The influence of methane blending ratio on the spontaneous combustion characteristics of high-pressure hydrogen leakage

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Abstract: Adding CH4 to high-pressure H2 is considered one of the effective and convenient measures to reduce high-pressure H2 leakage and spontaneous combustion, which is conducive to improving the safety of H2 energy storage. Based on the independently built high-pressure hydrogen leakage and self ignition experimental platform, the influence of CH4 on the critical self ignition pressure and flame of high-pressure H2 leakage and self ignition was tested. The results indicate that the addition of methane can effectively increase the critical spontaneous combustion pressure. When 20% CH4 is added, the critical self ignition pressure can be increased by 151.58%. Under similar discharge pressure conditions, the flame velocity in the pipeline decreases from 1224.64m/s for pure H2 to 1024.07m/s for 10% CH4. In addition, after mixing CH4, the dispersion time of the jet flame is advanced, the flame duration is shortened, and the flame brightness is reduced. There are two main reasons for the mixed inhibition of spontaneous combustion by CH4. On the one hand, it reduces the Mach number of shock wave propagation, thereby lowering the ignition temperature. On the other hand, the activity of the fuel system decreases, and the heat required for self ignition increases.

1. Introduction

According to statistics, among accidents involving combustion and explosion caused by high-pressure H2 leakage, nearly 61.98% of accident disasters cannot determine the external ignition source[1]. Such accidents are usually considered to be spontaneous combustion after H2 leakage. Adding CH4 has a greater effect on reducing the possibility of spontaneous combustion [2]. CH4 is added to H2 fuel in a certain way to form a new combustible mixture gas, called H2-rich natural gas (HCNG). When used, it can effectively combine the advantages of CH4 and H2, ensuring the combustion calorific value while reducing risks[3]. Today, with the rapid development of H2 energy, research on the characteristics and mechanisms of the special combustion phenomenon of H2-CH4 mixed gas leakage and spontaneous combustion is of great significance for reducing the possibility of H2 leakage and spontaneous combustion accidents and promoting the further promotion and use of H2 energy.

Experimental research on the high-pressure leakage and spontaneous combustion of mixed gases of H2 and CH4 mainly focuses on the critical pressure, ignition delay time, and flame evolution characteristics of H2 spontaneous combustion after mixing with CH4. Rudy et al[2] first compared the differences in spontaneous combustion phenomena after mixing 5% and 10% CH4 in pipelines with pipe diameters of 6, 10, and 14 mm and pipe lengths of 40, 50, 75, and 100 mm. The results showed that adding 5% CH4 to H2 significantly increased the pressure required for spontaneous combustion. When the pipe length was 75mm, the critical pressure increased by 1.49 times for a 10mm diameter pipe and by 2.67 times for a 6mm diameter pipe. For 10% CH4 addition, no self-ignition phenomenon occurred for all diameters with a pipe length of 100 mm and a discharge pressure within 15MPa. Sergey et al. [4] tested the ignition delay time change in a pipe with a length of 185mm and an inner diameter of 5mm under an initial pressure range of 3MPa-15MPa and a CH4 molar volume ratio concentration of 0-18%. The results showed that after adding 18% The H2-CH4 ignition delay time increases 16 times. Zeng et al[5] conducted an experimental study on the propagation characteristics of autoignition flame of high-pressure H2-CH4 mixed gas through pipelines. The ratio of CH4 to H2 is 2.5% by volume. The experimental pipeline is a rectangular tube with a window, a cross-sectional size of 15mm*15mm, and a length of 400mm. The results show that for the addition of 2.5% CH4, the minimum burst pressure required for autoignition increases from 2.89MPa to 4.68MPa. Moreover, the addition of CH4 increases the initial ignition time, weakens the flame intensity, reduces the propagation speed of the flame in the tube relative to the tube wall, and the complete flame in the entire tube is formed closer to the rear end of the tube. In terms of ignition mechanism, in 1973, Wolanski et al[6] first proposed the "diffusion natural" theory to explain this unique spontaneous combustion phenomenon. This theory believes that strong shock waves are one of the most
important reasons for spontaneous combustion. Golub et al. [7,8] studied the spontaneous ignition phenomenon of high-pressure ammonia leakage through experiments and numerical simulations. They believed that the temperature increase at the H₂-air contact surface after the shock wave was the key factor leading to ignition.

