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NUMERICAL SIMULATION AND EXPERIMENTAL STUDY ON FORMATION OF HIGH CONCENTRATION OF H_2 GENERATED BY GAS EXPLOSION

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ABSTRACT

In coal mine fire rescues, if the abnormal increase of gas concentration occurs, it is the primary thing to analyze the reasons and identify sources of the abnormal forming, which is also the basis of judge the combustion state of fire area and formulate proper fire reliefs. Nowadays, related researches have recognized the methane explosion as the source of high concentration of H_2 formation, but there are few studies about the conditions and reaction mechanism of gas explosion generating high concentration of H_2.Therefore, this paper uses the chemical kinetic calculation software, ChemKin, and the 20L spherical explosion experimental device to simulate the generating process and formation conditions of H_2 in gas explosion. The experimental results show that: the decomposition of water vapor is the main base element reaction (R84) which leads to the generation of H_2.The free radical H is the key factor to influence the formation of H_2 generated from gas explosion. With the gradual increase of gas explosion concentration, the explosive reaction becomes more incomplete, and then the generating quantity of H_2 increases gradually. Experimental results of 20L spherical explosion are consistent with the change trend about simulation results, which verifies the accuracy of simulation analysis. The results of explosion experiments show that when gas concentration is higher than 9%, the incomplete reaction of methane explosion increases which leads to the gradual increase of H_2 formation

Keywords: gas explosion, high concentration of H_2, numerical simulation, explosion experiment

INTRODUCTION

Since the ignition sources are very difficult to approach in fire zone, it is the most important method to judge the combustion status of coal mine fire by gas analysis method. Once the exceptions of gas composition or gas concentration occurs, the basic action for developing rational fire disaster relief plan and preventing secondary disasters is to analyze causes for the exceptions with gas analysis method(Xinquan,2013). Nowadays, studies about the change law and abnormal variations of indicator gas (CO, CO_2, C_2H_4, C_2H_2, C_2H_6 etc.) in coal mine fire have gained abundant achievements(Singh et al.,2007;Kim et al.,2004;Deng et al.,2015;Lingqi et al.,2008), but there are relatively less studies of the change patterns of H_2, especially lacks in researches on formation mechanism of high concentration of H_2 in in fire area.

H_2 is a kind of flammable gas with its explosion limits from 4% to 74.2%. There are many sources of H_2 in coal mine, during normal operation, the pyrolysis of coal(Handong,2001; Arenillas et al.,1999), the leakage of battery, bacterial decomposition of wood(Xinquan et al.,2013) in coal mines, etc, will all produce H_2. But when the mine fire happens, the H_2 in the fire area mainly comes from the oxidized spontaneous combustion with coal, so it is practical to analyze combustion state(Peng et al.,2010; Nehemia et al.,1999; Grossman et al.,1996) and verify whether the re-ignition exists according to the change of H_2 concentration in fire area(Fubao et al.,2010;Shao et al.,2014; Yang et al.,2015). In common mine fire, the concentrations of

H_2 are usually no higher than 2% due to the coal pyrolysis and incomplete combustion(AMSA,2008). However, sometimes the concentration of H_2 could be monitored to be higher than 2%, reaching to 7% or even higher. Due to the lower explosion limit, high concentration of H_2 have high risks of explosion. Therefore, it is crucial to analyze the formation mechanism of high concentration of H_2 for perfecting gas analysis theory and implementing fire relief measures.

Through literature reviews (AMSA,2008;Yingmei et al., 2009;Lianhua Dong,1999), it could be found that gas explosion is an important source of high concentration of H_2. Researchers had detected high concentrations of H_2 (about 4%) after gas explosion in Dashan coal mine of Fushun early in 1917. High concentration of H_2 (higher than 3%) was also detected by the American Mining Bureau and French Institute of Metrology in the process of gas explosion experiment. AMSA(2008) proposed that high concentration of H_2 was generated when gas explosion reactions were not complete. However, the formation conditions and mechanism of high concentration H_2 after gas explosion are still absent of sufficient studies.

