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Effect of hydrogen on explosion of methane-air mixture

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ABSTRACT
Gas explosion is one type of coal mine accidents in China. The main composition of the gas in coal seam is methane, but hydrogen is contained in some coal seams and increases the risk of gas explosion. The main reaction path of methane-air mixture explosion process and elementary reactions characteristics at high temperature are analyzed using detailed mechanism of methane combustion. Different fraction of H_2/CH_4/Air mixture explosion is simulated, and temperature, pressure, mole fraction of different species and elementary reactions rate are analyzed. The simulation results show that hydrogen will reduce the priming induction period of gas explosion and has influence on the temperature and pressure of gas explosion.
KEYWORDS: hydrogen; methane-air explosion; hydrogen; elementary reaction; induction time; reaction rate

1. INTRODUCTION

Gas is produced in the process of coal-forming. The main component of gas all over the world is methane, and there are also C_2H_6, C_3H_8 and other combustible gases of heavy hydrocarbon in some coal seams (Zhou,1999) . In addition, there is a small amount of hydrogen in some coal seam because thermal decomposition of coal at a high temperature (Yu and Wang, 2005). Meanwhile, combustible gases of CO, C_2H_4, C_2H_6, C_3H_8, etc. are produced in the process of coal spontaneous combustion (Xiao et al., 2007; Zhang, 2000). So in addition to main specie methane, there may be a small amount of H_2, CO, C_2H_4, C_2H_6 and C_3H_8 and other combustible gases in coal seam. Explosion limits and severity of gas mixture explosion depends on species and fraction of the gas mixture. Combustible gas mixture in methane will influence explosive limits and increase risk of explosion (Pan et al., 2008; Guo, 2002).

Although there is a little hydrogen in methane, risk of explosion can increased greatly because lower explosive limit (LEL) of hydrogen is very low compared to methane. H_2/CH_4/Air mixtures have lower LEL compared to CH_4/Air methane when mole fraction of CH_4 is same, and it is easy to explode. Explosion power and explosion hazard will increase even if there is little hydrogen in CH_4/Air mixture (Ma, 2015).

Many research had been carried out on explosion characteristic of H_2/CH_4/Air mixture(Li et al.2008; Shrestha,1999).Ma(2015) showed in their publication that temperature and pressure of H_2/CH_4/Air mixture explosion is very different when using different mixing ratios. Pan et al. (2008) demonstrated that hydrogen influences LEL of H_2/CH_4/Air mixture and can increase explosion risk. Luo et al. (2015) showed in their publication that combustion gas CO, H_2, C_2H_4 and C_2H_6 affect explosion limit of CH_4/Air mixture. Ren et al. (2013) conducted methane explosion experiment and found that explosion limit range was extended with fraction of H_2S, CO and H_2 increasing. Jia et al. (2016) analyzed effects of different concentration CO and H_2 mixture on the gas explosion by numerical analysis. Hu et al. (2010) analyzed pressure waves of H_2/CO/CH_4/air mixture explosion and found that hydrogen is key element affecting the explosion. Mahdi et al. (2016) obtained maximum pressure rise rate and deflagration index of methane, hydrogen and their mixtures and examined influence of equivalence ratio, initial temperature and initial pressure on the maximum pressure rise rate and deflagration index. Li et al. (2012) found that the presence of molecular hydrogen yield from coal spontaneous heated process would significantly increase the maximum explosion pressure and pressure rise rate of H_2/CH_4/air mixtures. Li et al. (2015) carried out the explosion experiments of hydrogen/air and methane/air for different gas volumes and found that the flame propagation speed of hydrogen/air explosion is higher than that of methane/air, while the flame duration of methane/air is longer than that of hydrogen/air.

In this paper, the influence of combustible gas hydrogen in coal mine on the explosion mixture of methane air was studied using the chemical kinetic software CHEMKIN. Pressure, temperature and free radicals of mixture gas explosion are analyzed, and

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the influence of the mixed combustible gas on methane-air mixture explosion is obtained. CHEMKIN developed by Sandia laboratory and Kee R.J et al. can solve the problem of gas-phase chemical reaction in the combustion process. Subroutine of Senkin is used in this simulation. Senkin is a Fortran computer program block, which can simulate the tendency of premixed homogeneous gas reaction with time charge in a closed container (Li, 2011). Detailed chemical reaction mechanism of H2/air mixture is relatively simple, which is included in GRI-Mech 3.0, so the simulation of H_2/CH_4/air mixture explosion reaction is calculated by data files GRI-Mech3.0.