Current experimental research on the impact of higher CH₄ blending ratios on the spontaneous combustion of high-pressure H₂ leakage is still relatively insufficient, especially in terms of the critical pressure for the occurrence of spontaneous combustion and flame propagation. This article relies on the high-pressure gas leakage and spontaneous combustion experimental platform to test the critical release pressure changes of H₂–CH₄ and the flame changes in the visualized pipeline and protective box under the volume ratio of 0%, 5%, 10%, 15% and 20% CH₄. And the reasons why CH₄ affects the spontaneous combustion characteristics of high-pressure H₂ leakage are analyzed.

2. Experimental equipment and methods

The physical diagram (Fig.1) and structural schematic diagram (Fig.2) of the high-pressure gas leakage spontaneous combustion experimental platform used in this article are as follows. When studying flame characteristics, high-speed cameras are used for recording. The main experimental steps are as follows:

(1) Before starting the experiment, install and debug the experimental system according to the experimental system structure diagram shown in Fig.2. Selecting a suitable bursting disc and install it in the holder. At the same time, the pressure testing system, camera system, data acquisition system and other measurement devices are turned on.

(2) Open the nitrogen control valve, fill the experimental device with nitrogen at a certain pressure and maintain it for a period of time, and carefully check the air tightness of the leakage simulation device. If the air tightness of the device is good, discharge the nitrogen in the device through the reserved exhaust valve port.

(3) Use a vacuum system to evacuate the leakage simulation device to about 30kPa.

(4) Open the fuel control valve, and the high-pressure pump will fill the fuel into the high-pressure storage thread until the bursting disc ruptures. The fuel in the storage tank will be discharged into the protective box through the downstream visualization pipeline, and high-speed camera shooting will be started at the same time. The shooting state is entered when the experiment begins.

(5) Open the nitrogen control valve, fill the leakage and self-ignition simulation device with nitrogen, and purge the high-pressure tank and the undischarged atmosphere in the visual pipeline (Fig.3).

(6) After a high-pressure gas release experiment is completed, store the pressure data recorded by the data collector and the flame image data captured by the camera device, and then prepare for the next set of experiments.

3. Results and discussion

3.1. Effect of CH₄ mixing ratio on critical pressure of spontaneous combustion leakage

When the pressure in the high-pressure storage tank exceeds the withstand pressure of the bursting disc, the bursting disc ruptures. A pressure sensor installed on the high-pressure storage tank records the pressure changes within the tank. Fig.4 shows the pressure changes in the storage tank under the discharge pressure conditions of three groups of pure H₂ experiments. Since the bursting discs used in each set of experiments cannot be guaranteed to be completely consistent, there is a certain error in the actual bursting pressure. For example, the actual bursting pressure of the bursting disc with a bursting pressure of 7 MPa is 7.605 MPa. The actual bursting pressure of the bursting disc is defined as \( P_b \). The pressure difference between adjacent bursting discs is 2 MPa. When two adjacent pressure experiments have ignition and no ignition, the actual bursting disc pressure \( P_b \) at which ignition occurs is defined as the autoignition critical pressure.

