

Study on critical ambient temperature of cylindrical battery

Zerong Guo · Quan Xia · Peiyu Yan ·
Zhiming Du

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Abstract In order to study the thermal safety of cylindrical battery and solve the three-dimensional cylindrical battery thermal explosion problem, a common thermal explosion physical model of cylindrical battery and three-dimensional thermal explosion mathematical model of cylindrical fireworks with non-uniform heat dissipation of the lateral surface were established for the first time. By applying the theory of heat transfer, the boundary conditions of cylindrical battery were simplified reasonably. The seven-point difference method was introduced to disperse the model. The three-dimensional numerical program was written by homotopy continuation method and Newton iteration method based on Matlab. Comparison of two-dimensional numerical solutions obtained by taking $\phi = 0$ and classical solutions proved the accuracy of model. A common kind of fireworks was calculated in this paper. When this single cylinder firework stored individually, the criterion of thermal explosion is 1.796, and critical ambient temperature is 450.484 K. When stored in combination form (that is battery), the criterion of thermal explosion is 1.363 and critical ambient temperature is 447.964 K. The results show that the cylindrical fireworks stored in combination form is more dangerous than this single cylinder firework stored individually, so the cylindrical battery is the focus of safety prevention of fireworks.

Keywords Cylindrical battery · Critical ambient temperature · Non-uniform heat dissipation · Three-dimensional thermal explosion

List of symbols

χ	Heat transfer coefficient
χ_r	Cylinder radial heat transfer coefficient
χ_z	Cylinder axial heat transfer coefficient
k	Heat transfer coefficient of propellant
T	System temperature
T_a	Ambient temperature
E	Activation energy
Q	Reaction heat
A	Pre-exponential factor
R	Universal gas constant
δ	Frank-Kamenetskii number
δ_{cr}	Criterion of thermal explosion
H	Length diameter ratio
ε	The dimensionless activation energy
θ	The dimensionless temperature rise
Bi_r	Biot number of the lateral surface
Bi_{z1}	Biot number of the upper surface
Bi_{z2}	Biot number of the lower surface
ρ_1	Dimensionless coordinate variable in the r direction
ρ_2	Dimensionless coordinate variable in the z direction
ρ_3	Dimensionless coordinate variable in the z direction
R_c	Thermal contact resistance
R_r	Thermal resistance of the lateral surface (paper shell)
R_{z1}	Thermal resistance of the upper surface (sealing power)
R_{z2}	Thermal resistance of the lower surface (mud shell)
R_a	Thermal resistance of the air layer
λ_a	Air thermal conductivity

Introduction

Fireworks and crackers are traditional handicrafts of China with a long history. It plays an important role in meeting the needs of the folk custom, economic development and

Z. Guo (✉) · Q. Xia · P. Yan · Z. Du
State Key Laboratory of Explosion Science and Technology,
Beijing Institute of Technology, Beijing 100081, China
e-mail: zeronguo@gmail.com

export. However, fireworks and crackers as civil explosives are made from pyrotechnic, occurring thermal hazard in the production, storage, transport and use process. What is more, the thermal imbalance of fireworks system will lead to burning and explosion accidents. According to statistics, from 1985 to 2005, 8,532 fireworks safety accidents occurred in China and 9349 people were killed [1]. From 2007 to 2011, a total of 503 fireworks accidents occurred in China and 998 people were killed [2]. Thus, it is of importance to study the thermal safety of fireworks and firecrackers.

Pyrotechnic is a typical energetic material. Thermal safety evaluation method of energetic material includes mainly estimate evaluation method, test evaluation method [3] and simulation method based on thermodynamics [4], in which the basic stability test evaluation method and simulation method based on thermodynamics are suitable for evaluation of the thermal safety of pyrotechnics. However, the basic stability test evaluation method mainly targets at small dose and is not suitable for thermal safety evaluation of fireworks and crackers which contain a large amount of pyrotechnics. Simulation method, based on thermodynamics method, involves thermal analysis kinetics and thermal explosion theory. The purpose of thermal analysis kinetics is to obtain kinetic triplet including activation energy E , pre-exponential factor A and mechanism function $f(a)$ [5, 6], which can describe dynamics equation of a reaction. In this paper, thermal analysis kinetics can provide basic data for solving the problems of thermal safety of fireworks and crackers.

Since thermal explosion theory has been founded, a lot of theoretical research has been made by scholars [7–12]. But the problem of three-dimensional thermal explosion has not been solved commendably so far, and thermal explosion theory was still limited to two dimensional. On the other hand, the study on the application of thermal explosion theory in thermal safety of fireworks is only a few. Until 2010, Zhou [13] using the thermal analysis method to obtain the thermodynamic parameters of black powder, fulminating powder, green powder and other pyrotechnic solved the one-dimensional thermal safety criticality problems of spherical fireworks by introducing thermal explosion theory for the first time. Whereafter, three-different structural thermal explosion models of spherical fireworks were established, and the critical ambient temperature of one-dimensional spherical fireworks was obtained with shooting method by Liu [14], etc. In 2012, thermal explosion model of two-dimensional single cylinder cylindrical fireworks, in which the cooling conditions of the upper surface, lower surface and lateral surface are different, was studied by Ji [15]. However, in the overwhelming majority of cases, fireworks and crackers are stored in complex surrounding environment or the form

