materials

The experimental system is composed of experimental pipeline, transient pressure acquisition devices, gas distribution systems, and ignition devices. A schematic of this system is shown in Figure 1.

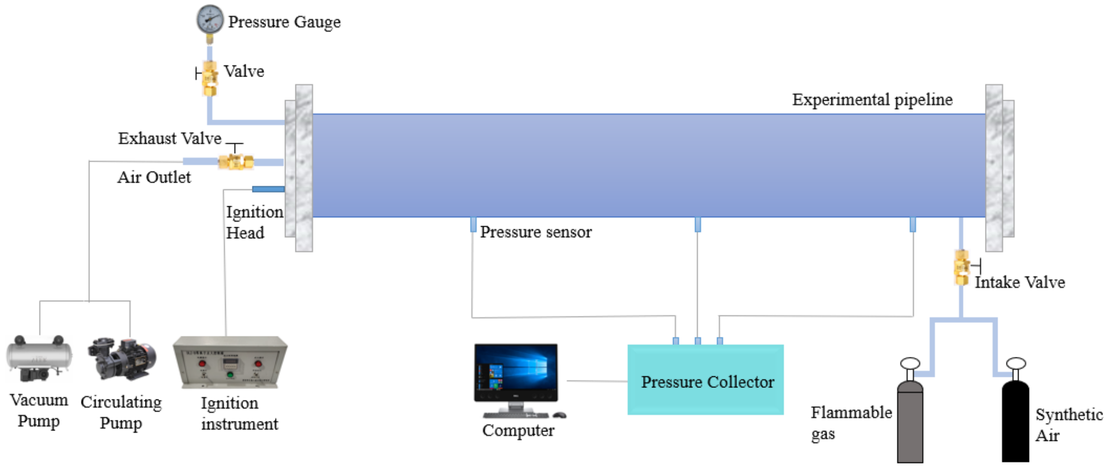
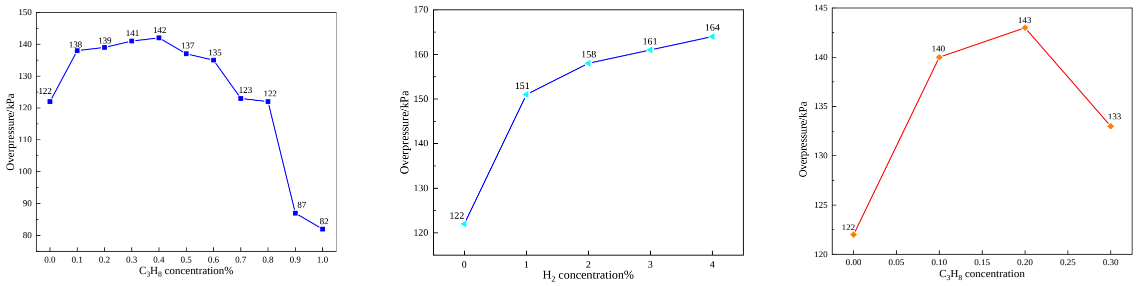


Figure 1: Schematic of gas explosion experiment device

As shown in the schematic in Figure 1, the cylindrical experimental pipeline of length 1000mm, inner diameter of 100mm and thickness of 6mm is pressure-resistant pipeline and equipped with a bursting disc. Three pressure sensors are installed in the pipeline to measure the pressure at different positions. The No. 1 pressure sensor was set to 30 cm from the ignition end, and the No. 2 pressure sensor was set to be 30 cm away from sensor No. 1 in a horizontal direction. Pressure sensor No. 3 was set to 30 cm in a horizontal direction to sensor No. 2. The transient pressure system consists of Kistler-211B3 sensors and a data collector. The software was set to a collection frequency of 80 kHz, that is, 80 times/ms of data collection. The process was operated using measurement software. The gas distribution system includes vacuum pump, circulating pump and two valves. The ignition system consists of a high-energy igniter instrument and an ignition head. The ignition head is located at left of pipeline. The experimental gas materials include CH_4, C_3H_8, H_2 and synthetic air with a purity of 99.9999 %.
Chapter 2 All experiments were carried out at room temperature and normal pressure. The experimental steps are as follows: The gas seal of the experimental system was checked. A vacuum of <667 Pa (according to GB/T 12474–2008) was established in the experimental pipeline by the vacuum pump, and the pressure remained unchanged within 5 min as observed through a pressure gauge, which indicated that the experimental instruments were appropriate for the experiment. The combustible gas of calculated volume was injected into the pipe in the vacuum environment, and then synthetic air was injected into the pipe until atmospheric pressure. The gas in the pipe was mixed for 2 min by the circulation pump and standing for 5 min to ensure uniformity mixing gas according to the law of Dalton partial pressure method with an accuracy of 0.1%. The combustible gas is ignited by the ignition system, and the pressure data are collected. The residual gas in the pipeline was treated harmlessly by physical (adsorption) and chemical (catalytic combustion) methods to avoid polluting the atmosphere.

