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Chemical kinetic characteristics of methane/air mixture explosion and its affecting factors

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ABSTRACT

Gas explosion in coal mines caused a large number of deaths, injuries and property losses. Gas explosion still happens occasionally in recent years. It is known that most people died from CO poisoning in gas explosion. But the details of toxic gases produced and their impacts on people need further investigation. In order to study the products and species in gas explosion, an analysis of chemical kinetic characteristics was conducted using CHEMKIN III with detailed mechanism (GRI-Mech3.0) package. A closed homogeneous 0-D reactor was adopted to investigate the kinetic behavior of gas explosion. The initial conditions were set, similar to those in the real tunnel environment. The profiles of four reactants, toxic gases and free radicals were obtained. The threshold values of people exposed to different poisonous gases were analyzed to study their impacts on people. Sensitivity analysis of key elementary reaction to free radical was performed to find possible reactions which can suppress gas explosion. The results show that the ignition delay time is the longest at fuel-rich condition. The O_2 concentration decreases from 19% to 2% at stoichiometric ratio, which could not support normal respiration after explosion. It is found that the concentration of CO ranks the highest among the four toxic gases. Toxicity analysis indicates that those exposed to such condition will soon die of asphyxia. This is consistent with the accident investigation findings that the majority of fatalities result from inhalation of CO. The concentration of CO at fuel-rich condition is higher than that at fuel-lean condition. The relationship between the final free radical concentration and initial CH_4 concentration exhibits a reverse U shape. Sensitivity analysis reveals that free radicals are mostly sensitive to the intermediate reaction R156 (forward direction) and R158 (reverse direction). It provides a possible direction to research the corresponding chemicals for gas explosion suppression. This work would provide theoretical support for gas explosion suppression technology and decision-making of personal protection in rescuing trapped coal miners. It is of great importance for developing suppression chemicals of gas explosion.

1. Introduction

Methane-air mixture is life-threatening particularly in underground coal mines, which is considered as a huge risk source worldwide (Kundu et al., 2016). China has suffered from 25 accidents that separately caused more than 100 deaths since 1949 in underground coal mines, 21 of which resulted from gas explosion or gas/coal dust explosion. Gas explosion leads to macroscopic impact and the secondary disaster. Much attention has been paid to the flame acceleration, shock wave propagation, maximum overpressure and the deflagration to detonation transition (DDT) (Nie et al., 2015; Wang et al., 2015; Wang et al., 2016; Wen et al., 2012). This work aims at the physical aspects such as flame and shock wave velocity and maximum pressure which damage the facilities and tunnel roofs. Some studies focus on the prevention and mitigation of gas explosions. There have been a lot of proven ways to mitigate gas explosion severity, such as using inert gas or powder injection, water mist spray, wire mesh and foam ceramics obstruction (Ciccarelli, 2012; Nie et al., 2011; Pei et al., 2016; Ranganathan et al., 2015). The suppression effect of CO_2 dilution on gas explosion is calculated using chemical kinetic method (Hu et al., 2014). At the same time, the suppression mechanism of

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Table 1
Initial conditions.

case	Initial temperature (K)	Initial pressure (atm)	Mole fraction			Time (s)
			CH_4	O_2	N_2	
1	1200	0.9	0.0600	0.1974	0.7426	0.1
2	1200	0.9	0.0800	0.1932	0.7268	0.1
3	1200	0.9	0.0950	0.1900	0.7150	0.1
4	1200	0.9	0.1100	0.1869	0.7031	0.1
5	1200	0.9	0.1400	0.1806	0.6794	0.1

these methods remains to be studied.