Chemical reaction kinetics simulation is an effective method to analyze gas explosion process, it can analyze the influences that the intermediate component or activation center have on gas explosion processes, and the kinetics factors of explosive gas products generation could also be analyzed. Xiangcun(2016) had studied the influences of different concentrations of gas on the gas explosive products and TKERS(The key elementary reaction steps). The chemical kinetic characteristics of gas explosion were simulated and analyzed by Na(2014). Baoshan(2013) had compared the inhibition effect of N_2 and CO_2 on gas explosion in the view of TKERS, while Yuntao(2009) had analyzed the explosion suppression characteristics with chemical kinetics model. The above studies are related to the change analysis of gas products after explosion, but the gas products are limited to carbon oxides and nitrogen oxides.

This paper takes research on the formation mechanism of high concentration of H_2 in gas explosion by numerical simulation and experiment. Firstly, it analyzed the change trend of mole fraction , TKERS and free radical of some catastrophic gases (CO, CO_2 and H_2) during the gas explosion process by using constant volume reactor model which be in Chemkin. Then, the 20L spherical explosion experimental device is applied to verify the H_2 quantity generated by gas explosion.

GAS EXPLOSION REACTION DYNAMICS ANALYSIS

REACTION MECHANISM

Gas explosion reaction process is not a single step chemical reaction, but a kind of complex "hot chain" reaction, and it is directly influenced by the generation and disappearance of free radicals. In order to analyze the kenetics characteristics of gas explosion, the article used the detailed chemical kinetics mechanism of methane combustion from Livermore Lawrence National Laboratory of the United States, which includes 53 components, 325 reactions (Gregory et al.,2016). The calculation has been verified by a large number of researchers at home and abroad. Table one shows parts of the reaction steps of chain reaction of gas explosion. Table one shows parts of the reaction steps of chain reaction of gas explosion.

Table 1 partial reaction basis in the chain reaction of gas explosion

No.	elementary reaction
R3	$O + H_2 \Leftrightarrow H + OH$
R53	$H + CH_4 \Leftrightarrow CH_3 + H_2$
R58	$H + CH_2O \Leftrightarrow HCO + H_2$
R75	$H + C_2H_4 \Leftrightarrow C_2H_3 + H_2$
R84	$OH + H_2 \Leftrightarrow H + H_2O$
R126	$CH + H_2 \Leftrightarrow H + CH_2$
R284	$O + CH_3 \Leftrightarrow H + H_2 + CO$

INITIAL CALCULATION CONDITION

In order to analyze the reaction kinetics of H_2 in gas explosion in confined space, it used the constant volume reactor model in Chemkin software to solve the energy equation of gas explosion process. The solving procedure assumes that the enclosed space is an ideal adiabatic environment, the reaction rate keeps the same for every position in the computation space with no gradient difference of temperature and concentration. In the calculation condition, the volume fraction of O2 and N2 is 79/21. In this paper, 6 kinds of gases with different gas concentration are calculated in the gas explosion experiment processes. Its initial conditions are set as shown in table 2.

Table 2 Initial parameters of gas explosion

No.	Initial temperature (K)	Initial pressure (Mpa)	CH_4 (%)	O_2 (%)	N_2 (%)	Computing time (s)
1	1300	0.1	6	19.74	74.26	0.02
2	1300	0.1	7	19.53	73.47	0.02
3	1300	0.1	9	19.11	71.89	0.02
4	1300	0.1	11	18.69	70.31	0.02
5	1300	0.1	13	18.27	68.73	0.02
6	1300	0.1	15	17.85	67.15	0.02

RATE OF PRODUCTION ANALYSIS

When analyzing the gas explosion process, distinguish the most influential elementary reactions for H_2 generation is very important to understand of the formation process of H_2. In this paper, the ROP analysis in Chemkin software is used to analyze the elementary reaction affecting the H_2 generation.

Rate of production analysis (ROP for short) could be used to quickly extract and analyze which element reactions are most important to the generation or consumption of a component, it could also be used to analyze the direction of the chemical reaction at the same time. The calculation formulas of ROP are as follows:

$$P_K = \omega_K = \sum_{i=1}^{I} v_{ki} q_i \quad (1)$$

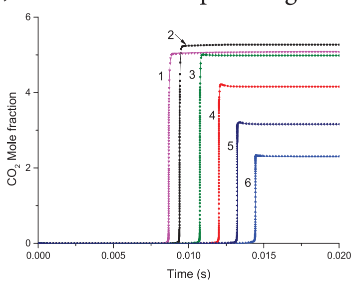
$$\overline{C_{Ki}}^{P} = \frac{\max(v_{Ki}, 0) q_i}{\sum_{i=1}^{I} \max(v_{ki}, 0) q_i} \quad (2)$$

Where P_K is the molar production of a species per unit volume, v_{ki} is the stoichiometric for the gas reactions, q_i is the rate of progress of the I gas-phase reactions. The calculation results of $\overline{C_{Ki}}^{P}$ are indicators to judge the importance degree of different element reactions.

