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Effects of C_2H_4 on chemical kinetic characteristics of CH_4-air explosion

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Abstract. There is a small amount of other flammable gases other than the major constituent of methane in mine gas. The flammable gases have critical effects on gas explosion. Appropriate understandings of the effects of flammable gases on chemical kinetic characteristics of CH_4-air explosion are essential to prevent and control gas explosion in mine. Therefore, the numerical simulations are conducted through the software of CHEMKIN to investigate the effects. The present study is mainly to analyse the variation of the pressure, temperature, products, free radicals and sensitivity of CH_4 in the process of the gas explosion after addition of C_2H_4. The results obtained show that the addition of C_2H_4 makes the explosion time shorter, maximum explosion pressure and maximum explosion temperature larger, that the addition of C_2H_4 contributes to the increase of the product of CO and the decrease of NO and NO_2, and makes CO_2 increase first, and then decrease, and that the addition of C_2H_4 can improve the gas explosion due to the fact that the addition of C_2H_4 has a great effect on the reaction #38 and #119, making the two reaction dominant, thereby generating a large number of free radicals.

1. Introduction

Gas explosion has always been one of the most major disasters in coal mines. Not only does it usually cause a large number of deaths, injuries and property losses, but it leads to the secondary disaster, so gas explosion is also considered as one of the most severe. In recent years, gas explosion still happens occasionally. How to prevent and control gas explosion in mine effectively and efficiently, therefore, becomes a critical problem which should be solved quickly. A great number of researches are performed by scholars at home and abroad to resolve this problem. Much attention has been paid to the blast-pressure evolution [1, 2], flame propagation [3, 4], explosion venting [5, 6], and the influences of obstacles on CH_4 explosion [7-9]. It can be concluded that these work aims at the physical aspects and focused on the explosion characteristics of CH_4-air mixtures. 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 [10, 11]. Despite the extensive researches of gas explosion conducted by scholars at home and abroad, few people study the effect other flammable gases on gas explosion. As we all know, mine gas is a mixture of gases and there is a small amount of other flammable gases other than the major constituent of methane. Many studies have shown that the content of the flammable gases is very small, but they have a critical influence on gas explosion. Besides, mixing CH_4 with other combustible gases is often inevitable in some processes of chemical production, so

from this viewpoint to ensure safety in production, it also is necessary to investigate the influences of the flammable gases on gas explosion.

CHEMKIN is a powerful software system to solve complex chemical kinetics problems, which 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. To investigate the effects of C_2H_4 on the chemical kinetic characteristics of CH_4-air explosion, the numerical simulations are conducted through the software of CHEMKIN with GRI-Mech 3.0 mechanism. In the present work, we focus on the influence of C_2H_4 on the chemical kinetic characteristics of CH_4-air explosion. The variation law of reactants, products, free radicals and sensitivity of CH_4 in the process of gas explosion are analyzed. The aim of the present study is to reveal the law of influence of C_2H_4 on the chemical kinetic characteristics of CH_4-air explosion, to help the rescuer establish rescue strategy to prevent them from injury and to explain gas explosion from chain reaction theory, thereby providing theoretical guidance for preventing and controlling mine gas explosion effectively and efficiently.

2. Modeling details

The CHEMKIN software is employed to calculate the gas explosion process with GRI-Mech 3.0 mechanism, which contains 325 reactions and 53 species, and 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, and thus there is no exchange of mass or energy (adiabatic).

2.1. Governing equations

The species equation is as follows:

$$\frac{dY_i}{dt} = v\dot{w}_i M_i \qquad (\, i = 1, 2; 3, \ldots, K_g) \tag{1}$$

where Y_i and M_i represent the mass fraction and relative molecular mass of species i respectively; t and v denote time and specific heat capacity of mixture; K_g is the total number of species. w_i is the reaction rate of species i and N_g is the number of reaction steps, given by

$$\dot{w}_i = \sum_{k=1}^{N_g} v_{ik} k_{fk} \prod_{j=1}^{K_g} (X_j)^{v'_{ik}} \qquad (\, i = 1, 2; 3, \ldots, K_g) \tag{2}$$

where (X_j) denotes the mole fraction of species j; K_{fk} is the positive reaction rate constant of elementary reaction steps k.