2. CHARACTERISTICS OF CH_4/AIR MIXTURE EXPLOSION

2.1 The Main Elementary Reaction of CH_4/air Mixture Explosion

Methane has a tetrahedron molecular structure and bond energy of C-H, which make methane oxidation process complex (Stephen, 2015). In the early 20th century, people have confirmed that all gas phase reaction are conducted by a series of elementary reaction, the complex chain reaction of gas explosion reaction is composed of the elementary reaction (Lin et al., 2013). At present, there are more than a dozen of detailed chemical mechanisms, but methane combustion reaction mechanism by the Lawrence Livermore National Laboratory is generally accepted, which includes 53 species and 325 elementary reactions. Methane combustion process is very complex, but there is only one key oxidation path, and some key elementary reactions.

According to detailed mechanism, in the process of gas explosion, elementary reactions $H+CH_3(+M)=CH_4(+M)$ and $HO_2+CH_3=O_2+CH_4$ produce free radicals and initiate reaction. When initial temperature is low, $HO_2+CH_3=O_2+CH4$ initiate reaction mainly, and $H+CH_3(+M)=CH_4(+M)$ initiate reaction mainly when the initial temperature is high. Lin et al. (2012)shows that when temperature is more than 2000T, explosion is initiated by $H+CH_3(+M)=CH_4(+M)$ only.

CH_4 is mainly consumed by following three reactions: $H+CH_4=CH_3+H_2$, $OH+CH_4=CH_3+H_2O$ and $O+CH_4=OH+CH_3$.Compared with H and OH, amount of CH4 consumed by O is much smaller (Peter, 1985). So $O+CH_4=OH+CH_3$ is less important compared with other two reactions. CH_3 is mainly oxidized by the following reactions: $O+CH_3=H+CH_2O$, $OH+CH_3=CH_2(S)$ $+H_2O$, $OH+CH_3=CH_2+H_2O$ and $HO_2+CH_3=OH+CH_3O$. Compared with OH and HO_2, CH_3 is mainly consumed by reaction with O. Combination reaction of $CH_3+CH_3=C_2H_6$ generates hydrocarbon of C_2 series, which is important when CH_4 is rich. CH_2O is mainly oxidized by the two reactions $H+CH_2O=HCO+H_2$ and $OH+CH_2O=HCO+H_2O$. HCO is mainly oxidized by the two reactions HCO+M=H+CO+M and $HCO+O2=HO_2+CO$. CO is oxidized essentially by the reaction $OH+CO=H+CO_2$, and the reaction of CO with O and O_2 can be in general neglected. The consumption of oxygen and the formation of radical by the reactions $H+O_2=OH+O$, $OH+H_2=H+H_2O$, $2OH=O+H_2O$ and $O+H_2=H+OH$. The last three of these are linearly dependent. Reaction $H+O_2=OH+O$ is very important as a chain branching reaction since it produces more radicals than it consumes. Finally, chain breaking occurs mainly through three body reactions $H+O_2+M=HO_2+M$ and $H+OH+M=H_2O+M$.While other recombination reaction can be neglected.

2.2 Heat Production of Elementary Reaction

In a reaction, energy produced by old chemical bond breaking and new chemical bond forming can cause heat release. In the process of gas explosion, lots of elementary reaction release heat for a second, which cause temperature and pressure rise immediately and lead to disaster.

Detailed mechanism includes 325 elementary reactions. Some absorb heat and some release heat .Because all the reaction is reversible, a reaction may release heat and absorb heat in different time. But release heat or absorb heat can be identified by positive and negative of a reaction total heat release. Except for 106 elementary reactions which nitrogen oxides participate in, there are 175 heat release reactions and 44 heat absorption reaction during the process of gas explosion. In the process of gas explosion, chain initiation elementary reactions absorb heat when meeting heat source, and produce free radical. So at first, gas explosion system absorbs heat. And then lots of elementary reactions release heat, and there is a peat point of heat release.

CHEMKIN software and closed homogeneous model are used to simulate heat release of mixture CH_4/Air explosion. Initial temperature is 1300K, and initial pressure is 1atm.Reactor volume is 1cm^3, and mole fraction of CH4 is 0.095.

Fig.1 shows system heat releases at different time during explosion process. The total heat release is 0.5124J. Fig.2 shows top ten total heat release of different elementary reactions. In the process of gas explosion, reaction $HCO+O_2=HO_2+CO$ 、 $O+CH_3=H+CH_2O$ and $CH_3(+M)=C_2H_6(+M)$ are top three heat release reactions.The total heat releases of the three release is 0.0489J、0.0435J and 0.0358J respectively. Total heat release of the three releases account for more than twenty percent of system total heat release.Key absorbtion heat release reaction is $H+O_2=O+OH$, total heat release is 0.072J.