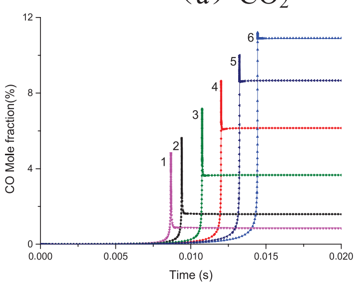
CALCULATION RESULTS AND ANALYSIS

The influences of gas concentration on gas compositions

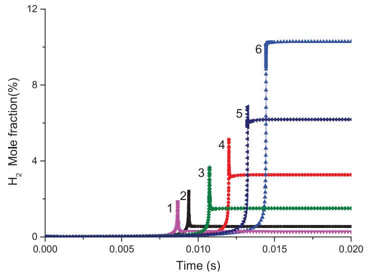
Figure 1 is the change regulation of main gas products CO, CO_2 and H_2 with different gas concentrations in dry and moist air environment. According to Figure 2, the explosion reaction processes within 5 to 10 milliseconds, the products concentration increased rapidly in the moment of explosion, and then stabilized quickly as well. With the increase of gas concentration, the time of the explosion gradually delayed.



(a) CO_2



(b) CO



(c) H_2

Fig. 1 The change trend of CO_2, CO and H_2 mole fraction in gas explosion process

From Figure 1 (a), with the increase of gas concentration, the mole fraction of CO_2 increased firstly and then decreased gradually. From Figure 1 (b) (c) it shows that CO and H_2 firstly increased rapidly and then rapidly decayed in the explosion with low concentration of methane during explosion reaction process. With the increase of explosion concentration, the increment of CO and H_2 becomes more significant, and the decline range gradually decreases. Eventually the final production of CO and H_2 would increase gradually. It indicates that the CO and H_2 formation is inevitably produced in the process of gas explosion, but parts of the CO and H_2 will quickly participate in the explosion reaction and then be consumed

$CO/(CO+CO_2)$ is known as the combustion balance ratio. The ratio change indicates the severity of reaction. It shows that the greater the value is the more incomplete the reaction is, and vice versa. In order to analyze the relationship between H_2 generation and the degree of explosive reaction, the change of H_2 mole fraction under different test conditions is shown in Figure 3, and the ratio of $CO/(CO+CO_2)$ is plotted in Figure 4.