K_{fk} is given by Arrhenius function:

$$k_{fk} = A_k T^{b_k} \exp\left(\frac{-E_k}{RT}\right) \qquad (\, k = 1, 2; 3, \ldots, N_g) \tag{3}$$

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_k is activation energy of reactions k. R is mixed gas constant.

Energy equation:

$$c_v \frac{dT}{dt} + v \sum_{i=1}^{k_g} e_i \dot{w}_i M_i = 0 \qquad (\, i = 1, 2, 3, \ldots, N_g) \tag{4}$$

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 can be expressed as:

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

where $Z = (Y_1, Y_2, \ldots, Y_{kg})$ is the mass fraction of species k_g; $a = (A_1, A_2, \ldots, A_{Ng})$ represents pre-exponential factor.

As the value a of reaction changes, the corresponding mass fraction varies. Sensitivity analysis is to determine the extent of variation of species fraction which is dependent on value a. The coefficient of sensitivity can be expressed as:

$$w_{l,i} = \frac{\partial Z_l}{\partial a_i} \tag{6}$$

where Z_l is the variable number l, and a_i is the pre-exponential factor of reactions i. To differentiate Eq. (6) with regard to a_i yields:

$$\frac{dw_{l,i}}{dt} = \frac{\partial F_l}{\partial Z} W_{l,i} + \frac{\partial F_l}{\partial a_i} \tag{7}$$

2.3. Initial conditions

The numerical simulation was carried out in a constant volume reactor. The mole fraction of CH_4 is 7% and that of C_2H_4 ranges from 0 to 2%. According to the volume fraction in the air, the mole fraction of nitrogen to oxygen is 79/21. Since the pressure in underground space is lower than that on the surface, the initial pressure is set at 1 atm. The initial conditions are shown in Table 1.

Table 1. Initial conditions.

Cases	Temperature	Pressure	mole fraction				Time(s)
			CH_4	O_2	N_2	C_2H_4	
1	1300K	1 atm	0.07	0.1953	0.7347	0.000	0.02
2	1300K	1 atm	0.07	0.1945	0.7315	0.004	0.02
3	1300K	1 atm	0.07	0.1936	0.7284	0.008	0.02
4	1300K	1 atm	0.07	0.1928	0.7252	0.012	0.02
5	1300K	1 atm	0.07	0.1919	0.7221	0.016	0.02
6	1300K	1 atm	0.07	0.1911	0.7189	0.020	0.02

3. Results and analysis

3.1. Effect of C_2H_4 Content on Pressure and Temperature
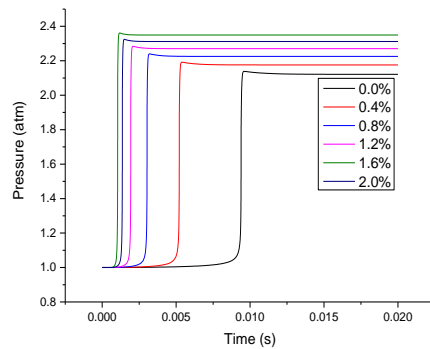
Figure 1. Pressure in the process of gas explosion.
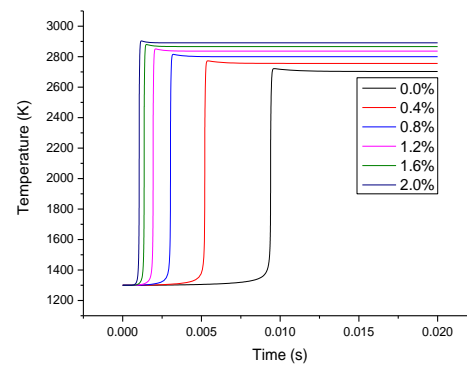
**Figure 2.** Temperature in the process of gas explosion.

The variations of gas pressure and temperature in the explosion process of CH_4-air with different C_2H_4 additions are plotted in Figure 1 and Figure 2 respectively. It can be seen that the changing trend of the temperatures is similar with that of the pressures and the additions of C_2H_4 have a positive influence on the maximum of gas pressure and temperature.

