Numerical estimation of thermal ignition conditions for reactive medium with Gaussian distribution of activation energy

I G Donskoy
130 Lermontov st., Irkutsk, Russian Federation, 664033
donskoy.chem@mail.ru

Abstract. The article investigates the solutions of the one-dimensional stationary integro-differential heat equation. The source of heat release is determined through the Gaussian distribution function of the activation energy. In such a statement, the critical conditions for the existence of a bounded solution depend on the distribution variance. With the help of numerical methods, such dependences are obtained; for their explanation, the analytical approximations of the thermal explosion theory are used.

1. Introduction
In the classical stationary theory of thermal explosion, the following heat balance equation is considered for a quasi-stationary (slow) exothermic reaction in a plane-parallel reactor with an isothermal wall:

$$\theta'' + Fk \exp \left( \frac{\theta}{1 + Ar \theta} \right) = 0,$$

(1)

with boundary conditions:

$$\theta'(0) = 0, \quad \theta(1) = 0.$$  

(2)

The parameter $Ar$ is small; usually it can be neglected.

The bounded solution to the differential equation exists under constraints on the value of Fk. For $Ar = 0$, the critical value of Fk equal to 0.88 was obtained by Frank-Kamenetskiy [1]. Various modifications of equation (1) were studied in [2-5]. The non-stationary thermal explosion equation was investigated in [5-8]. Alternative statements of the problem are discussed in [9, 10].

When considering reactions in the condensed phase or at the interface (catalytic processes, oxidation of polymers or natural materials), the reaction rate depends on the local configuration in which the reaction center is located. Then the reactivity of the material is described by the distribution over these configurations. Experimental methods for determining the parameters of such a distribution were proposed in [11-13] for coals, biomass and artificial polymers. Introducing the variable $s$, which is relative deviation of activation energy from averaged value, one can write the equation:

$$\theta'' + Fk \exp \left( \frac{\theta}{1 + Ar \theta} \right) \int \exp \left( - \frac{s}{Ar} \right) \exp \left( \frac{s \theta}{1 + Ar \theta} \right) f(s) ds = 0.$$  

(3)
It can be seen that if \( f(s) = \delta(s) \), then eq. (3) is equivalent to eq. (1). In this paper, we consider the Gaussian distribution functions with variance \( \sigma \). This allows evaluation of the integral in eq. (3), so we can rewrite eq. (3) as follows:

\[
0^* + Fk \exp \left[ \frac{0}{1 + Ar\theta} \right] \exp \left[ \frac{\sigma^2}{2} \left( \frac{0}{1 + Ar\theta} - \frac{1}{Ar} \right)^2 \right] = 0.
\] (4)

Mean value of \( s \) is of the order of \(-\sigma^2/Ar\) (because the critical value of \( \theta \) is usually about 1). The aim of the paper is to study the dependence of critical conditions for eq. (4).

2. Numerical solution
Equation obtained in previous section is nonlinear. Therefore, instead of an exact solution, we try to solve it numerically using a uniform spatial grid. Let us consider approximation \( Y^k \) for the solution \( \theta \). Then, the next approximation can be estimated using the scheme with splitting into physical processes [14]. The source term is calculated using an explicit formula, and then the problem of thermal conductivity is solved with a given heat sources:

\[
Y_{i-1}^{k+1} + Y_{i+1}^{k+1} - 2Y_i^{k+1} = -h^2 S(Y_i^k).
\] (5)

Here \( h \) is the step of the spatial grid. Boundary conditions (4) in the difference form are written as follows:

\[
Y_1^{k+1} - Y_2^{k+1} = 0, \quad Y_{N_y}^{k+1} = 0.
\] (6)

The resulting approximation is refined again until the maximum differences between the approximations \( Y^k \) and \( Y^{k+1} \) become less than the specified error \( 10^{-3} \). If the parameter \( Fk \) is higher than the critical one, then the solution blows up (the \( Y \) values become too large, the iterative process diverges). If the iterative process converges to a stationary solution \( Y \), then the selected parameter \( Fk \) corresponds to the safe range. The critical conditions for a thermal explosion are determined by the bisection method.