of composition (such as battery). The thermal explosion theory of single cylinder fireworks is no longer applicable in this case. Therefore, a scientific and reliable thermal safety evaluation method of battery is vital. And it is necessary to study the thermal safety of battery. Previously, there are a certain theoretical research on cylindrical three-dimensional heat transfer equation both at home and abroad. In 2011, the three-dimension heat transfer problem of non-isothermal decomposition for a solid cylindrical particle was studied by Nowicki [16], etc. The non-stationary thermo-chemical system of two nonlinear integro-differential equations was solved by the semi-analytical method. In 2014, a three-dimensional model including three directions of heat dissipation (x, y, z) was established by Xia [17], etc. They did some research on thermal conductivity of porous materials which is hampered by their highly random internal structure. Base on thermal analysis kinetics, the thermal safety problem of cylindrical battery by applying thermal explosion theory was studied in this paper. Three-dimensional thermal explosion mathematical model of cylindrical fireworks with non-uniform heat dissipation of the lateral surface were established for the first time. The boundary conditions of cylindrical battery were simplified reasonably. The model was dispersed by the seven-point difference method. The three-dimensional numerical program was written by homotopy continuation method and Newton iteration method based on Matlab. The three-dimensional thermal explosion problem of cylindrical battery was solved for the first time in this paper.

Thermal explosion model of cylindrical battery

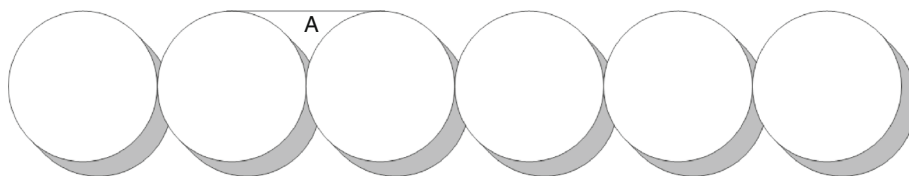
Physical thermal explosion model of cylindrical battery

Cylindrical battery is made up of multiple single cylindrical fireworks. Each single cylindrical firework is an independent reaction system. The difference between battery and single cylinder is that single cylinder in battery system interacts with each other mainly in thermal influence, which leads to non-uniform heat dissipation. It assuredly increases the dimensions of the problem of thermal explosion and the difficulty of the model calculation. Thus, thermal explosion model of fireworks and crackers should not only conform to the actual situation, but also should be easy to solve, which needs a scientific hypothesis. A common battery was studied in this paper as shown in Fig. 1.

As a system, cylindrical battery should satisfy the law of conservation of energy. In addition to meet the basic characteristics of the thermal explosion model, the assumptions were made as follows:

1. System is composed of multiple identical single cylinder fireworks which are parallel vertical closely

Fig. 1 Diagrammatic sketch of cylindrical battery



arranged. The cooling conditions on both sides of each single cylinder fireworks are the same. That is, the ignition point of single cylinder is still in the center of the geometry.

- Ignore thermal influence of the fireworks which is not adjacent. In view of the internal temperature gradient of single cylinder fireworks is the same with the adjacency, there is no heat transfer in the contact part because of no difference in temperature. And the heat transfer weaken place is mainly in the area between fireworks (such as zone A). For no pyrotechnic in the zone A, the influence of geometry can be ignored, and we assume the effect of air layer as increase of the thermal resistance of cylindrical boundary.

In the system of battery, as long as thermal imbalance occurs in one of the single cylinder fireworks, thermal explosion will eventually happen with constant thermal feedback. So the model of battery can be solved by solving one of the single cylinder.

Mathematical thermal explosion model of cylindrical battery

According to the physical model and the law of conservation of energy, the mathematical thermal explosion steady-state model of cylindrical battery with radius a_0 and height $2Ha_0$ was established. The three-dimensional coordinate system and the solution region of cylindrical battery are shown in Fig. 2 as follows.

$$k \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \phi^2} + \frac{\partial^2 T}{\partial z^2} \right) + QA \exp\left(-\frac{E}{RT}\right) = 0 \tag{1}$$

The boundary conditions of cylindrical battery:

$$r = 0, \quad \partial T / \partial r = 0 \tag{2}$$

$$\phi = 0, \quad \partial T / \partial \phi = 0 \tag{3}$$

$$z = 0, \quad \partial T / \partial z = 0 \tag{4}$$

$$r = a_0, \quad k \partial T / \partial r + \chi_r (T - T_a) = 0 \tag{5}$$

$$\phi = 2\pi, \quad \partial T / \partial \phi = 0 \tag{6}$$

$$z = Ha_0, \quad k \partial T / \partial z + \chi_z (T - T_a) = 0 \tag{7}$$

The boundary conditions vary from angle ϕ in the model of cylindrical battery established in this paper. Introduce

the dimensionless parameters: dimensionless coordinate variables ρ_1, ρ_2 and ρ_3 , dimensionless temperature rise θ , dimensionless activation energy ε , Frank-Kamenetskii number δ and Biot number Bi . The dimensionless conservation equation of thermal explosion steady-state model:

$$\frac{\partial^2 \theta}{\partial \rho_1^2} + \frac{1}{\rho_1} \frac{\partial \theta}{\partial \rho_1} + \frac{1}{\rho_1^2} \frac{\partial^2 \theta}{\partial \rho_2^2} + \frac{1}{H^2} \frac{\partial^2 \theta}{\partial \rho_3^2} + \delta f(\theta) = 0 \tag{8}$$