From the Figure 1, it can be indicated that the explosion time generally shortens with the addition of C_2H_4. Specifically, when CH_4-air explosion happens, the time is about 0.0095s, while with 0.4% C_2H_4 being added, the time of gas explosion is some 0.0055s. In other words, compared with CH_4-air explosion, the time of CH_4-air explosion with 0.4% C_2H_4 is smaller, almost equivalent to its half. Furthermore, when the amount of added C_2H_4 increases, such as 0.8%, 1.2%, 1.6%, 2.0%, the effect of C_2H_4 on CH_4-air explosion is increasingly great, and the time becomes shorter and shorter. It can be also revealed that all the maximum of pressures in the process of explosion becomes larger with the

addition of C_2H_4. Moreover, the more the amount of added C_2H_4, the larger the increment of maximum pressure becomes.

There are some variations of temperature shown in the Figure 2 similar to that of pressure. These variations can be expressed that with the addition of C_2H_4, the time of gas explosion generally shortens, and the more the amount of added C_2H_4, the larger the decrement of time becomes. In addition, all the maximum of temperatures in the process of explosion becomes larger with the addition of C_2H_4. Moreover, the more the amount of added C_2H_4, the larger the increment of maximum temperature becomes.
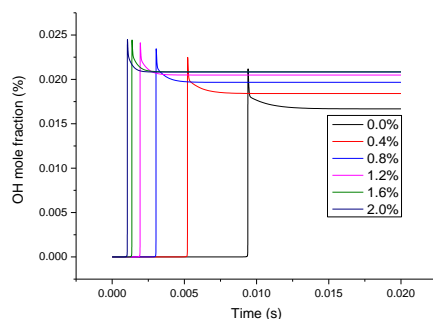
3.2. Effect of C_2H_4 content on Free Radicals
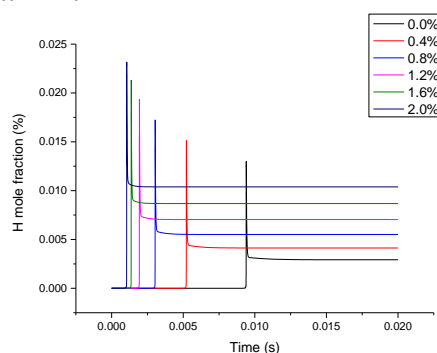
Figure 3. Free radical H in the process of gas explosion.
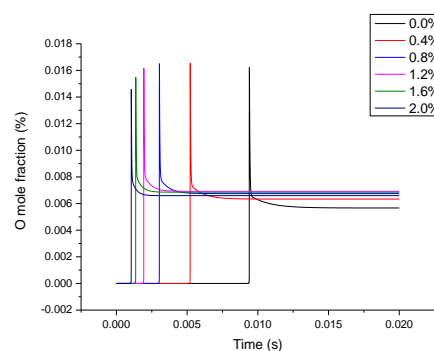
Figure 4. Free radical O in the process of gas explosion.

Figure 5. Free radical OH in the process of gas explosion.

Table 2. The key reactions.

Reaction	Equation
#38	$H+O_2 \rightarrow O+OH$
#52	$H+CH_3 (+M) \rightarrow CH_4 (+M)$
#53	$H+CH_4 \rightarrow CH_3+H_2$
#75	$H+C_2H_4 \rightarrow C_2H_3+H_2$
#98	$OH+CH_4 \rightarrow CH_3+H_2O$
#101	$OH+CH_2O \rightarrow HCO+H_2O$
#112	$OH+C_2H_4 \rightarrow C_2H_3+H_2O$
#118	$HO_2+CH_3 \rightarrow O_2+CH_4$
#119	$HO_2+CH_3 \rightarrow OH+CH_3O$
#155	$CH_3+O_2 \rightarrow O+CH_3O$
#156	$CH_3+O_2 \rightarrow OH+CH_2O$
#157	$CH_3+H_2O_2 \rightarrow HO_2+CH_4$

Gas explosion is a radical chain reaction. The chain reactions are dominated by free radicals in the process of gas explosion, especially oxygen radical O, hydrogen H and hydroxyl radical OH. The variation of concentration of these radicals directly determines the explosion flame propagation speed and severity. Therefore, the variations of the three radicals in the explosion process of CH_4-air with different C_2H_4 additions are plotted in Figure 3, Figure 4 and Figure 5.