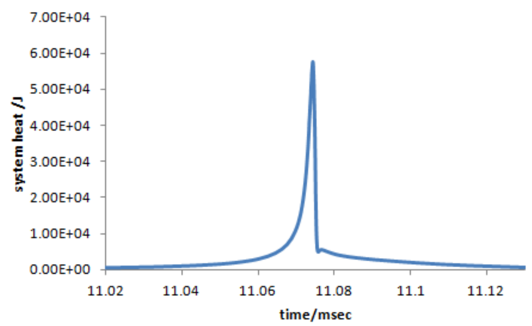

Figure 1: System heat releases at different time

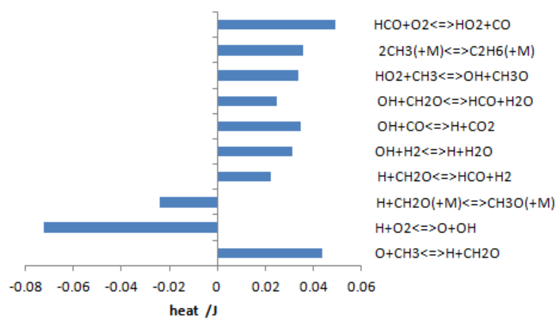

Figure 2: Total heat release of different elementary reactions

3. CHARACTERISTICS OF H_2/CH_4/AIR MIXTURE EXPLOSION

3.1 Characteristics of H_2/CH_4/air Mixture explosion

Considering actual situation, when designing simulation schemes, mole fraction of hydrogen in every scheme should be small because there is little hydrogen in coal seams. Five schemes are designed in the simulation, as is shown in Tab.1. In the five schemes, mole fraction of methane is 8%, mole fraction of hydrogen are 0, 0.5%, 1%, 2% and 4% respectively. Air is assumed consisting of 79% nitrogen and 21% oxygen by volume.

Table 1: Mole fraction of each species of five schemes

species	1	2	3	4	5
CH_4	0.08	0.08	0.08	0.08	0.08
O_2	0.1932	0.19215	0.1911	0.189	0.1848
N_2	0.7268	0.72285	0.7189	0.711	0.6952
H_2	0	0.005	0.01	0.02	0.04

CHEMKIN software and closed homogeneous model are used to do the simulation. Initial temperature is 1300K, and initial pressure is 1atm.

Tab.2 shows max temperature, pressure and percentage increase of temperature and pressure of the five schemes. Max temperature and pressure increase with increase of mole fraction hydrogen, but percentage increase is low. When mole fraction of hydrogen is 4%, percentage increase of temperature and pressure are 2.79% and 2.24% respectively.

Table 2: Max temperature, pressure and percentage increase of temperature and pressure

schemes	1	2	3	4	5
Temperature(K)	2776	2787	2798	2819	2853
Temperature Percentage increase(%)	-	0.41	0.8	1.53	2.79
Pressure(atm)	2.20	2.21	2.21	2.23	2.25
Pressure Percentage increase (%)	-	0.33	0.65	1.24	2.24

Fig.3 shows explosion induction of the five schemes. As can be seen from Fig.3, induction time decreases with the increase of initial hydrogen concentration. Percentage decreases are 45%, 64%, 81% and 92% respectively when the mole fractions of hydrogen are 0.5%, 1%, 2% and 4%.Hydrogen influence induction time of explosion greatly. When there is little hydrogen in CH_4/Air, induction time will change greatly.

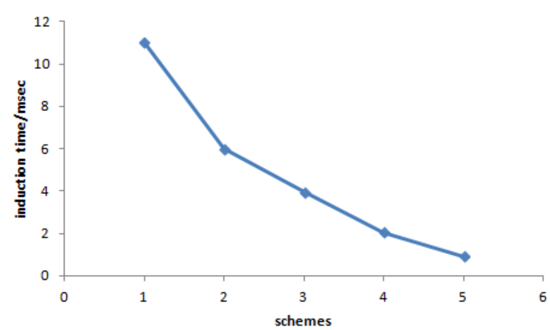

Figure 3: Explosion induction time of the five schemes

Fig.4-Fig.6 is the main free radical change curve with time of different schemes. As is showed in Fig.4-Fig.6, when explosion occurs, the mole fraction of each free radical increases for a section and reaches the peak point, and then decreases rapidly to a stable condition. The mole fraction of O reduces slightly with H_2 increasing. Because with hydrogen increasing, the reactions rate of $O+H_2=H+OH$ and $OH+H_2=H+H_2O$ increase, and H increase, which cause chain reaction rate of $H+O_2=O+OH$ increase.