The dimensionless boundary conditions of cylindrical battery:

$$\rho_1 = 0, \quad \partial \theta / \partial \rho_1 = 0 \tag{9}$$

$$\rho_2 = 0, \quad \partial \theta / \partial \rho_2 = 0 \tag{10}$$

$$\rho_3 = 0, \quad \partial \theta / \partial \rho_3 = 0 \tag{11}$$

$$\rho_1 = 1, \quad \partial \theta / \partial \rho_1 + Bi_r \theta = 0 \tag{12}$$

$$\rho_2 = 2\pi, \quad \partial \theta / \partial \rho_2 = 0 \tag{13}$$

$$\rho_3 = 1, \quad \partial \theta / \partial \rho_3 + HBi_z \theta = 0 \tag{14}$$

Treatment of boundary conditions

Proper treatment of boundary conditions can simplify the solution of models. Literature [15] explained the calculation of effective Biot number of the upper, lower and lateral surface with uniform heat dissipation. However, the boundary conditions of the single cylinder fireworks in battery include not only complex shell conditions, but also complex external environment. In order to solve the problems of three-dimensional thermal explosion, the cooling conditions of the upper surface and lower surface are considered the same. And the effective Biot number of the upper and lower surface can be calculated. The followings are the shell condition and external environment analysis of the lateral surface of battery.

In battery, the changes of external environment lead to non-uniform heat dissipation of the lateral surface. It can be seen from Fig. 3 that the heat transfer weaken place is mainly in zone A. In practice, to avoid the battery corroded or damaged during storage and transport, the thin plastic wrapping paper is usually used for packaging. So, the air in zone A is motionless and the thermal resistance of thin plastic wrapping paper can be ignored. In addition, the shell of lateral surface consists of multiwall Kraft paper and straw board. There are four steps during the process of practical heat conduct of lateral surface.

Fig. 2 Three-dimensional coordinate system and solution region of cylindrical battery

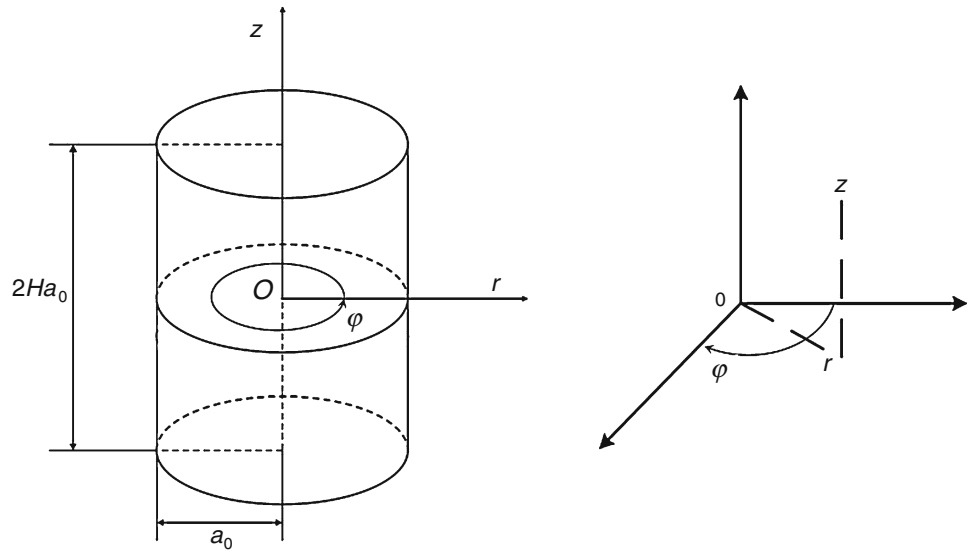
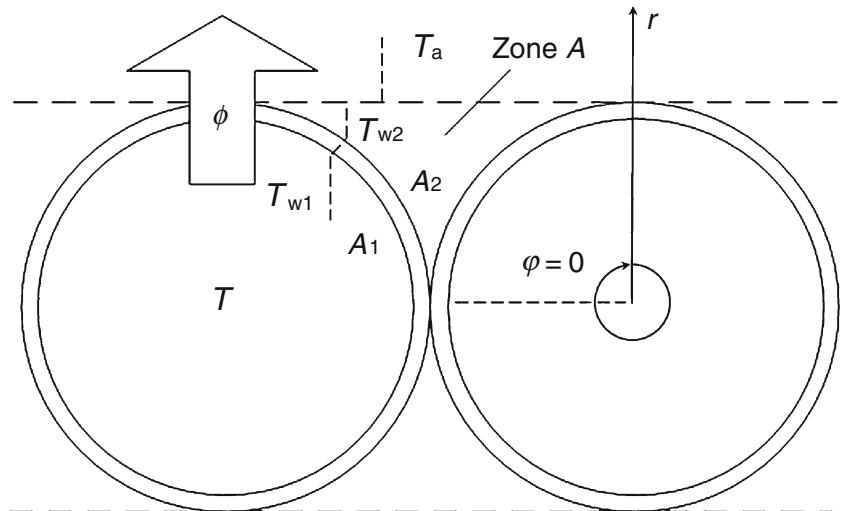