3. Results analysis

The explosion pressure of $CH_4/C_3H_8/H_2$/air premixed multicomponent gas was shown in Figure. 2.



2a 9.5%CH_4+C_3H_8 2b 9.5%CH_4+H_2 2c 9.5%CH_4+1%H_2+ C_3H_8

Figure 2: multicomponent gas explosion pressure under different working conditions

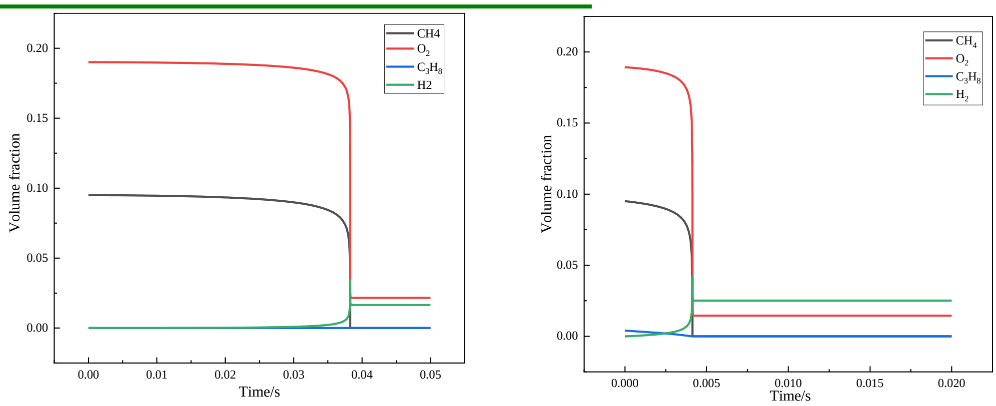
It can be seen from Figure. 2a that with the increase of C_3H_8 concentration, the explosion pressure of CH_4 shows a trend of first promoting and then inhibiting. The explosion pressure of C_3H_8/CH_4/ air mixture was the largest and increased 16.369% when the C_3H_8 concentration was 0.4%. When the C_3H_8 concentration was 0.8 %, the explosion pressure was the same as the blank group. When the C_3H_8 concentration exceeds 0.8 %, the explosion pressure decreases greatly.
It can be seen from Figure. 2b that the H_2 concentration was positively correlated with the explosion pressure of the multicomponent gas. The greater the H_2 concentration was, the greater the explosion pressure was. When the H_2 concentration was 1%, the explosion pressure increased the fastest, rising by 23.77%. With the increase of H_2 concentration, the rise was indeed gentle. When the H_2 concentration reached 4%, the explosion pressure of the mixed gas increased by 34.43% compared with the blank group.
It can be seen from Figure 2c that in the C_3H_8/H_2/CH_4/air mixture, the concentration of C_3H_8 was changing, the concentration of H_2 was 1%, and the concentration of CH_4 was 9.5%. With the increase of C_3H_8 concentration, the peak explosion pressure first increased and then decreased. Compared with the blank group, the addition of C_3H_8 and H_2 still promoted the explosion pressure. When the propane concentration was 0.2%, the peak explosion pressure increased by 17.21%.