Because OH is mainly produced by the reaction $H+O_2=O+OH$, free radical OH increase. But with the increase of hydrogen content, the total content of oxygen in the mixture decreased slightly, so the O produced by the explosion is slightly reduced, which cause the rate of OH increase less than H.

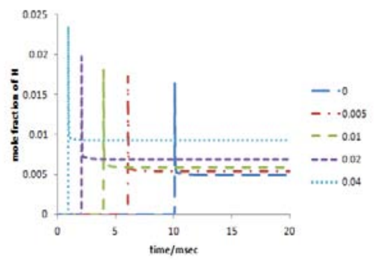

Figure 4: Time-H curve of different hydrogen mole fraction

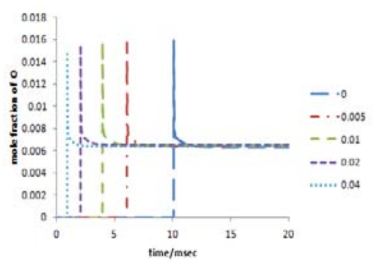

Figure 5: Time-O curve of different hydrogen mole fraction

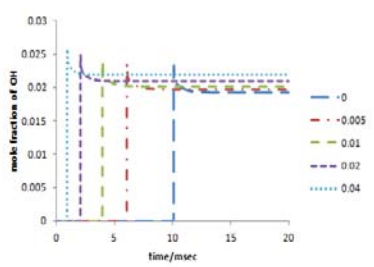

Figure 6: Time-OH curve of different hydrogen mole fraction

The free radicals of CH_3, CH_2O, and HCO reach the maximum value at the moment of explosion, and then reduced instantly to zero after the explosion, the process is very fast. Fig.7 is the maximum mole fraction CH_3, CH_2O, and HCO of different scheme during explosion. Fig.7 shows that mole fraction of CH_3 and HCO increase with the increase of hydrogen concentration, but mole fraction of CH_2O reduce reduces with the increase of hydrogen concentration. Because CH_4 is mainly oxidized by the reaction $H+CH_4=CH_3+H_2$.And in the reaction, CH_3 will be produced. Because mole fraction of H increases with the increase of hydrogen concentration, mole fraction of CH_3 will increase too. CH_3 is mainly oxidized by the reaction $O+CH_3=H+CH_2O$. With the increase of H_2 content, the content of O decreases, so the CH_2O generated by the explosion is reduced. Oxidation reaction of CH_2O is mainly reacted by the elementary reaction $H+CH_2O=HCO+H_2$. Mole fraction of H increase lead to the reaction rate of $H+CH_2O=HCO+H_2$ increasing, so mole fraction of HCO increase.

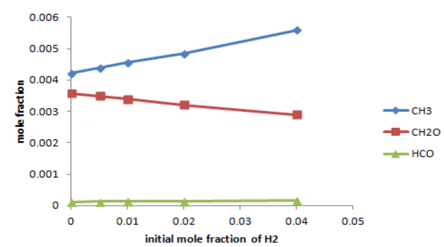

Figure 7: Max mole fraction CH_3, CH2O, HCO of different hydrogen mole fraction

Final products of explosion are mainly CO, CO_2 H_2O, and the mole fractions of each product are not the same. In the explosion, the mole fraction of H_2O and CO_2 reaches the maximum value at the moment of the explosion and then remains the same; but the mole fraction of CO reaches the maximum value at the moment of the explosion and then reduces to a certain value. Therefore max mole fraction of H_2O and CO_2 of each scheme are analyzed, as is shown in Fig.8, but mole fraction of CO varying with time is analyzed, as in showed in Fig.9.

