

## 2. Approximate Solution of Powered Materials Spontaneous Combustion Problem for Reaction of $\nu$ -order

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### ABSTRACT

The problem of defining the conditions of spontaneous combustion of powdered materials under oxidation for reaction of  $\nu$ -order and a wide range of heat and mass exchange parameters has been solved in this paper. The mathematical model tested on the laboratory apparatus and the test rig allows to calculate and to predict the behaviour of bulk powdered porous stuff of any dimensions and shape during its processing, transportation or storage.

Self-ignition of small-dispersal organic materials is a widely-spread phenomenon in practice of storage, processing and transportation of substances and materials. Self-ignition is characterized by the fact that it does not require outer impulse or high temperature to start. Self-ignition comes into existence by the reaction of heterogeneous oxidation in large volumes of the product under relatively small temperature of environment and it is accompanied by foundation of gaseous products of the reaction. Because of low heat-conductivity of small-dispersed material mass, heat accumulation in the volume, growth of temperature, speed of the chemical reaction and, in the long run, ignition of the material come into existence.

Practical interest to processes of heat explosion depends on principal opportunity to calculate in proper time fire safe conditions of processing and storage of dispersed materials under which self-ignition is impossible.

In classical theory, mathematical formulation of the task with heat-explosion consists of the following [1-4]: some volume is considered, and inside it there is a reactant. Physico-chemical constants characterizing heat-exchange and reaction of burning, heat-emission inside the volume, initial and boundary conditions are considered to be known.

This paper is an attempt to find an approximate solution of powdered materials self-ignition problem under their oxidation in the reaction of  $\nu$ -order and change of parameters of heat-mass-exchange in large diopason. The task comes to known equations of heat-conductivity with a distributed source of heat and speed of chemical reaction.

$$c\rho \frac{\partial T}{\partial t} = \rho \frac{dq}{dt} + \lambda \left( \frac{\partial T}{\partial x^2} + \frac{n}{x} \cdot \frac{\partial T}{\partial x} \right); \quad (1)$$

$$\frac{dq}{dt} = K_0 C_0^m Q \left( 1 - \frac{q}{Q} \right)^{\nu} e^{-E/RT}. \quad (2)$$

Boundary and initial conditions are:

$$x = 0 \quad \text{if} \quad \frac{\partial T}{\partial x} = 0; \quad (3)$$

$$x = r \quad \text{if} \quad -\lambda \frac{\partial T}{\partial x} = a(T - T_0); \quad (4)$$

$$t = 0 \quad \text{and} \quad \frac{\partial T}{\partial x} = 0 \quad \text{if} \quad T = T_H; \quad q = 0. \quad (5)$$

Equation(1) is an equation of heat-conductivity with distributed source of heat in a bulk of a material, and equation(2) characterizes speed of the chemical reaction. Boundary conditions formulate absence of heat stream on the axis of symmetry of considered volumes and heat-exchange with the environment according to Newton's law. Three symmetrical volumes are considered in the task: flat-parallel ( $n = 0$ ), cylindrical ( $n = 1$ ), and spherical ( $n = 2$ ), and the following symbols are taken:  $T_H$ ,  $T_0$ ,  $T$  - initial temperature, temperature of the environment and current temperature in the reaction zone correspondingly;  $x$ ,  $r$  - current coordinate and typical dimension, correspondingly;  $t$  - time,  $Q$  - heat effect of the reaction,  $E$  - energy of activation,  $K_0$  - exponential factor;  $\lambda$ ,  $c$ ,  $\rho$  - heat-conductivity, heat-capacity and density of substance correspondingly;  $a$  - heat-emission coefficient,  $R$  - gas constant,  $C_0$  - concentration of oxidant in the environment;  $q$  - quantity of heat educing in the reaction per unit of solid phase;  $m$ ,  $\nu$  - order of the reaction according to oxidant and fuel;  $a$  - heat-emission coefficient.

Let us define the average temperature according to volume

$$\bar{T} = \frac{1+n}{r^{1+n}} \int_0^r T x^n dx \quad (6)$$

and approximately take into account distribution of temperature on the parabola of the second order,

where  $A$  and  $B$  - coefficients (time function) defined from the boundary conditions (3)-(5).