As is shown from the figures, under different conditions, at the last moment, before gas explosion occurred, the concentration of free radicals H, O and OH increased sharply, and then their concentration rapidly decreased after the explosion and finally stabilized. This is because when there is a high-temperature heat source, a branching reaction of CH_4 is caused to generate highly active radicals such as H, O and OH, thereby forming an extremely high concentration of activation centres and finally contributing to a gas explosion. The chain carrier that led to the partial chemical reaction was destroyed by the explosion, causing the concentration of free radicals such as H, O and OH to decrease rapidly, and stabilized to a certain extent.

It can be seen from Figure 3 and Figure 5 that compared with no addition of C_2H_4, with the addition of C_2H_4, the maximum of free radical H and OH all increases and the more the amount of added C_2H_4, the larger the increment of the maximum of free radicals H becomes. From the Figure 4, when the amount of addition of C_2H_4 is smaller, with the addition of C_2H_4 the maximum of free radical O increases; when the amount of addition of C_2H_4 exceed a certain value, with the addition of C_2H_4 the maximum of free radical O decreases.

3.3. Effect of C_2H_4 Content on Products after Gas Explosion
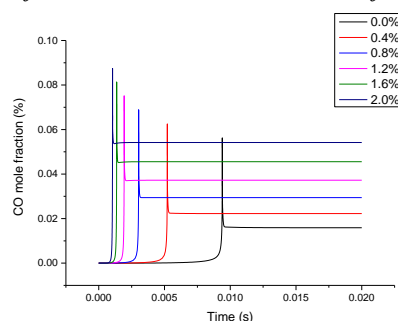
Figure 6. CO in the process of gas explosion.
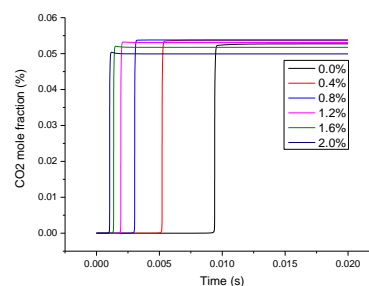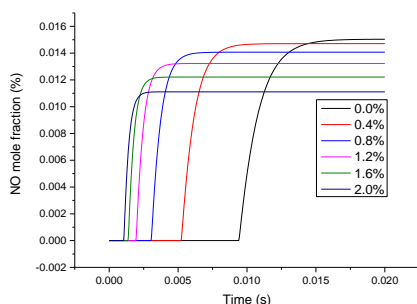

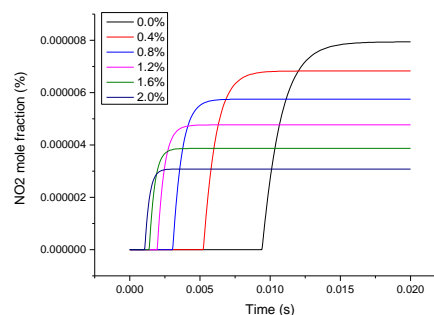**Figure 7.** CO_2 in the process of gas explosion.

Harmful and toxic gases produced after gas explosion, such as CO, CO_2, NO and NO_2, are responsible for a large number of deaths and injuries. Therefore, the law of gas production after gas explosion is studied, as is shown in the Figure 6, Figure 7, Figure 8 and Figure 9.

From the Figure 6, it is seen that compared with no addition of C_2H_4, with the addition of C_2H_4, regardless of 0.4%, 0.8%, 1.2%,1.6% or 2.0%, the CO produced after gas explosion all increases and the more the amount of added C_2H_4, the larger the increment of CO becomes. This is because C_2H_4 reacts with O_2, which produces CO in the process of gas explosion.

It is found from the Figure 7 that compared with no addition of C_2H_4, when the amount of addition of C_2H_4 is smaller, with the addition of C_2H_4 the CO_2 produced after gas explosion increases; when the amount of addition of C_2H_4 exceed a certain value, with the addition of C_2H_4 the CO_2 decreases. This may be because when the amount of addition of C_2H_4 is smaller, the added C_2H_4 reacts with O_2 completely, so the CO_2 after gas explosion increases; when the amount of addition of C_2H_4 exceed a certain value, with O_2 being inadequate, the added C_2H_4 reacts with O_2 incompletely, so the CO_2 decreases.