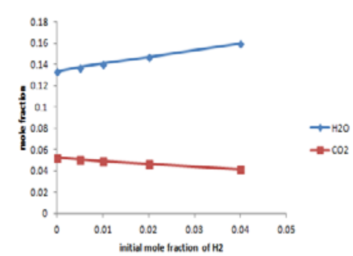

Figure 8: Max mole fraction of H_2O, CO_2 of different hydrogen mole fraction

Fig.8 shows that mole fraction of H_2O increases with the increase of hydrogen, but CO_2 decreases. As showed in Fig.9, the maximum value of CO is almost same at the moment of explosion, but final value of CO decreases with the increase of hydrogen. Because H_2O is mainly produced by the elementary reaction $OH+H_2=H+H_2O$ and CO is mainly oxidized by the elementary reaction $OH+CO=H+CO_2$, and they compete for OH. Therefore, reaction rate of $OH+H_2=H+H_2O$ increases and $OH+CO=H+CO_2$

decreases with hydrogen increasing, so mole fraction CO_2 will decrease

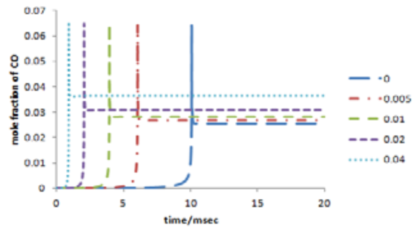

Figure 9: Time-CO curve of different hydrogen mole fraction

Fig.10 is the maximum values of main elementary reactions rate. As shown in Fig.10, the reaction rate of each elementary reactions increase with the increase of hydrogen concentration, so hydrogen can improve mail elementary reaction rate in if there are some hydrogen in methane-air mixture.

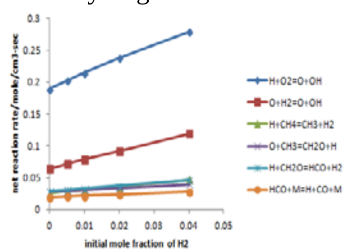

Figure 10: Maximum rate of main elementary reaction of different hydrogen mole fraction

3.2 Effect of hydrogen to gas explosion

Gas explosion which is a kind of special reaction is the chain reaction, and is also called the linked reactions. These reactions include free atoms or radicals. Free radicals are unpaired electron atoms or groups. Besides, it has a highly reactive chemical speciation, which can react with other molecules and form new free radicals, and the new free radicals quickly take part in the reaction to produce other new free radicals. These processes link together closely, until reactions come to end. Chain reactions include the straight chain reaction and the branched chain reaction. Gas explosion is branched chain reaction.

In the process of explosion, breakup reaction are $H+CH_3(+M)=CH_4+CH_3(+M)$ and $HO_2=O_2+CH_4$, this reaction forms actively free radicals which can causes and accelerates explosion reaction, but rate of the two chain initial reaction are slow, so the gas explosion needs a certain induction period. The oxidation rate of methane to form hydrogen is slow, because CH_4 need dehydrogenation at first, then through a series of elementary reaction to form hydrogen. The gas explosion branched chain reaction will be accelerated if there are hydrogen in it. For example $H_2+M=H+H+M$, $O+H_2=H+OH$ and $H+O_2=O+OH$ et al.. These branched chain reactions make the mole fraction of free radicals O, OH and H increase in geometry level, and will accelerated the explosion. Therefore, induction period of explosion will be shorter if there is some hydrogen in methane-air mixture

The mail oxidation path of methane-air explosion are through the elementary reactions $H+CH_4=CH_3+H_2$, $O+CH_3=CH_2O+H$, $H+CH_2O=HCO+H_2$ and $OH+H_2=H+H_2O$, the rate of which are influenced by hydrogen and rate of these reaction will increase with the increase of hydrogen concentration. Max temperature and pressure are not influenced very much by hydrogen because low heat release of hydrogen explosion. Besides, some oxygen is used in the process of hydrogen oxidation, which causes lower oxidation degree of CH_4.

4. CONCLUSIONS

(1) Main oxidation path of methane-air explosion is CH_4-CH_3-CH_2O-HCO-CO-CO_2. Except for 106 elementary reactions which nitrogen oxides participate in, there are 175 heat release reactions and 44 heat absorption reaction during the process of gas explosion. $HCO+O_2=HO_2+CO$ 、 $O+CH_3=H+CH_2O$ and $CH_3(+M)=C_2H_6(+M)$ are top three heat release reactions.

(2) If there are some hydrogen in methane-air mixture, branch chain reactions $O+H_2=H+OH$ and $H+O_2=O+OH$ will be accelerated in the process of explosion, and will produce more active free radicals, which will accelerate other main elementary reactions. Rate of main reaction of explosion will be increased

(3)Hydrogen influences induction period of H_2/CH_4 /Air explosion greatly. And with the mole fraction of hydrogen increase, the induction period will be shorter. But hydrogen has little influence on max temperature and pressure.

5. ACKNOWLEDGEMENTS

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