In order to study the influence of CH₄ on the critical pressure of H₂ leakage and autoignition, the critical pressure of pure H₂ leakage and autoignition in this experimental platform was first measured. When \( P_b \) was 3.210 MPa and 5.219 MPa, no spontaneous combustion occurred when observing the high-speed camera images in the visual pipeline and protective box. When \( P_b \) continued to increase to 7.605 MPa, no spontaneous combustion occurred in the pipeline. When the bursting disc ruptures, the pipeline will vibrate slightly, and this vibration will be amplified in the high-speed camera. The initial moment
When the high-speed camera captures the vibration of the pipeline in the lens is defined as the bursting disc rupture moment \((t_g=0\mu s)\). When \(P_b=7.605\) MPa, an obvious jet fire occurred in the protective box downstream of the visualized pipeline (Fig.5). Define the frame before the flame appears at the outlet of the discharge pipe in the protective box as the initial moment \((t_f=0)\). The analysis found that at \(t_f=22.61\mu s\), the flame is extremely weak, which is consistent with the characteristics of the initial stage of flame germination. Therefore, it can be inferred that \(P_b=7.605\) MPa pure H₂ gas spontaneously ignited in the connection section between the visualization pipeline and the downstream protective box, where the high-speed camera cannot directly photograph, forming a flame and continuing to spread. In summary, the critical pressure of pure H₂ high-pressure release and self-ignition tested on this experimental platform is \(P_b=7.605\) MPa.

Fig.4. Relationship between pressure with time in 5, 7 and 9MPa bursting disc of high-pressure storage tank

When 5% CH₄ gas was added, the pressure increase to \(P_b=9.938\) MPa. No self-ignition phenomenon is found in the visualized pipeline, but self-ignition occurs in the protective box and a jet flame is formed. As shown in Fig.6. Therefore, the critical pressure of self-ignition after adding 5% CH₄ is \(P_b=9.938\) MPa.

Fig.5. Autoignition flame image of pure H₂ \(P_b=7.605\) MPa protective box

When the relief pressure continues to increase to \(P_b=11.853\) MPa, as shown in Fig.7, a natural phenomenon occurs in the visualized pipeline, so the autoignition critical pressure rises to \(P_b=11.8523\) MPa after adding 10% CH₄.

Fig.6. Image of autoignition flame in 5% CH₄-95% H₂ \(P_b=9.938\) MPa protective box

When the pressure increases to \(P_b=14.512\) MPa, as shown in Fig.8, an autoignition point first appears on the lower wall of the pipeline at \(t_g=90\mu s\), and then propagates forward along the upper wall of the visualized pipeline. The critical pressure of autoignition after adding 15% CH₄ is \(P_b=14.512\) MPa.

Fig.7. Image of spontaneous combustion flame in 10% CH₄-90% H₂ \(P_b=11.853\) MPa pipeline

When \(P_b=19.133\) MPa, the high-speed camera was used to detect the presence of a self-igniting flame light at the end of the visualized pipe, and it was determined that self-ignition occurred. Fig.9 shows the image inside the visualized pipeline under working conditions. Therefore, the critical pressure of self-ignition after adding 10% CH₄ is \(P_b=19.133\) MPa.

In summary, adding CH₄ can increase the critical pressure at which high-pressure H₂ leaks and spontaneously ignites. As shown in Fig.10, when 5% and 10% CH₄ are added, the auto-ignition critical pressure increases by 30.68% and 55.86% respectively. When the further addition ratio reaches 15% and 20%, increasing by 90.82% respectively, and 151.58%.

Fig.8. Autoignition flame image of 15% CH₄-85% H₂ \(P_b=14.512\) MPa pipeline

Fig.9. Image of spontaneous combustion flame of 20% CH₄-80% H₂ \(P_b=19.133\) MPa pipeline
3.2. Effect of CH₄ on flame of visual pipeline leakage

In order to reduce the impact of bursting disc rupture pressure difference on leakage and spontaneous combustion flames, the \( P_b \) difference is within 1MPa. Analyzed the effect of CH₄ blending ratio on H₂-CH₄ leakage and spontaneous combustion. Fig.11 and Fig.12 show the images of autoignition flames in the pipeline when pure H₂ has a \( P_b \) of 12.779MPa and 10% CH₄-90% H₂ has a \( P_b \) of 11.862MPa. The \( P_b \) difference is 0.917MPa.