Fig. 3 The process of heat transfer of the lateral surface



1. Heat transfer between the propellant and the shell of lateral surface (refers to thermal contact resistance).
2. Heat transfer between the hot side and the cold side of the shell of lateral surface (refers to thermal conductivity).
3. Heat transfer between the cold side of shell and the air of zone A (refers to thermal conductivity of air).
4. Heat transfer between the air of zone A and ambient environment (refers to heat transfer coefficient).

According to the theory of heat transfer and the definition of effective Biot number [18], boundary condition of the lateral surface was obtained:

$$r = a_0, \quad kA_1 \frac{\partial T}{\partial r} + \frac{T - T_a}{R_c + R_r + R_a + \frac{1}{\lambda A_2}} = 0 \quad (15)$$

The effective Biot number of lateral surface of battery can be defined as:

$$Bi'_r = \frac{a_0}{kA_1} \times \frac{1}{R_c + R_r + R_a + \frac{1}{\lambda A_2}} \quad (16)$$

where the air thermal resistance R_a is:

$$R_a = \frac{L}{\lambda_a A_2} \quad (17)$$

A_1 and A_2 represent the inner surface and the external area of lateral surface, respectively. Air resistance R_a varies from angle ϕ , shown as the change of the air layer thickness L . The relation between L and known parameters are obtained from the Fig. 3.

$$L = (1 - |\sin \phi|) \cdot a_0 \quad (18)$$

Numerical solutions and results analysis

Numerical solution

The mathematical thermal explosion model of cylindrical battery is made up of the Eqs. (1)–(7) or the dimensionless Eqs. (8)–(14). Because the solution domain is cylindrical, the coefficient of partial differential Eq. (1) is singular at $\rho_1 = 0$. Only when $\rho_1 > 0$ equations make sense. So assuming the equation is bounded at $\rho_1 = 0$ (the origin of coordinates is a removable singularity). The seven-point difference method [19] was introduced to disperse the model. The steps of variables ρ_1, ρ_2 and ρ_3 is h_r, h_ϕ and h_z , respectively (to express convenient, r_i, ϕ_j and z_k stand for the discrete point coordinates in the following discrete equation). Note: If the value of r_0 is too large, the calculation error is big. Conversely, if the value is too small, the calculation procedure will not converge. After much experimenting, the value of r_i, ϕ_j and z_k was obtained as follows.

$$r_i = (i + 0.1)h_r \quad i = 0, 1, 2, \dots, I - 1 \tag{19}$$

$$\phi_j = (j + 1)h_\phi \quad j = 0, 1, 2, \dots, J - 1, \quad h_\phi = 2\pi/J \tag{20}$$

$$z_k = (k + 1)h_z \quad k = 0, 1, 2, \dots, K - 1 \tag{21}$$

Using the central difference quotient formula:

$$\begin{aligned} \left[\frac{1}{\rho_1} \frac{\partial}{\partial \rho_1} \left(\rho_1 \frac{\partial \theta}{\partial \rho_1} \right) \right]_{(r_i, \phi_j, z_k)} &= \frac{\partial^2 \theta}{\partial \rho_1^2} + \frac{1}{\rho_1} \frac{\partial \theta}{\partial \rho_1} \\ &\approx \frac{1}{r_i} \frac{r_{i+0.9}\theta_{i+1,j,k} - (r_{i+0.9} + r_{i-0.1})\theta_{i,j,k} + r_{i-0.1}\theta_{i-1,j,k}}{h_r^2} \\ &\quad + \frac{1}{r_i} \frac{\theta_{i+1,j,k} - \theta_{i-1,j,k}}{2h_r^2} \end{aligned} \tag{22}$$

$$\left[\frac{1}{\rho_1^2} \frac{\partial^2 \theta}{\partial \rho_2^2} \right]_{(r_i, \phi_j, z_k)} \approx \frac{1}{r_i^2} \frac{\theta_{i,j+1,k} - 2\theta_{i,j,k} + \theta_{i,j-1,k}}{h_\phi^2} \tag{23}$$

$$\left[\frac{\partial^2 \theta}{\partial \rho_3^2} \right]_{(r_i, \phi_j, z_k)} \approx \frac{\theta_{i,j,k+1} - 2\theta_{i,j,k} + \theta_{i,j,k-1}}{h_z^2} \tag{24}$$

The boundary conditions of dimensionless discrete partial differential equations were obtained as follows.