**Figure 8.** NO in the process of gas explosion.

**Figure 9.** NO_2 in the process of gas explosion.

From the Figure 8 and Figure 9, it is found that compared with no addition of C_2H_4, with the addition of C_2H_4, regardless of 0.4%, 0.8%, 1.2%,1.6% or 2.0%, the NO and NO_2 produced after gas explosion all decreases and the more the amount of added C_2H_4, the larger the decrement of CO

becomes. N_2 is an inert gas and C_2H_4 coexists with N_2. According to the chemical principle concerned, under high-temperature and high-pressure environment, C_2H_4 has priority to react with O_2, which make the O_2 in the mixture inadequate, contributing to the decrease of NO and NO_2 produced after gas explosion.
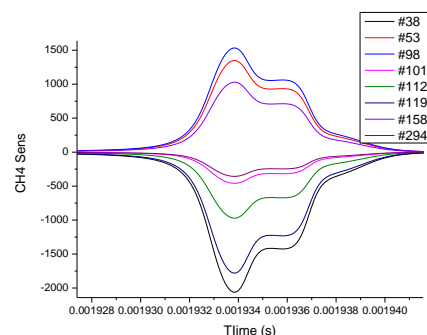
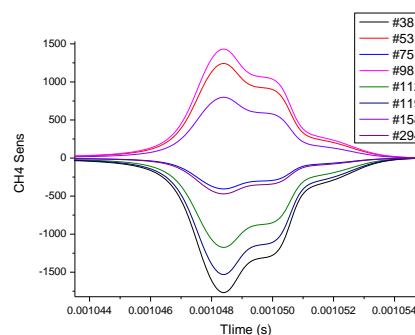### 3.4. Effect of C_2H_4 Content on the Key Reactions
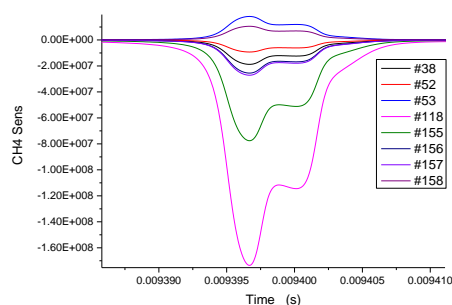
Figure 10. Sensitivity of CH4 in Case 1.
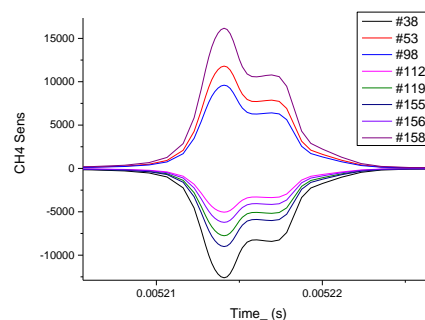
Figure 11. Sensitivity of CH4 in Case 2.

Figure 12. Sensitivity of CH4 in Case 4.

Figure 13. Sensitivity of CH4 in Case 6.

The sensitivity of CH_4 to the intermediate reaction is conducted to find possible ways to keep gas explosion from happening or to reduce gas explosion intensity. It is important to reveal the reactions that affect consumption of CH_4. The top eight reactions that affect CH_4 consumption under different conditions are obtained, as shown in Figure 10, Figure 11, Figure 12 and Figure 13.

From the Figure 10, it can be seen that the critical reactions affecting the amount of CH_4 in the process of explosion are reaction #118, #155, #157, #156, #38, #52, #158, #53. Detailed reaction equations are listed in Table 2. The former six reactions all improve the combustion of CH_4.The reaction#118, #157 and #52 all recompose CH_4, making the concentration of CH_4 increase and then enabling the reaction severer. The reaction #155, #156 and #38 all generate the free radicals, such as O, OH and CH_3O, contributing the increase of the concentration of active center and then improving the combustion of CH_4. The latter two reactions restrain the combustion of CH_4 by the consumption of the free radicals, such as H and CH_3.