4. Simulation analysis

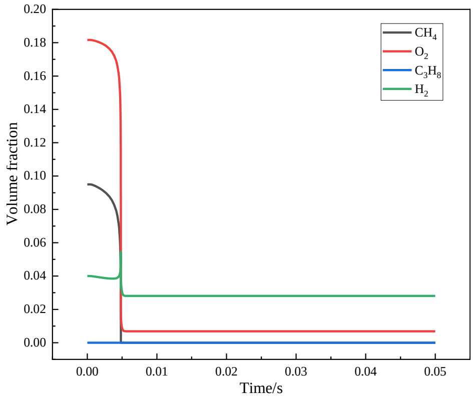
The simulation software was Chemkin-pro, and the mechanism file was GRI Mech 3.0 of Hai Wang team. (Wang et al., 2007) The closed homogeneous Batch Reactor model was used to simulate the transient gas reaction. The blank group and the three conditions of adding 0.4%C_3H_8, 4%H_2 and0.2%C_3H_8 +1%H_2 were simulated. Because these three conditions had the greatest promotion effect on CH_4 explosion pressure.

Table 1: simulated conditions

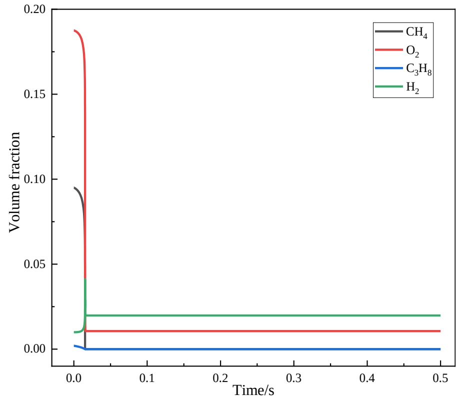
Serial	CH_4/vol.%	C_3H_8/vol.%	H_2/vol.%
1	9.5	0	0
2	9.5	0.4	0
3	9.5	0	4
4	9.5	0.2	1