Then the average temperature is:

$$\begin{aligned} \bar{T} &= \frac{1+n}{r^{1+n}} \int_0^r \left( A - AB \frac{x^2}{r^2} \right) x^n dx \\ &= A \left( 1 - \frac{1+n}{3+n} B \right). \end{aligned} \quad (7)$$

Let us express equations (1) and (2) through the average temperature. To do this, let us multiply all members of these equations by  $x^n \cdot dx$  integrate from 0 till  $\infty$

$$\begin{aligned} c\rho \frac{d\bar{T}}{dt} &= \rho K_0 C_0^m Q \left( 1 - \frac{q}{Q} \right)^v e^{-E/R\bar{T}} \\ &\quad - \frac{2(1+n)}{r^2} AB; \end{aligned} \quad (8)$$

$$\frac{d(\bar{T})}{dt} = K_0 C_0^m Q \left( 1 - \frac{q}{Q} \right)^v e^{-E/RT}. \quad (9)$$

Let us define product  $AB$  through the average temperature  $\bar{T}$ . From (4) and (10) we shall find the following

$$\frac{2\lambda}{r} AB = \alpha [A(1-B) - T_0]. \quad (10)$$

Let us change (8) till it looks like

$$\begin{aligned} \bar{T} &= A \left( 1 - \frac{1+n}{3+n} B \right) \\ &= A(1+n)B + \frac{2}{3+n} AB, \end{aligned} \quad (11)$$

now we have that

$$A(1-B) = \bar{T} - \frac{2}{3+n} AB. \quad (12)$$

Putting (13) into (11) we find that

$$AB = \frac{3+n(\bar{T} - T_0)}{2 \left[ 1 + \frac{(3+n)\lambda}{\alpha r} \right]}. \quad (13)$$

Taking into account (14) and equality of criteria  $B_i = \alpha r/\lambda$ , system of equations (1) and (2) will look like (averaging sign is omitted)

$$\begin{aligned} c\rho \frac{d\bar{T}}{dt} &= \rho K_0 C_0^m Q \left( 1 - \frac{q}{Q} \right)^v e^{-E/R\bar{T}} \\ &\quad - \frac{\lambda(1+n)(3+n)(T - T_0)}{r^2 \left( 1 + \frac{3+n}{B_i} \right)}; \end{aligned} \quad (14)$$

$$\frac{dq}{dt} = K_0 C_0^m Q \left( 1 - \frac{q}{Q} \right)^v e^{-E/RT}. \quad (15)$$

To come the received system to the task solved in paper (6), Let us change expression  $(1 - q/Q)$  in the exponent

$$\left( 1 - \frac{q}{Q} \right) \approx e^{\mu q}; \quad (16)$$

where

$$\mu = \frac{v}{Q}. \quad (17)$$

When taking into consideration (17), equations (1) and (2) with dimensionless variables will be rewritten in the following way if

$$\begin{cases} \frac{dQ}{d\tau} = e^\eta \cdot e^{\theta/1+\beta\theta} - \frac{\theta}{x}; \\ \frac{d\eta}{d\tau} = \gamma e^{-\eta} \cdot e^{\theta/1+\beta\theta}; \\ \tau = 0 \text{ if } \theta = -\theta_H; \eta = 0 \end{cases} \quad (18)$$

where

$$\eta = \mu q \text{ if } \theta = -\theta_h; \quad (19)$$

$$\theta_H = \frac{E(T_0 - T_H)}{RT_0^2}; \quad (20)$$

$$x = \frac{QEK_0 C_0^m \rho r^2 \left( 1 + \frac{n+3}{B_i} \right) e^{-E/RT}}{(1+n)(3+n)\lambda RT^2}; \quad (21)$$

$$\gamma = \frac{vc}{Q} \cdot \frac{RT_0^2}{E} \text{ and } \beta = \frac{RT_0}{\lambda}; \quad (22)$$

$$\theta = \frac{E(T - T_0)}{RT_0^2}; \quad (23)$$

$$\tau = \frac{QEK_0 C_0^m e^{-E/RT}}{cRT_0^2}; \quad (24)$$

System of equations (19) strictly coincides with the analogical system given in paper [6]. Critical condition found in this paper is defined by the expression

$$x_{cr} - 3r = \frac{1}{e}.$$

Taking into account (22) and (23) and symbols given above, we have

$$\frac{QEK_0 C_0^m \rho r^2 e^{-E/RT_{cr}}}{\lambda RT_{cr}^2} \cdot \frac{\left( 1 + \frac{3+n}{B_i} \right)}{(1+n)(3+n)} - \frac{3vcR_{cr}^2}{QE} = \frac{1}{e}. \quad (25)$$

This critical condition differs from that deduced in paper [6] by member

$$F(B_i) = \frac{1 + \frac{3+n}{B_i}}{(1+n)(3+n)}, \quad (26)$$

It takes into account heterogeneity of temperature distribution in the sample.