When H₂ \( P_b=12.779\)MPa releases and ignites spontaneously, the autoignition point occurs on the upper wall of the pipe at \( t_g=10\)µs. At this time, the flame length (the horizontal distance from the front of the flame to the end of the flame) is 9.5mm. After that, the flame gradually lengthens, it thickens and develops towards the lower wall of the pipeline. When \( t_g=220\)µs, a self-igniting flame is born on the lower wall of the pipeline. The two flames merge into one when \( t_g=240\)µs, and the width occupies the entire pipeline. When \( t_g=240\)µs, the flame front propagates to the far right side of the visual pipe glass window, the flame length increases to 64.67mm, which lasts 230µs, and the average flame propagation speed during the entire process is 1224.64m/s. When \( t_g=320\)µs, the end of the flame completely leaves the visualization pipeline, and the entire autoignition flame propagation process in the visualization pipeline lasts 310µs.

When 10%CH₄-90%H₂ releases and spontaneously ignites at \( P_b=11.862\)MPa, weak spontaneous combustion points are simultaneously generated on the upper and lower walls of the pipeline at \( t_g=30\)µs, and the flame lengths are both approximately 3mm. Then the two flames moved up and down to avoid horizontal movement toward the pipe outlet. At \( t_g=260\)µs, the two flames gradually merged into one near the horizontal centerline of the pipe and continued to move. At \( t_g=300\)µs, the flame front propagated to the visualized pipe glass. On the far right side of the window, the flame length reaches the longest, lasting 270µs. The average flame propagation speed during the entire process is 1024.07m/s. When \( t_g=380\)µs, the flame end completely leaves the visualization pipeline. The duration of the entire autoignition flame propagation process is 350µs. Compared with the self-ignition flame of pure H₂, the brightness of the self-ignition flame after mixing 10% CH₄ also dropped significantly.

As can be seen from the comparison in Fig.13, after blending 10% CH₄, the flame front position is delayed compared to that of pure H₂, the overall flame propagation speed is lower, and the maximum flame propagation instantaneous speed is reduced from 1734.4m/s to 1440.2m/s.

3.3. Effect of CH₄ mixing ratio on spontaneous combustion flame of leakage in protective box

When Fig.14, Fig.15 and Fig.16 respectively show pure H₂ at a \( P_b \) of 9.965MPa, 5% CH₄-95% H₂ at a \( P_b \) of 9.938MPa and 10% CH₄-90% H₂ at a \( P_b \) of 11.86MPa. Autoignition flame image, \( P_b \) range is 1.92MPa.

When high-pressure gas is ejected from the visual pipe, flame splitting behavior occurs. The specific content refers to the flame gradually splitting into two parts in the protective box. One part of the flame is stable near the pipe mouth, while the other part of the flame propagates downstream. By comparison, it was found that when the CH₄ doping ratio increased from 0% to 5% and 10%, the completion time of flame splitting decreased from \( t_f=248.71\)µs to 170.84µs and 113.05µs. The flame splitting behavior outside the tube was mainly due to the near mouth of the tube. The vortex formed. The short flame splitting time indicates that the addition of CH₄ changes the flow properties of the mixed gas, thereby changing the vortex condition at the pipe outlet, causing the flame to develop in the direction of early splitting.

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At the same time, the addition of CH₄ reduces the duration of the jet fire. When pure H₂ or mixed with 5% CH₄, the flame still exists at the limit of high-speed camera recording, that is, when τ is 172446.47 and 597384.77 µs respectively (Fig.17 and Fig.18, Fig.19), but when 10% CH₄ was mixed, the remaining discrete flame was extinguished after τ = 13950.37 µs. The above experimental results show that the CH₄ mixing ratio has a clear tendency to inhibit spontaneous combustion of H₂ leakage.