It is found from the Figure 11, Figure 12 and Figure 13 that the addition of C_2H_4 has an obvious influence on both the sensitivity coefficients of CH_4 and the critical reactions. Specifically, with the gas of C_2H_4 added, regardless of 0.4%, 1.2% or 2.0%, the sensitivity coefficients of CH_4 all decrease sharply, and from the picture, it can also be seen that compared with no addition of C_2H_4, with the addition of C_2H_4, the critical reactions are different.

With the gas of C_2H_4 being added, the reaction #118 and # 155, which are the top two critical reactions improving the combustion of CH_4, become # 38 and #119. From the chemical reaction equation of #38 and #119, it can be seen that the two reactions all generate the free radicals, such as O

and OH, which are dominant in the process of gas explosion. After addition of C_2H_4, the reaction #53 and #158, which are the top two critical reactions restraining the combustion of CH_4, become #98 and #53. From the chemical reaction equation of #98 and #53, the two reactions all consume the free radical, such as OH and H. It is seen from the pictures and equations that the addition of C_2H_4 has a greater influence on the reactions improving the combustion of CH_4 than on the reactions restraining the combustion of CH_4, so the addition of C_2H_4 can improve the gas explosion. Specifically, the addition of C_2H_4 mainly improve the reaction #38 and #119, making them dominant. The two reactions generate the free radicals, such as O and OH, increasing the concentration of activation center, and then contributing the gas explosion severer.

4. Conclusions

To investigate the effects of C_2H_4 on chemical kinetic characteristics of CH_4-air explosion, the numerical simulations of the gas explosion are conducted through the software of CHEMKIN. The reactants, products, free radicals and sensitivity of CH_4 are analysed in the process of gas explosion. The results obtained show that the addition of C_2H_4 makes the explosion time short, maximum explosion pressure and maximum explosion temperature large, that the addition of C_2H_4 contributes to the increase of product CO and the decrease of NO and NO_2, and makes CO_2 increase first, and then decrease, and that the addition of C_2H_4 can improve the gas explosion due to the fact that the addition of C_2H_4 has a great effect on the reaction #38 and #119, making the two reaction dominant, thereby generating a large number of free radicals.

References

[1]   Zhang B, Xiu G, Bai C 2014a Explosion characteristics of argon/nitrogen diluted natural gas-air mixtures *Fuel* **124** 125-132
[2]   Zhang B, Ng HD 2015 Explosion behavior of methane-dimethyl ether/air mixtures *Fuel* **157** 56-63
[3]   Huang Z, Liu Z, Chen S, Zhang Y, Zhang 2012 Numerical simulation and study on the transmission law of flame and pressure wave of pipeline gas explosion *Saf Sci* **50** 806-810
[4]   Liu Q, Zhang Y, Niu F, Li L 2015 Study on the flame propagation and gas explosion in propane/air mixtures *Fuel* **140** 677-684
[5]   Bao Q, Fang Q, Zhang Y, Chen L, 2016 Effects of gas concentration and venting pressure on overpressure transients during vented explosion of methane-air mixtures *Fuel* **175** 40-48
[6]   Kasmani RM, Andrews GE, Phylaktou HN 2013 Experimental study on vented gas explosion in a cylindrical vessel with a vent duct *Process Saf Environ Prot* **91** 245-252
[7]   Fairweather M, Hargrave GK, Ibrahim SS, Walker DG 1999 Studies of premixed flame propagation in explosion tubes *Combust Flame* **116** 504-518
[8]   Na'inna AM, Somuano GB, Phylaktou HN, Andrews GE 2015 Flame acceleration in tube explosions with up to three flat-bar obstacles with variable obstacle separation distance *J Loss Prev Process Ind* **38** 119-124
[9]   Oh KH, Kim H, Kim JB, Lee SE 2001 A study on the obstacle-induced variation of the gas explosion characteristics *J Loss Prev Process Ind* **14** 597-602
[10] Ciccarelli G 2012 Explosion propagation in inert porous media *Philosophical Trans R Soc Lond A Math Phys Eng Sci* **370 (1960)** 647-667
[11] Ranganathan S, Lee M, Akkerman V, Rangwala AS 2015 Suppression of premixed flames with inert particles *J Loss Prev Process Industries* **35** 46-51