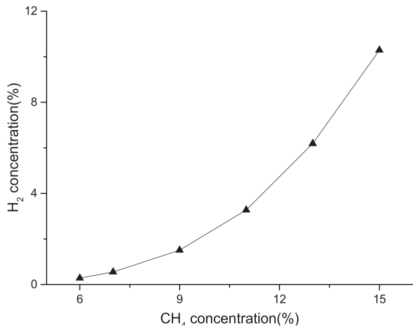


Fig. 3 H_2 mole fraction contrast curve

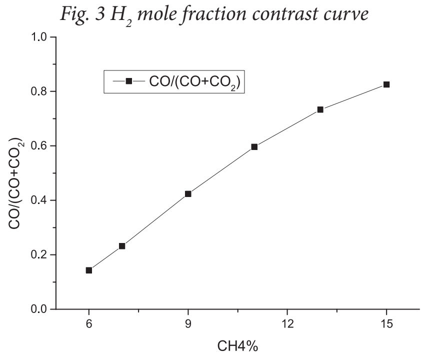


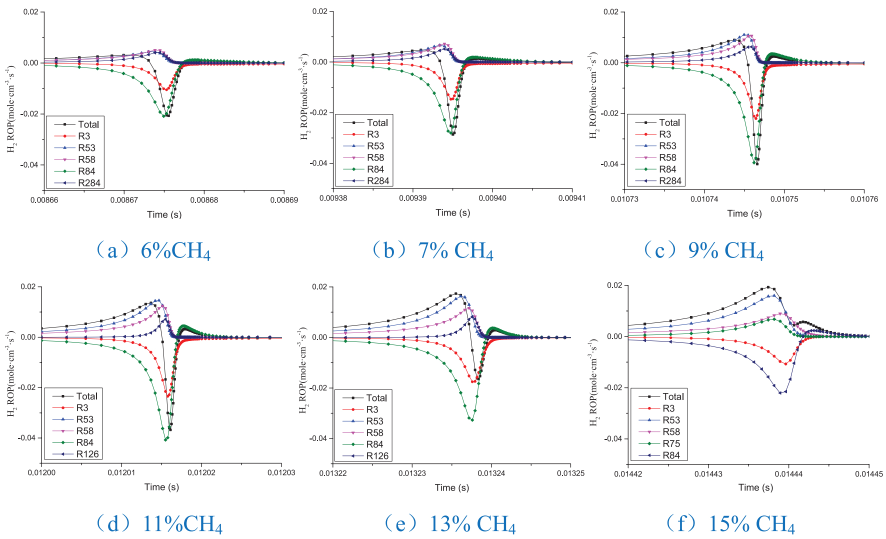
Fig. 4 The change trend of $CO/(CO+CO_2)$

The contrast analysis between Figure 3 and Figure 4 shows that with the increase of concentration of gas explosion, the amount of H_2 is gradually increased, and $CO/(CO+CO_2)$ also gradually increases. Therefore, it is implied that H_2 is mainly produced by incomplete gas explosion. And the greater the incomplete reaction degree of gas explosion is, the greater amount of H_2 is generated. In order to demonstrate this point, this paper makes further analyses of changes of TKERS and free radicals which affect the H_2 formation.

Analysis of TKERS and free radicals affecting H_2 generation

After the gas explosion, the gas composition balance is quickly completed, therefore, in order to effectively extract TKERS which affect the H_2 generation, ROP analysis was carried out to analyze the moment of explosive reaction. Use the ROP analysis tool in Chemkin software to search out 5 basic elements that have most important effects on the rate of H_2 generation, which are shown in Figure 5.

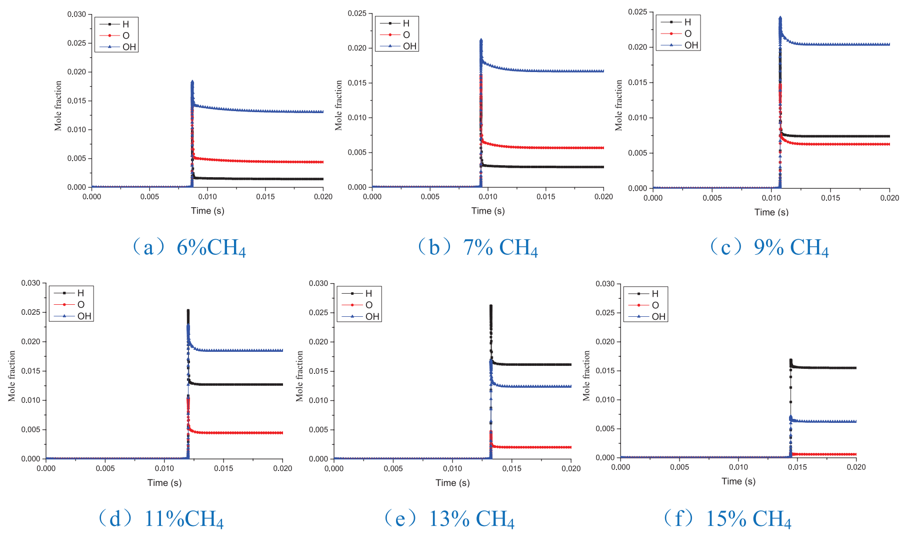
If the value of ROP is positive, it means the undergoing reaction is to promote the generation of H_2. If the value of ROP is negative, the reaction is to suppress H_2 generation. The greater the absolute value of ROP is, indicates the larger promotion (or suppression) effects on H_2 generation. Through observation of Figure 5, with different gas concentrations, the TKERS are not the same all the time. However, in all test conditions, the reaction step of greatest impacts to H_2 formation responses are R84($OH+H_2 \Leftrightarrow H+H_2O$). In the early stage of explosion, R84 reaction mainly consumes free radicals OH and H_2 to generate water, thereby inhibiting the generation of H_2. And in the later stage of the explosion, R84 is mainly to promote formation of H_2, that is, the decomposition of H_2O under the influence of free radical H to generate H_2. With the increase of the gas concentration, the promotion effects of R53 and R58 on H_2 formation becomes more and more obvious , while the effects of R3 consuming H2 is getting smaller and smaller, resulting in the increments of H_2 generation quantity after gas explosion. The analysis result also reveals that the existence of water vapor in the explosion