### 3.4. Analysis of the inhibition mechanism of CH₄ mixing ratio on spontaneous combustion

According to the diffusion ignition theory, the shock wave generated by high-pressure gas release is a prerequisite for
spontaneous ignition, and the autoignition process can be considered a shock wave-induced ignition mode. The shock-induced ignition process is as follows. The compressed gas is suddenly released from the high-pressure equipment into a low-pressure environment. Due to the high pressure, a highly under-expanded jet will be formed in the air. At the same time, a shock wave will be formed in the front of the jet. Since the propagation speed of the shock wave is greater than the propagation speed of the gas jet, a certain area of shock wave action will be formed between the jet and the leading shock wave. The pressure, density and temperature of the shock wave area will be significantly increased due to the compression of the shock wave. Once the temperature of the shock-heated air exceeds the threshold temperature for self-ignition of compressed combustible gas, ignition may be induced. The blending of CH4 will reduce the tendency of high-pressure H2 leakage and self-ignition from two aspects.

First, the blending of CH4 can reduce the leader shock wave velocity of H2. When the gas is released, the shock wave propagation speed in the pipeline can be obtained based on the pressure distribution of the four pressure sensors above the pipeline. When the shock wave is transmitted to the sensor position, it will cause the sensor pressure to rise. Therefore, based on the time interval between the rises of the two pressure sensors, the average speed of the shock wave through this distance can be deduced. When 100% H2, \( P_b = 12.779 \text{MPa} \), the shock wave propagates from sensor1 to sensor4 for 230µs. After adding 10% CH4 and 15% CH4, it is extended to 240µs and 260µs respectively. The corresponding stress wave speed is 1304.35m/s respectively, 1250m/s and 1153.85m/s(Fig.20). According to formula [9]:

\[
\frac{T_2}{T_1} = \frac{[2\gamma M_1^2 - (\gamma - 1)] [(\gamma - 1)M_1^2 + 2]}{\gamma (\gamma + 1)}
\]  

(1)

In the formula: \( T_1 \) and \( T_2 \) are the temperatures before and after the shock area respectively, \( M_1 \) is the gas shock Mach number, its value is the ratio of the gas shock velocity to the local sound speed [10], and \( \gamma \) is the adiabatic index of the gas. According to equation (1), the temperature \( T_2 \) behind the shock wave region is proportional to the shock wave speed. Therefore, when the shock wave speed is faster, the temperature rise will be higher. The increase in the blending amount of CH4 reduces the shock Mach number, which in turn reduces the temperature rise. This will be detrimental to the occurrence of auto-ignition flames.

On the other hand, the blending of CH4 can reduce the activity of the H2-CH4 system [11] and significantly increase the temperature required for spontaneous combustion [12]. This phenomenon has been widely proven in other studies [13]. In addition, under the same conditions, the density of CH4 is five times that of H2. The blending of CH4 can reduce the mobility of H2, which promotes the reduction of turbulent flame speed [14].

4 Conclusion

Through experiments, the changes in the critical pressure and flame characteristics of high-pressure H2 spontaneously igniting during pipeline propagation after mixing with CH4 were compared. Concluded as follow

1) The blending of CH4 will increase the critical pressure of high-pressure H2 leakage and spontaneous combustion. When blending 5%, 10%, 15% and 20%, the critical spontaneous combustion pressure increases by 30.68%, 55.86%, 90.82% and 20% respectively. 151.58%.

2) The blending of CH4 can significantly reduce the brightness of the auto-ignition flame in the pipeline, the time of the auto-ignition flame, the length of the flame and the propagation speed of the flame. At the same time, blending CH4 can reduce the splitting time of the jet flame at the pipe outlet and greatly reduce the duration of the flame.

3) The impact of CH4 on H2 leakage and spontaneous combustion lies in two aspects. On the one hand, the blending of CH4 can reduce the shock wave propagation speed in the pipeline and thereby reduce the shock wave heating level. On the other hand, the blending of CH4 can reduce the activity of H2 and increase the temperature required for spontaneous combustion. The CH4-H2 system has a higher density and weaker fluidity than pure H2, which is not conducive to flame propagation.
References