$$\begin{aligned} &\frac{1}{r_i} \frac{r_{i+0.9}\theta_{i+1,j,k} - (r_{i+0.9} + r_{i-0.1})\theta_{i,j,k} + r_{i-0.1}\theta_{i-1,j,k}}{h_r^2} \\ &+ \frac{1}{r_i} \frac{\theta_{i+1,j,k} - \theta_{i-1,j,k}}{2h_r^2} + \frac{1}{r_i^2} \frac{\theta_{i,j+1,k} - 2\theta_{i,j,k} + \theta_{i,j-1,k}}{h_\phi^2} \\ &+ \frac{1}{H^2} \frac{\theta_{i,j,k+1} - 2\theta_{i,j,k} + \theta_{i,j,k-1}}{h_z^2} + \delta \exp\left(\frac{\theta_{i,j,k}}{1 + \varepsilon\theta_{i,j,k}}\right) = 0 \end{aligned} \tag{25}$$

$$\rho_1 = 0, \frac{\theta_{i+1,j,k} - \theta_{i-1,j,k}}{2h_r} = 0 \tag{26}$$

$$\rho_2 = 0, \frac{\theta_{i,j+1,k} - \theta_{i,j-1,k}}{2h_\phi} = 0 \tag{27}$$

$$\rho_3 = 0, \frac{\theta_{i,j,k+1} - \theta_{i,j,k-1}}{2h_z} = 0 \tag{28}$$

$$\rho_1 = 1, \frac{\theta_{i+1,j,k} - \theta_{i-1,j,k}}{2h_r} + Bi_r \theta_{i,j,k} = 0 \tag{29}$$

$$\rho_2 = 2\pi, \frac{\theta_{i,j+1,k} - \theta_{i,j-1,k}}{2h_\phi} = 0 \tag{30}$$

$$\rho_3 = 1, \frac{\theta_{i,j,k+1} - \theta_{i,j,k-1}}{2h_z} + HBi_z \theta_{i,j,k} = 0 \tag{31}$$

Based on Matlab, the three-dimensional numerical program was written to solve the dimensionless discrete partial differential equations by homotopy continuation [20, 21] method and Newton iteration method [22]. The mathematical thermal explosion model can be solved by this three-dimensional numerical program, and the critical parameters can be obtained.

Results analysis

The greater the difference discrete degree of model is, the smaller the calculation error is. Meanwhile, the difficulty of calculation increases as the discrete degree increases. Similarly, if the discrete degree in r and z direction are greater, the numerical results are more close to the value in literature [12] (literature solutions are shown in brackets of Table 1). However, high discrete degree will lead to a huge amount of calculation, and even equations cannot be computed. This is because the matrix $r \cdot \phi \cdot z$ is too large. Considering the error and computational difficulty, this paper took $I = 15, J = 0, K = 15, H = 1, \varepsilon = 0$ and compared the numerical results with the results of two-dimensional thermal explosion (that is, literature solutions) to verify the accuracy of three-dimensional numerical program. The results are shown in Table 1.

From Table 1, it can be seen that the errors between the numerical solutions and literature solutions are $< 10^{-2}$. It verifies the accuracy of the three-dimensional model of battery and the numerical calculation method.

The results also show that when the model is not discrete in the angle ϕ direction, this thermal explosion model is equal to the two-dimensional thermal explosion cylindrical model studied before. When taking $I = 15, J = 0$ and $K = 15$, the calculation results are close to actual situation. Similarly, the three-dimensional thermal explosion cylindrical model can be calculated by dispersing the angle ϕ direction. And increasing the discrete degree of angle ϕ direction will facilitate the analysis of heat dissipation in

Table 1 Verification of the effect of Biot number on δ_{cr} , $\theta_{0,cr}$ in three-dimensional numerical program

Bi_r	$Bi_z = 10^5$		$Bi_z = 10^1$		$Bi_z = 10^0$		$Bi_z = 10^{-1}$		$Bi_z = 10^{-4}$ (infinite long cylindrical)	
	δ_{cr}	θ_{cr}	δ_{cr}	θ_{cr}	δ_{cr}	θ_{cr}	δ_{cr}	θ_{cr}	δ_{cr}	θ_{cr}
10^4	2.750 (2.764)	1.610 (1.612)	2.614 (2.629)	1.610 (1.610)	2.226 (2.244)	1.520 (1.525)	2.017 (2.037)	1.410 (1.411)	1.983 (2.000)	1.400 (1.386)
10^1	2.423 (2.435)	1.600 (1.607)	2.286 (2.289)	1.600 (1.603)	1.888 (1.899)	1.510 (1.518)	1.676 (1.688)	1.390 (1.399)	1.642 (1.654)	1.390 (1.378)
10^0	1.426 (1.423)	1.400 (1.405)	1.280 (1.283)	1.400 (1.400)	0.838 (0.841)	1.290 (1.311)	0.608 (0.611)	1.200 (1.207)	0.573 (0.576)	1.200 (1.188)
10^{-1}	0.947 (0.951)	1.200 (1.212)	0.798 (0.800)	1.210 (1.211)	0.342 (0.342)	1.120 (1.132)	0.107 (0.107)	1.040 (1.041)	0.072 (0.072)	1.030 (1.024)
10^{-3}	0.879 (0.880)	1.180 (1.187)	0.730 (0.729)	1.180 (1.182)	0.271 (0.271)	1.100 (1.105)	0.016 (0.016)	0.040 (0.036)	—	—

the angle ϕ direction. Let $J = 40$ after a lot of numerical trials.