The chemical kinetic calculation software, CHEMKIN, provides a useful method to study gas explosion mechanism and its affecting factors. The detailed mechanism GRI-Mech 3.0 is widely acknowledged due to its reliability in predicting methane explosion reaction. The proposed detailed kinetic mechanism was used to calculate the ignition delay time and laminar flame speed (Basevich et al., 2015). Three chemical kinetic mechanisms of CH_4 combustion were studied by Ennetta. One-step global reaction mechanism, four-step mechanism and the standard detailed scheme GRIMECH 3.0 were used to study the differences of methane combustion in internal combustion engine. It was found that the four-step mechanism was in agreement with the detailed mechanisms in predicting temperature and main species profiles (Ennetta et al., 2008). A kinetic software, Dsmoke, was used to predict the kinetics of natural gas cracking (Rodat et al., 2009). It was discovered that the CH_4 oxidation paths depended on combustion temperature (Loeffler et al., 2002). Many studies have paid attention to the differences between detailed and reduced mechanisms in predicting combustion. The profiles of products and free radicals generated in gas explosion were obtained (Mansha et al., 2010a,b). Few literature reported the effects of toxic products on the underground miners. The influence mechanism of intermediate reaction on free radicals is also rarely investigated in detail.

The objective of this work is to obtain the variation of toxic gases against time and find out the interaction between harmful gases and human body in underground situation. Thus the initial pressure is set to be negative which is similar to the actual environment. The key elementary reactions and the affected free radical formation are expected to be carried out. The determined intermediate reactions will provide a further understanding of suppressing mechanism and a guidance to research the chemicals for gas suppression. Some factors that have influence on gas explosion are also analyzed. This work proposes the possibility of gas explosion prevention method.

2. Modeling details

The gas explosion process is calculated by CHEMKIN III Pro using GRI-Mech 3.0 mechanism (Smith et al.), which contains 325 reactions and 53 species. In this study, we focus on the hazardous products and intermediate free radicals. A closed homogeneous 0-D reactor is adopted to investigate the kinetic behavior of gas explosion. The gas in the reactor is isolated from exterior, thus there is no exchange of mass or energy (adiabatic).

2.1. Governing equations

The species equation is as follows:

Table 2
Relationship between hypoxia symptoms and the O_2 concentration in the air.

O_2 concentration/%	Symptoms
17	Faster, deeper breathing
15	Dizziness, buzzing in ears, rapid heart beat
13	May loss consciousness if exposure prolonged
9	Fainting, unconsciousness
7	Life endangered
6	Convulsive movements, death

$$\frac{dY_i}{di} = \nu \dot{w}_i W_i \quad (i = 1, 2, 3, \ldots, k_g) \tag{1}$$

where Y_i and W_i represent the mass fraction and molecular weight of species i. ν denotes specific heat capacity of mixture. k_g is the total number of species. N_g is the reaction steps number. w_i is the reaction rate of species i, given by

$$\dot{w}_i = \sum_{k=1}^{N_g} \nu_{ik} k_{fk} \prod_{i=1}^{k_g} X_j^{\nu'_{ik}}, \quad (i = 1, \ldots, k_g). \tag{2}$$

(X_j) denotes the mole fraction of species j. t represents time. K_{fk} is the positive reaction rate constant of elementary reaction steps k. K_{fk} is given by Arrhenius function:

$$k_{fk} = A_k T^{bk} \exp\left(\frac{-E_{ak}}{RT}\right) \quad (k = 1, \ldots, N_g) \tag{3}$$

where A_k and b_k are the pre-exponential factor and thermal constant of positive reactions k, respectively. T is the temperature of the mixture, E_{ak} is activation energy of reactions k. R is mixed gas constant.

Energy equation:

$$c_\nu \frac{dT}{dt} + \nu \sum_{i=1}^{k_g} e_i \dot{w}_i W_i = 0 \tag{4}$$

where c_v is constant-volume specific heat, and e_i stands for the internal energy of species i.

2.2. Sensitivity analysis

It is assumed that the variable Z, which can be expressed as,

$$\frac{dZ}{dt} = F(Z, t, a) \tag{5}$$

where $Z = (Y1, Y2, \ldots, Y_{kg})$ is the mass fraction of species k_g. $a = (A1, A2, \ldots, A_{Ng})$ represents pre-exponential factor.

As the value of reaction changes, the corresponding mass fraction varies. Sensitivity analysis is to determine the extent of

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