3a 9.5%CH_4 3b 9.5%CH_4+0.4%C_3H_8



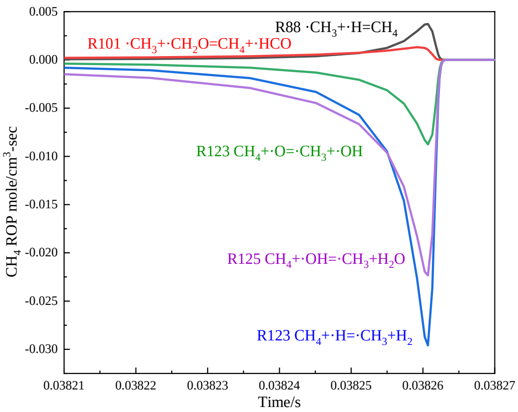
3c 9.5% CH_4+4% H_2



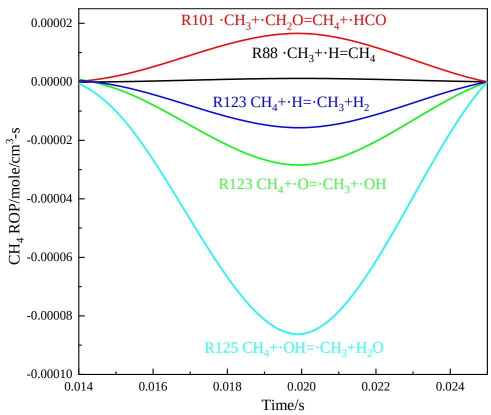
3d 9.5%CH_4+0.2%C_3H_8+1%H_2

Figure 3: volume fraction of reactants under different working conditions

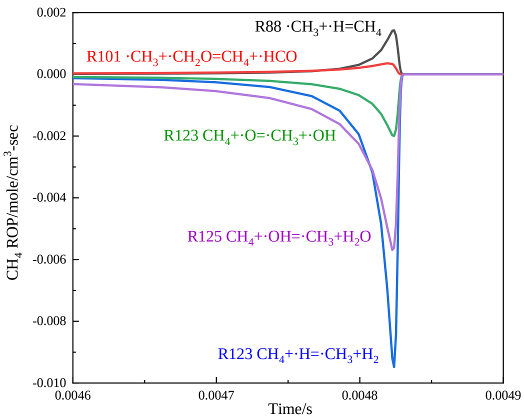
It can be seen from Figure 3 that the residual amount of CH_4 in the blank group was the least. After the addition of 0.4% C_3H_8, the residual amount of CH_4 increased, indicating that in C_3H_8/CH_4/air multivariate gases, C_3H_8 would be preferentially consumed, and then CH_4 was consumed. The addition of H_2 also increased the CH_4 residue, proving that H_2 reacted earlier than CH_4 in the H_2/CH_4/air multicomponent system. When C_3H_8 and H_2 were homochromous added, the remaining amount of CH_4 increased, and the remaining amount of C_3H_8 also increased, indicating that in the multi-system of C_3H_8/H_2/CH_4/air, H_2 reacted preferentially than C_3H_8.



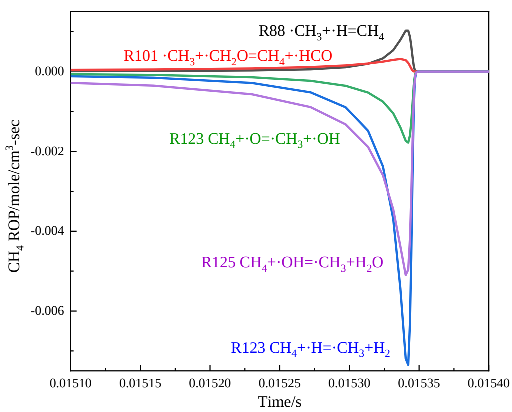
4a 9.5%CH_4



4b 9.5%CH_4+0.4%C_3H_8



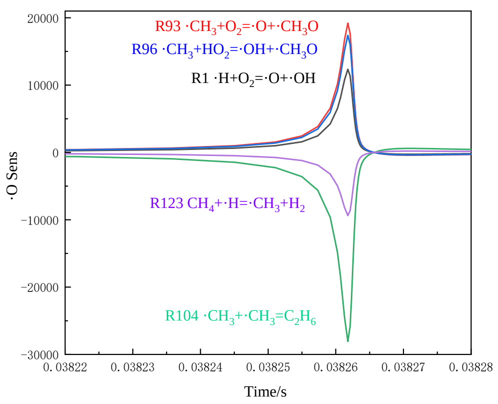
4c 9.5% CH_4+4% H_2



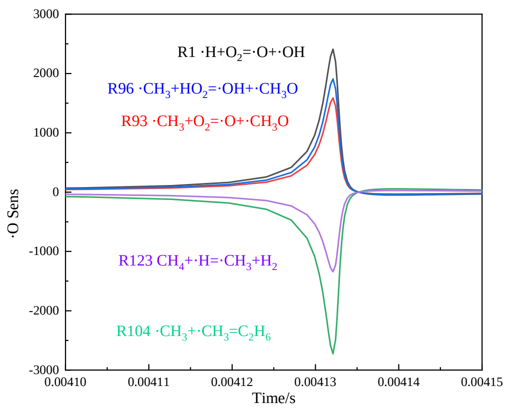
4d 9.5%CH_4+0.2%C_3H_8+1%H_2

Figure 4: CH_4 ROP under different working conditions

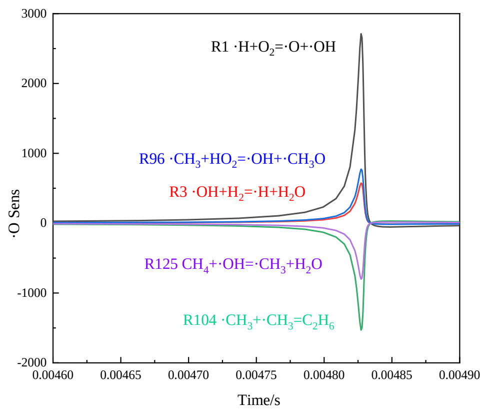
Positive represented the elementary reaction to produce CH_4, negative represented the elementary reaction to consume CH_4. It can be seen from Figure 4 that the first five elementary reactions of CH_4 explosion reaction were the same, but the reaction rates were different. R88·CH_3+·H= CH_4 and R101·CH_3+·CH_2O=CH_4+·HCO generated CH_4. R123CH_4+·O=·CH_3+·OH, R124CH_4+·H=·CH_3+H_2 and R125CH_4+·OH=·CH_3+H_2O were the main reaction of CH_4 consumption. CH_4 collided with massive ·H, ·O, ·OH to generated ·CH_3 and other products. The addition of C_3H_8 reduced the reaction rate of R88 and increased the reaction rate of R101. The addition of C_3H_8 and H_2 decreased the reaction rates of R123, R124 and R125, indicating that the addition of C_3H_8 and H_2 inhibits the CH_4 consumption reaction. It is considered that H_2 and C_3H_8 preferentially reacted with O_2, resulting in an increase in CH_4 residue.