The analysis of equation (26) shows that it quite coincides with Semenov's condition [1] and gives too high values in comparison with Frank-Kamenetsky's solution. By introducing coordinating function  $\Phi(B_i)$  (its values are calculated according to data given by Mirdzanov and collaborators in paper [3, 5]) into equation (26) (figure 1), quite satisfying agreement with Semenov's and Frank-Kamenetsky's solution of the task may be achieved in all diapason of parameter  $B_i$  change (from 0 till  $\infty$ )

$$\frac{QEC_0^m \rho r^2 e^{-E/RT}}{\lambda RT_{Kp}^2} \cdot \frac{\left(1 + \frac{3+n}{B_i}\right)}{(1+n)(3+n)\Phi(B_i)} - \frac{3vcRT^2}{QE} = \frac{1}{e}. \quad (27)$$

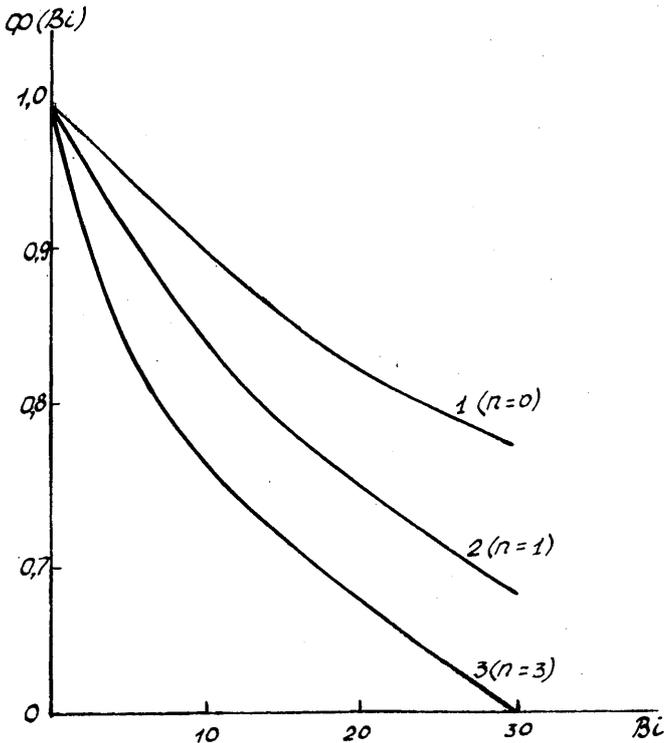


Figure 1: Dependence of function  $\Phi(B_i)$  on  $B_i$   
 1 – a plate, 2 – a cylinder, 3 – a sphere.

To decrease inexactitude appearing as a result of approximation of temperature distribution in combustible system by parable of second order, function  $\Phi(B_i)$  must be taken into account in equation (28).

To calculate critical values of temperature ( $T_{cr}$ ) and typical dimension ( $r$ ) in equation (28), we need values of kinetic parameters:  $E, K_0$  and  $v$ . Definition of these parameters is fulfilled grapho-analytically using thermal analysis [3, 7] from experimental curves "ΔT-time" (figure 2).

The mathematical model deduced above allows to calculate self-ignition conditions and to predict the behaviour of a bulk of powered material of any dimensions and shape.

Results of calculations for wide choice of vegetable stuff are shown in table 1. Period of induction for the stuff given in the table was calculated according to correlations given in paper [3].