Example analysis

To study the thermal safety of battery, take a kind of fireworks called “Charactizing a fine spring day” produced by Panda Fireworks Group Co., LTD as example. The simplified structure is shown in Fig. 4. Considering that the cooling conditions of the upper surface and the lower surface are similar, this firework is suitable for case study in this paper.

Parameter calculation

The height of the single cylinder in this firework is 188 mm, the inside diameter is 94 mm and the thickness of the lateral shell (paper shell) is 2 mm. The thickness of the upper surface (sealing powder) and lower shell (mud shell) are both 30 mm. The propellant black powder is the main pyrotechnic producing heat. The charge density of black powder is 400 kg m^{-3} , and the charge height is 46 mm (Table 2).

Activation energy, pre-exponential factor and reaction heat of black powder are obtained by using thermogravimetric analysis under nitrogen atmosphere. The thermal conductivity coefficients of materials are obtained by the DRY Thermal Conductivity Coefficient Tester in the condition of $50 \text{ }^\circ\text{C}$ and 100 N pressure [13] listed in Table 3. The sealing power, paper shell and mud shell belong to the inert substance.

The heat transfer coefficient of the air natural convection χ is about $1\text{--}10 \text{ W m}^{-2} \text{ K}^{-1}$ generally, and $\chi = 5$ was used in calculation [18]. In view of the critical ambient temperature of pyrotechnic is common in the range of $100\text{--}300 \text{ }^\circ\text{C}$ [12], thermal conductivity of air is in the range of 3.21×10^{-2} to $4.60 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ correspondingly and approximate linearly increases with temperature in this temperature scope. The mid value of thermal conductivity of air was used and $\lambda_a = 3.905 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$ [18]. According to the theory of thermal resistance, thermal resistance of shells of the upper, lower and lateral surface were obtained and $R_{z1} = R_{z2} = 4.55 \text{ K W}$ and $R_r = 0.99 \text{ K W}$. Both the effective Biot number of the upper and lower surface are 1.1726 obtained by putting R_{z1} and R_{z2} into the computational formula of the effective Biot number [15]. In addition, when this single cylinder firework stored individually, $R_a = 0$, and the effective Biot number of the lateral surface calculated by the formula (16) is 2.7031. When stored in combination form, the formula of battery is this:

Fig. 4 Simplified structure of “Charactizing a fine spring day”

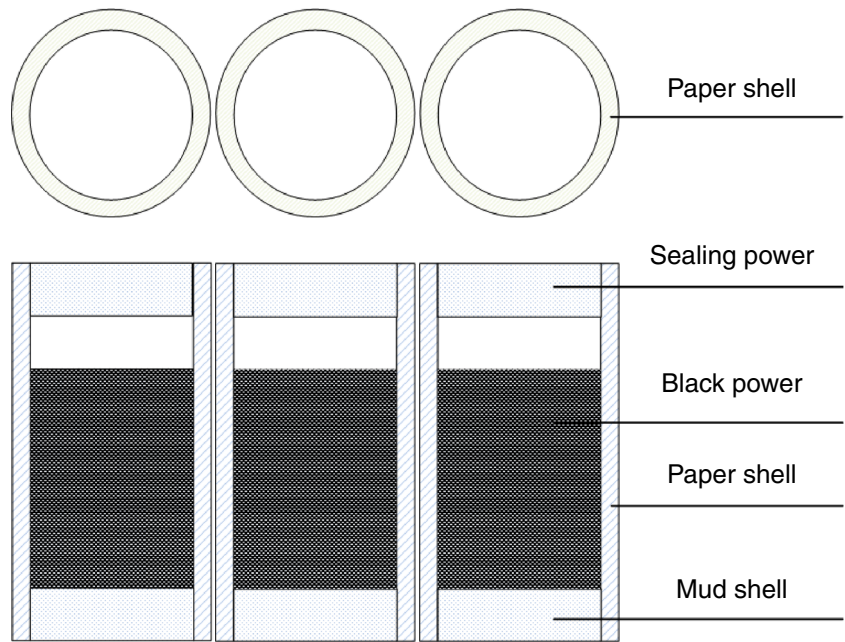


Table 2 Structural parameters of “Charactizing a fine spring day”

Tube height l/mm	Inside diameter r_1/mm	External diameter r_2/mm	Thickness of upper surface δ_1/mm	Thickness of lower surface δ_2/mm	Charge density $\rho/kg\ m^{-3}$	Charge height h/mm
188	47	49	30	30	400	46

Table 3 Physical and chemical parameters of propellant and materials

Propellant and materials	Activation energy/ $J\ kg^{-1}$	Pre-exponential factor/ s^{-1}	Reaction heat/ $J\ kg^{-1}$	Thermal conductivity coefficients/ $W\ m^{-1}\ K^{-1}$
Black powder	1.9100×10^5	1.4000×10^{16}	1.5263×10^6	0.0847
Sealing power	–	–	–	0.9500
Mud shell	–	–	–	0.9500
Paper shell	–	–	–	0.0357

$$Bi'_r = \frac{a_0}{kA_1} \times \frac{1}{R_c + R_r + \frac{(1-|\sin \phi|) \cdot a_0}{\lambda_a A_2} + \frac{1}{\chi A_2}} \quad (32)$$

Criticality calculation

The given length diameter ratio H of this single cylinder firework is 0.4894.