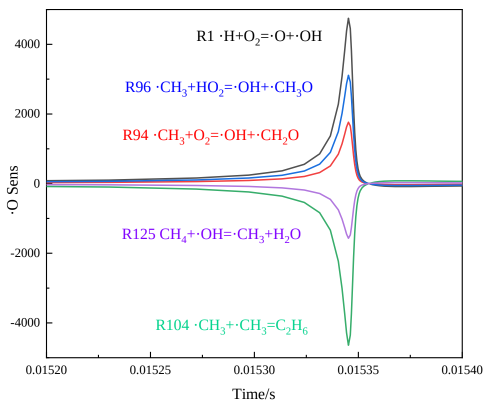
5a 9.5%CH_4



5b 0.4%C_3H_8+9.5%CH_4



5c 4%H_2+9.5%CH_4



5d 0.2%C_3H_8+1% H_2+9.5%CH_4

Figure 5: O sensitivities analysis under different working conditions

The addition of C_3H_8 and H_2 increased O_2 consumption, and the ·O sensitivity was analysed. The sensitivity coefficient was positive to promote O generation, that was, to promote explosion, while the negative was the opposite. It can be seen from Figure 5a that R1, R93, R96, R104 and R123 had great influence on ·O sensitivity. R93·CH_3+O_2=·O+·CH_3O had the greatest positive effect on ·O sensitivity and R96·CH_3+·HO_2=·OH+·CH_3O also has a greater positive impact on O, indicating that ·CH_3O promoted ·O and in turn promoted explosion. R104·CH_3+·CH_3=C_2H_6 was the chain termination reaction and produced larger molecular weight alkanes, which had the greatest negative impact on ·O sensitivity, indicating that R104 inhibits explosion.

It can be seen from Figure 5b that the elementary reaction with the greatest positive impact on ·O sensitivity changed from R93 CH_3+O_2=·O+·CH_3O to R1·H+O_2=·O+·OH after the addition of C_3H_8. C_3H_8 reacted with O_2 preferentially than CH_4. C_3H_8 decomposed into ·C_3H_7 and ·H, and O_2 decomposed into ·O. The addition of C_3H_8 increased the amount of CH_4 residue. This indicated that the reaction rate of ·CH_3 decreased, and the sensitivity of R93 and R96 to O decreased. ·CH_3O still had the positive impact on ·O sensitivity.

It can be seen from Figure 5c that compared with blank group, the elementary reaction with the greatest positive impact on ·O sensitivity changed from R93 to R1 after the addition of H_2. The sensitivity coefficient of R3·OH+H_2=·H+H_2O and R125CH_4+·OH=·CH_3+H_2O also increased. The number of ·H,·O and ·OH increased.

R96 still had positive impact on ·O sensitivity. R125 was the chain transfer reaction, from simple ·OH into $\cdot CH_3$. R125 had the negative impact on ·O sensitivity, indicating that R125 inhibits explosion.

It can be seen from Figure 5d that the elementary reaction with the greatest positive impact on ·O sensitivity changed from R93 to R1 when C_3H_8 and H_2 were added simultaneously. R104 still had the greatest negative impact. This indicated that R1 promoted explosion and R104 inhibited explosion. R96 still had positive impact on ·O, sensitivity indicating that $\cdot CH_3O$ still had the positive impact on ·O sensitivity. The addition of H_2 and C_3H_8 or the addition of H_2 both increased the sensitivity coefficient of R125, and the priority of H_2 reaction was higher than that of C_3H_8, indicating that the main reason for the increase of R125 sensitivity coefficient was the addition of H_2.