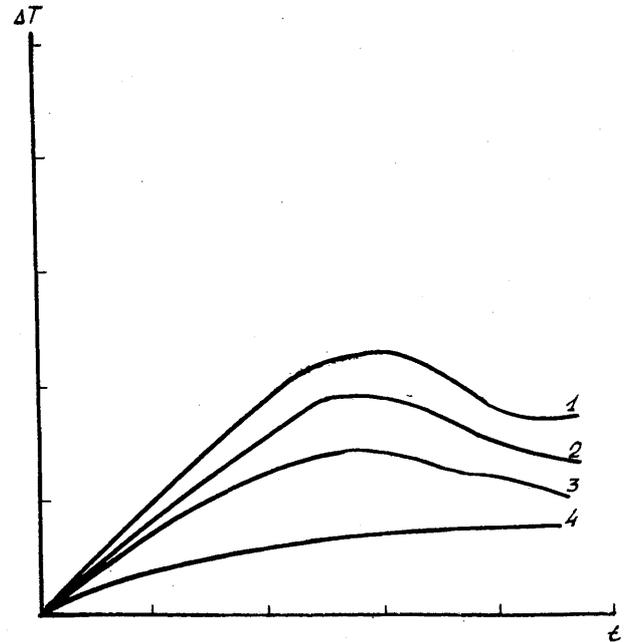


Figure 2: Kinetic curves of warming-up :  
 1 – 447K ; 2 – 450K ; 3 – 456K ; 4 – 458K .

Data from table 1 show that owing to the proposed scheme of calculation of heat self-ignition conditions it is possible not only to ascertain some potential danger of various combustible powered stuff but also to predict critical conditions of their storage (time of induction, dimension of the bulk).

Necessity to process a great number of thermal curves makes this method rather labour-intensive and hampers its use to get necessary information quickly. That is why some algorithms and a program for calculation of critical parameters was worked out on the computer. It allows to calculate fast critical parameters of powered combustible stuff self-ignition and to predict their behaviour during processing, transportation and storage.

Exactness of the chosen model for calculation of powered combustible stuff thermal self-ignition conditions was tested both on laboratory and field levels [8].

Warming-up of a material was investigated in laboratory conditions to get dependence  $T = f(t)$  and to determine kinetic characteristics. Field testing was carried out to investigate self-ignition in conditions close to real storage of materials.

The results of comparison of the calculation with the experiment are shown in table 2. Possibility to predict conditions of heat self-ignition by using the method described above (with precision enough for practical purposes) is clear from the table.

Table 1: Critical conditions of storage of various raw materials.

No	Name of product	$QK, J \cdot kg^{-1} \cdot s^{-1}$	$E, kJ \cdot mol^{-1}$	$v, 10^2$	$r = 1m$		$r = 5m$		$r = 10m$		$r_{cr}, m$
					$T_{cr}, K$	$t, days$	$T_{cr}, K$	$t, days$	$T_{cr}, K$	$t, days$	
1	Grass powder	$1.21 \cdot 10^{15}$	117	1.75	357.73	—	329.45	—	318.53	—	36
2	Sunflower solvent cake	$3.79 \cdot 10^6$	43.2	2.27	267.61	2.4	225.92	2.2	211.84	2.2	0.39
3	Sunflower oilcake	$1.51 \cdot 10^6$	42.0	1.2	274.44	4.0	229.48	3.6	214.50	3.5	0.5
4	Soy-bean oilcake	$4.36 \cdot 10^9$	47.3	1.85	292.61	13.0	247.03	9.2	231.64	9.1	0.8
5	Wheat flour	$1.94 \cdot 10^{10}$	81.2	3.02	348.88	—	310.45	—	296.42	1387.6	8.4
6	Wheat bran	$4.1 \cdot 10^8$	60.9	2.27	303.05	—	264.66	17.7	251.01	17.2	1.12
7	Barley flour	$2.04 \cdot 10^9$	73.6	2.61	344.91	—	303.61	—	288.76	548.1	5.63
8	Fodder yeast	$7.9 \cdot 10^{10}$	83.4	3.35	340.15	—	304.53	—	291.41	650.6	6.25
9	Mixed fodder for pigs	$8.89 \cdot 10^{11}$	93.5	1.41	352.05	—	317.92	—	305.18	—	8.1
10	Mixed fodder for birds	$3.79 \cdot 10^9$	71.6	1.78	326.35	—	288.31	136.0	274.57	120.6	2.8

Table 2:

Name of material	Size of sample, $m$	Temperature, $^{\circ}C$		$ \Delta t $
		calc, $t_p$	exper, $t_E$	
Shatura peat	0.05	128.0	139.0	11.0
Cotton solvent cake	0.05	147.0	150.0	2.5
Pinewood sawdust	0.05	166.0	170.0	3.4
Wheat flour, high qual	0.05	173.4	178.0	4.6
Soy-bean solvent cake	0.8	57.1	59.0	1.9

## LITERATURE

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