1. When this single cylinder firework stored individually, $Bi'_r = 2.7031$ and $Bi'_{z1} = Bi'_{z2} = 1.1726$.
2. When stored in combination form, $Bi'_{z1} = Bi'_{z2} = 1.1726$, and Bi'_r is shown in Eq. (28).

The critical parameters in steady state were obtained by numerical calculation shown in Table 4, in which the

Table 4 The calculation results of critical parameters in different location mode

Location mode	δ_{cr}	$\theta_{0,cr}$	$T_{a,cr}/K$
Single cylinder	1.796	1.38	450.484
Combination form	1.336	1.21	447.778

critical ambient temperature $T_{a,cr}$ was calculated by the expression of Frank-Kamenetskii number listed as follows.

$$\delta = \frac{a_0^2 Q E \sigma A \exp(-E/RT_a)}{\lambda RT_a^2} \quad (33)$$

Fig. 5 The dimensionless critical temperature rise of the center cross-section of cylinders in different location mode.

a Single cylinder.
b Combination form

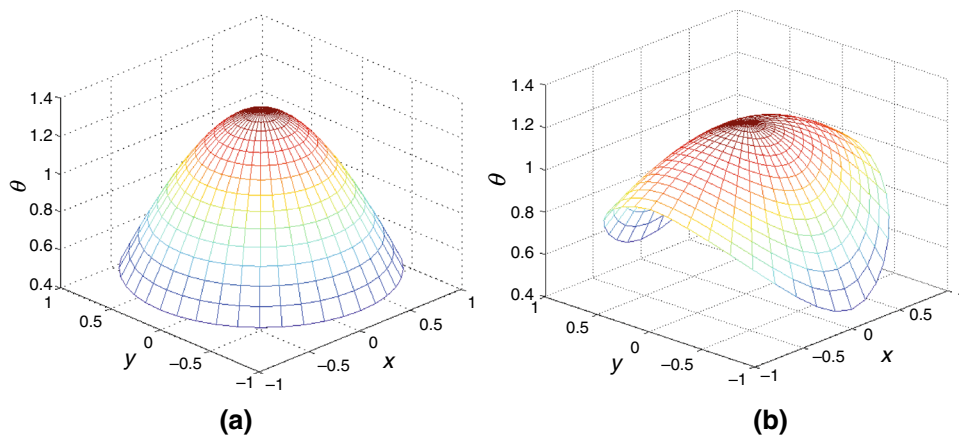


Table 4 shows that when stored individually, the criterion of thermal explosion is 1.796 and the critical ambient temperature is 450.484 K. When stored in combination form, the criterion of thermal explosion is 1.336 and the critical ambient temperature is 447.778 K. Obviously, the battery (combination form of the single cylinder firework) is more dangerous than the single cylinder firework, and the thermal explosion is more likely to happen in production, storage and transport. This is because the mutual interference of thermal field in the battery leads to a bad cooling condition. In addition, if the number of the single cylinder firework of battery increases and the complexity of battery enhances, the critical ambient temperature will reduce, which means poor thermal safety.

Figure 5 describes the dimensionless steady-state critical temperature rise of the center cross-section of cylinders in different location mode. Comparing (a) with (b), the critical center temperature rise of battery is lower than the single cylinder's. This is because the cooling condition of battery is worse and the thermal hazard is higher. The battery can reach critical state only by a lower temperature. It can be seen from Fig. 5b that the cooling condition of battery is bad on the Y axis and the dimensionless temperature rise is highest at $y = 0$ relative to the direction of X -axis. $Y = 0$ plane corresponds to the plane made up of $\phi = 0$ and $\phi = \pi$ in physical model of battery, and there is the same thermal fields of other fireworks in this direction. The closer to the other fireworks is, the greater the effect is and the higher the temperature is. Conversely, the cooling condition is relatively good in the X -axis direction. There is no other single cylinder firework in this direction. These results are in accordance with the actual situation. The difference between the single cylinder firework and battery of the dimensionless critical temperature rise of the center cross-section can be seen from the Fig. 6 clearly.