（a） 6%CH_4 （b） 7% CH_4 （c） 9% CH_4

（d） 11%CH_4 （e） 13% CH_4 （f） 15% CH_4

Fig. 5 Key basic element reaction step of gas explosion H_2



（a） 6%CH_4 （b） 7% CH_4 （c） 9% CH_4

（d） 11%CH_4 （e） 13% CH_4 （f） 15% CH_4

Fig. 6 Trend of free radical change in gas explosion process environment would accelerate H_2 generation.

Through the analysis of R3, R53, R58, R84, R126, it could be known that the higher proportion of free radical H there is, the smaller proportion of free radical O and OH is, therefore, the more amount of H_2 generation is from the explosion reaction. The changes of free radical H, O and OH in different gas concentrations during methane explosion process are drawn in Figure 6.

According to Figure 6, with the increase of the concentration of gas explosion, the mole fraction of free radical O and OH increased firstly in the enclosed space, it reaches the maximum at the 9% gas concentration, and then gradually decreased. The mole fraction of free radical H gradually increased, and then decreased slightly at the 15% gas concentration , and the free radical H is gradually increasing in the overall ratio of free radical H, OH and O. It shows that the proportion of free radical H is proportional to the amount of H_2 generated during the gas explosion.

EXPERIMENTAL STUDY ON GAS EXPLOSION

The numerical simulation of gas explosion shows that the higher the concentration of gas explosion is, the more incomplete the reaction is. And the amount of H_2 generated is greater. In order to analyze the reliability of simulation, this paper makes a comparative study on the numerical simulation results by measuring the variation of the gas concentration about H_2, CO and CO_2 in different gas concentrations.

EXPERIMENTAL DEVICE

The experimental devices are shown in Figure 7, which is mainly composed of explosion cavity, gas distribution device, ignition device, explosion control device and data acquisition device. The main body cavity is a 20L steel ball, which is composed of 3 parts, the cylinder, the top cover and the bottom cover. An observation hole is arranged on the cylinder body, and the internal gas explosion phenomenon can be observed through the observation hole. The air distribution device is mainly composed of a gas cylinder, a pressure reducing valve, a pressure stabilizing valve, a flow meter and a connecting gas path. The gas distribution are controlled the flow rate of different gases. The experiment used electric spark ignition, the ignition device can produce two kinds of strength of electric spark with energy 12J and 2J respectively. And a strong electric spark was used to carry out ignition during the experiment. Explosion control device is mainly to control the ignition energy and time, the sampling system, the system security .

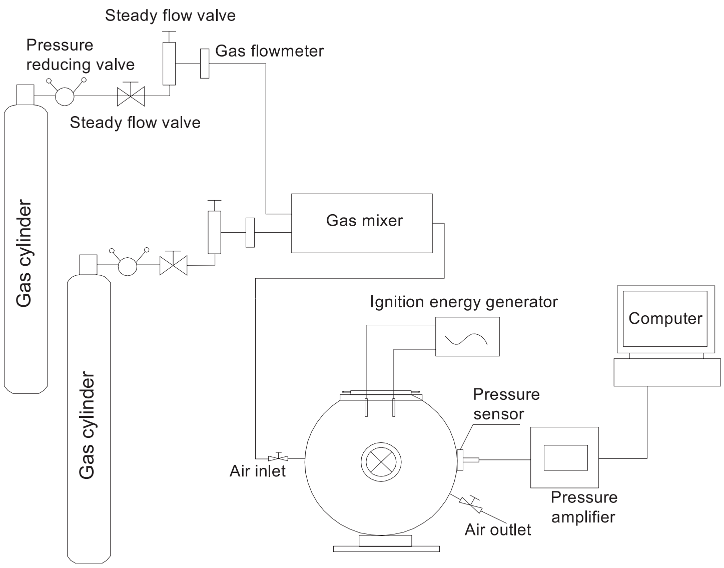


Fig. 7 The device of explosion experiment

EXPERIMENTAL PROCESS

Methane and air flows from the cylinder through pressure reducing valve, pressure srabilizing valve, flow valve successively into the mixing chamber in fixed air ratio. The mixed gas fills with explosive cavity, which is detonated by electric spark. The pressure generated by explosion acts on the pressure sensor inside the explosion tube and is converts to electronical pressure signal. When the pressure exceeds the original pressure by 7%, it indicates that the explosion experiment was successful. Then make analysis of gas collected through the air exhaust vent with gas chromatograph.