5. Conclusions

The addition of appropriate amount of C_3H_8 and H_2 in CH_4/air promoted CH_4 explosion, and 0.4% C_3H_8 had the largest promotion effect on CH_4 explosion. The higher the H_2 concentration, the more obvious the promotion effect of CH_4 explosion. The addition of 0.2% C_3H_8 and 1% H_2 had the greatest promotion effect on CH_4 explosion.

In the $C_3H_8/H_2/CH_4$/ air premixed multivariate gas, the reaction priority of H_2 was higher than C_3H_8, and that of C_3H_8 was higher than CH_4.

Elementary reaction $\cdot H+O_2 <=> \cdot O+\cdot OH$ promoted explosion and $\cdot CH_3+\cdot CH_3=C_2H_6$ inhibited explosion. In addition, $\cdot CH_3O$ was the important free radical in the explosion process and promoted the explosion.

Different concentrations and types of gases may have different effects on gas explosion reaction. The explosion reaction mechanism of multiple gases is a complicated topic. Therefore, the authors will continue to perform in-depth research in this direction.

Acknowledgments

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References

Chang, X.Y., Zhang B, Ng H.D., Bai C.H., 2020. The effects of pre-ignition turbulence by gas jets on the explosion behavior of methane-oxygen mixtures. Fuel, 277.

Li Q.Z., Lin B.Q., Dai H.M., Zhao S, 2012. Explosion characteristics of H_2/CH_4/air and CH_4/coal dust/air mixtures. Powder Technology , 229, 222-228.

Liang W.K., Liu Z.R., Law C.K., 2019. Explosion limits of $H_2/CH_4/O_2$ mixtures: Analyticity and dominant kinetics. Proceedings of the Combustion Institute, 37 (1), 493-500.

Luo Z.M., Su B, Li Q, Wang T, Kang X.F., Cheng F.M., Gao S.S., Liu L.T., 2019. Micromechanism of the Initiation of a Multiple Flammable Gas Explosion. Energy & Fuels, 33 (8), 7738-7748.

Pinaev A.V., Pinaev P.A., 2020. Combustion and Detonation Waves in Gas Mixtures of CH_4/Air, CH_4/O_2, and O_2/Coal Dust. Combustion, Explosion, and Shock Waves, 56 (6), 670-681.

Tan X, Schmidt M, Zhao P, Wei A, Huang W.X., Qian, X.M., Wu D.J., 2020. Minimum ignition temperature of carbonaceous dust clouds in air with CH_4/H_2/CO below the gas lower explosion limit. Fuel, 264.

Wang Y, Lin S, Feng H, Ji W.T., Ma H.Y., Zhang Y.M., 2021. Suppression of different functional group modified powders on 9.5% CH_4-air explosion and molecular simulation mechanism. Journal of Loss Prevention in the Process Industries, 69.

Wang H, Gu S, Chen T, 2020. Experimental Investigation of the Impact of CO, C_2H_6, and H_2 on the Explosion Characteristics of CH4. ACS Omega, 5 (38), 24684-24692.

Wang H.H., Ma H.H, Shen Z.W., 2020. Explosion characteristics of H_2/N_2O and CH_4/N_2O diluted with N2. Fuel, 260.

Wang H, YOU X.Q., AMEYA V.J., Scott G.D., Alexander L, Fokion E, Chung K.L., 2007. USC Mech Version II. High-Temperature Combustion Reaction Model of $H_2/CO/C_1$-C_4 Compounds[DB]. http://ignis.usc.edu/USC_Mech_II.htm.

Zhao P, Tan, X, Schmidt M, Wei A, Huang W.X., Qian X.M., Wu D.J., 2020. Minimum explosion concentration of coal dusts in air with small amount of CH_4/H_2/CO under 10-kJ ignition energy conditions. Fuel, 260.