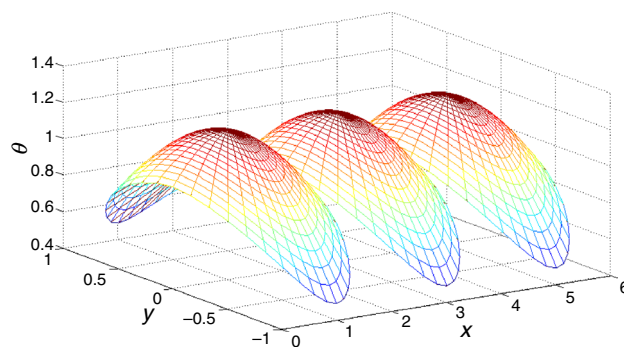


Fig. 6 The overall dimensionless critical temperature rise of the center cross-section of battery

Conclusions

In this paper, three-dimensional thermal explosion physical and mathematical model of cylindrical battery with non-uniform heat dissipation of the lateral surface were established for the first time. The boundary conditions of cylindrical battery were simplified reasonably by applying the theory of heat transfer. The seven-point difference method was introduced to disperse the model. The three-dimensional numerical program was written by homotopy continuation method and Newton iteration method based on Matlab. The model was solved by this three-dimensional numerical program. The criterion of thermal explosion in the location mode of single cylinder and combination form is 1.796 and 1.336, respectively, and the critical ambient temperature is 450.484 and 447.778 K correspondingly. The results show that both single cylinder and battery are safe to store at normal temperature obviously. And the cylindrical fireworks stored in combination form are more dangerous than this single cylinder firework stored individually, and therefore, the cylindrical battery is the focus of safety prevention of fireworks.

In the production, storage and transport of fireworks and crackers, ambient temperature may rise due to the influence of external factors such as hot weather, fire, poor ventilation and so on. The thermal explosion will happen when ambient temperature exceeds the critical ambient temperature with continuous heat accumulation. The results of this study provide basic data and theoretical guidance for safe store and use of firework products. The accident of thermal explosion of fireworks and crackers can be effectively prevented by monitoring the ambient temperature such as installing temperature sensor at the place where fireworks are stored, strengthening ventilated and so on. In practice, more attention should be paid to the safety of battery (the combined fireworks).

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References

1. Cao LX. Discussion on production safety accident causes and countermeasures of fireworks and crackers. *J Saf Sci Technol*. 2008;5(4):138–41 (In Chinese).
2. Yang NL. The 2007–2011 national production safety accident statistics analysis report of fireworks and crackers. *J Saf Sci Technol*. 2013;9(5):72–77 (In Chinese).
3. Fan RJ, Wang XJ, Liu DZ. Research progress of thermal stability and thermal safety evaluation method of energetic material. *Chem Propellants Polym*. 2004;2(2):22–4 (In Chinese).
4. Kossoy AA, Sheinman IY. Evaluating thermal explosion hazard by using kinetic-based simulation approach. *Process Saf Environ Prot*. 2004;82(B6):421–30.
5. Brown ME, Flynn RM, Flynn JH. Report on the Ictac-Kinetics-Committee. *Thermochim Acta*. 1995;256(2):477–83.
6. Vyazovkin S. Kinetic concepts of thermally stimulated Reactions in solid: a view from a historical perspective [J]. *Int Rev Phys Chem*. 2000;19(1):45–60.
7. Harris EJ. The thermal explosion of diethyl peroxide. *Proc R Soc Lond A*. 1940;175:254.
8. Frank-Kamenetskii DA. Diffusion and heat exchange in chemical kinetics. Princeton: Princeton University Press; 1955.
9. Wake GC, Walker IK. The heat balance in spontaneous ignition. 1. The critical state. *N Z J Sci*. 1961;7:227.
10. Feng CG. Thermal explosion theory. Beijing: Sci Press; 1988 (in Chinese).
11. Du ZM. Heat ignition in the exothermic system with limited space. Beijing: Beijing Institute of Technology; 1993 (in Chinese).
12. Wang LQ, Feng CG, Du ZM. Limited space explosion and ignition in theory and experiment. Beijing: Beijing Institute of Technology Press; 2005 (in Chinese).
13. Zhou GW. Study on thermal safety of fireworks and crackers. Beijing: Beijing Institute of Technology; 2010 (in Chinese).
14. Liu HY, Qian XM, Du ZM. Thermal explosion model and calculation of sphere fireworks and crackers. *J Therm Anal Calorim*. 2012;110(3):1029–36.
15. Ji LL. The study on critical ambient temperature and time to ignition of cylindrical hazardous chemicals with shells [D]. Beijing: Beijing Institute of Technology; 2012 (In Chinese).
16. Piddubniak O, Ledakowicz S, Nowicki L. New approach to a problem of heat transfer with chemical reaction in a cylinder of finite dimensions. *Int J Heat Mass Transf*. 2011;54(1–3):338–44.
17. Xia DH, Shen LT, Ren L, Guo SS. A binary array method for calculating thermal conductivity of porous materials. *J Therm Anal Calorim*. 2014;117(2):825–9.
18. Tao WQ. Heat transfer theory. Xi'an: Northwestern Polytechnical University Press; 2006 (in Chinese).
19. Thomas JW. Numerical partial differential equations: finite difference methods. Berlin: Springer; 1995. p. 193–203.
20. Li QY, Mo ZZ, Qi LQ. Numerical method for solving the non-linear equations. Beijing: Science Press; 1987 (in Chinese).
21. Sun ZZ. Numerical solution of partial differential equations. Beijing: Science Press; 2012 (in Chinese).
22. Leader JJ. Numerical analysis and scientific computation. Beijing: Tsinghua University Press; 2008.

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