In order to analyze the variation of H_2, CO_2 and CO after gas explosion at different gas volume fractions, 6 groups of gas explosion experiments were carried on with gas concentrations of 6%, 7%, 9%, 11%, 13%, 15% respectively.

EXPERIMENTAL RESULTS AND ANALYSIS

According to the results of different volume fraction in the gas explosion experiment, the change regulations of H_2, CO and CO_2 with the variations of gas volume fraction are shown in Figure 7, and the ratio of CO/ (CO+CO_2) is plotted in Figure 8.

By observing Figure 7 and Figure 8, it could be seen that when the concentration of CH_4 is lower than 9%, only small amounts of CO and H_2 production is produced. The main gas products are CO_2, so the calculation results of CO/(CO+CO_2) is nearly 0, which means the gas explosion is completely reaction. When the gas concentration is higher than 9%, the volume fraction of CO_2 decreases gradually, while the amount of H_2 and CO increased rapidly, and CO/(CO+CO_2) increased gradually, which shows that the degree of incomplete reaction of gas explosion is increasing gradually. The results are consistent with the trends of numerical simulation data, which shows that the formation of H_2 during gas explosion is mainly due to the incomplete reaction of gas explosion.

Through the comparison of experimental data of methane explosion generating H_2 and numerical simulation calculation data, it could be found that the results of simulation value is relatively higher. The deviation is mainly because the difference between experimental conditions and simulation conditions. In the numerical simulation it assumed confined space as an ideal diabetic environment, and the reaction rates are the same in every location in the calculation area with no temperature gradients and concentration gradients. Therefore, the calculation of explosion process is complete reaction, resulting in the simulation data is higher compared with practical experimental

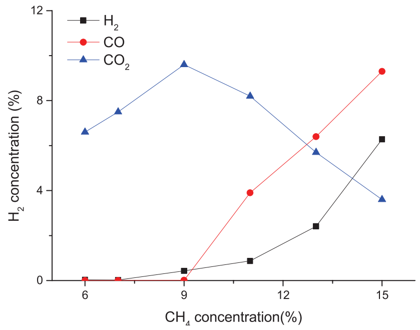


Fig. 8 Trend of gas product after gas explosion

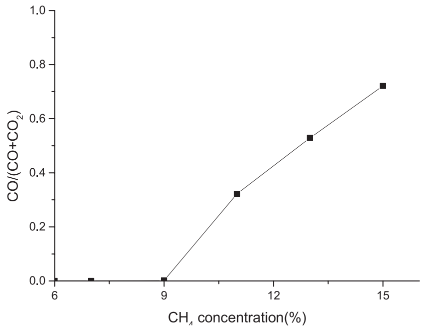


Fig. 9 change trend of $CO/(CO+CO_2)$

CONCLUSIONS

In this paper, the H_2 change rules and mechanism of gas explosion are firstly simulated with Chemkin, then the calculation results are verified by gas explosion experiment. The following conclusions are obtained:

(1) R84 is the greatest impact on H_2 generation in the process of gas explosion reaction, that is, the decomposition of water vapor is the main reason for the formation of H_2. The free radical H is the key factor to accelarate the H_2 formation and free radicals OH and O are the inhibiting factors for H_2 formation. With the increase of concentration of gas explosion, the explosion reaction is more incomplete, and the proportion of free radical H increases gradually. At the same time, free radical O and OH gradually decreases, resulting in a gradual decrease in the amount of H_2 consumption and gradual increase in the amount of H_2 formation.

(2) The experimental results of gas explosion are consistent with the changing trends of H_2, CO and CO_2 in simulation calculation. The experimental results show that the reaction of gas explosion is more sufficient when the concentration of gas explosion is lower than 9%, and the amount of H_2 generation is relatively small. When the gas concentration is higher than 9%, the degree of incomplete reaction of gas explosion process will increase gradually, leading to the gradual increase in the amount of H_2 generation. Therefore, high concentration of H_2 is mainly caused by the incomplete reaction of high concentration of gas explosion.

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