Usually, the activation energy in oxidation reactions ranges from several tens to several hundred kJ/mol. Then the parameter \( Ar \) will have the order of \( 10^3 \). The parameter \( \sigma \), according to the literature data, can be up to several tenths of a unit (such large values, however, are usually obtained not for exothermic reactions). In our calculations, the upper limit by the value of \( \sigma \) is 0.3.

The calculation results for the critical value of \( Fk \) are shown in Fig. 1. It can be seen that with a decrease in \( Ar \) and with an increase in \( \sigma \), the curves drop sharply \( (Fk << 1) \), i.e. an increase in the variance of the activation energy facilitates the ignition of the reaction system. The main contribution is concerned with the branch of the distribution, in which \( s < 0 \). A decrease in \( Ar \), in turn, increases the sensitivity of the reaction rate to the temperature, and therefore, even at small \( \sigma \), the critical value of the parameter \( Fk \) becomes small.

In previous work [15] the variational method was used to obtain critical conditions for eq. (3) using some additional approximations: the results of this method agree with present calculations.
3. Estimation of apparent activation energy

Obviously, such small critical values of $Fk$ no longer correspond to any physical picture of the phenomenon. Let us interpret the small critical values of $Fk$ in terms of changes in the effective activation energy. To this end, we consider $Fk$ for two reacting systems, in one of which the reaction proceeds with lower activation energy. With small values $\Delta s$, the main contribution to the decrease in the $Fk$ is concerned with the exponential term, and then we obtain the formula which allows an estimation of a relative change in the average activation energy of the combustion reaction:

$$\Delta s \approx Ar \ln \left( \frac{Fk}{Fk_0} \right).$$

(7)

Here $Fk_0$ is 0.88. Further, let us estimate dependence of $\Delta s$ on $\sigma$ and $Ar$ using approximation $Ar\theta \ll 1$. Exponent in eq. (4) can be written as follows:

$$\frac{\sigma^2}{2} \left( \frac{\theta}{1 + Ar\theta} - \frac{1}{Ar} \right)^2 = \frac{\sigma^2}{2} \left( \frac{\theta Ar - (1 + Ar\theta)}{Ar(1 + Ar\theta)} \right)^2 \approx \frac{\Delta s^2}{2Ar^2}.$$

(8)

As it is seen in Fig.1, the graphs look like right branches of Gaussian curves with the variance equal to $Ar$. Combining this approximation with (7) results in following estimation of $\Delta s$:

$$\Delta s \approx \frac{\sigma^2}{2Ar}. $$

(9)

A comparison of $\Delta s$ calculated from (7) and estimated from eq. (9) shows good agreement (Fig. 2). The deviations grow with increasing $Ar$: this is concerned with violation of approximation (7) applicability. The results obtained can be used to predict the conditions of thermal explosion in reaction systems, in which the reaction rate has more complex temperature dependence than the traditional Arrhenius formula (for example, heterogeneous catalytic reactions and low-temperature oxidation of solid fuels such as coal or biomass).
Conclusion
The conditions of thermal explosion are investigated for a reaction system with Gauss-distributed activation energy. The critical values of the parameter $F_k$ are obtained numerically for different values of the distribution variance of parameter $A_r$. The problem of a thermal explosion with distributed activation energy is reduced to the classical statement with new exponent taking into account the distribution parameters. Reduction of apparent activation energy is estimated using both numerical method and analytical approximation: results show good agreement for low values of activation energy deviations.

Acknowledgement
The research was carried out in Melentiev Energy Systems Institute under State Assignment Project (No. FWEU-2021-0005) of the Fundamental Research Program of Russian Federation 2021-2030. Computations were carried out using the resources of the High-Temperature Circuit Multi-Access Research Center (Ministry of Science and Higher Education of the Russian Federation of Russia, project no 13.ЦКП.21.0038).

References
[1] Frank-Kamenetskii D A Diffusion and Heat Exchange in Chemical Kinetics. Princeton Univ. Press, 2015.
[2] Li S and Liao S J 2005 Appl Math Comp 169 854
[3] Novozhilov V 2008 Combust Theor Model 12 433
[4] Merzhanov A G and Averson A E 1971 Combust Flame 16 89
[5] Gontkovskata V T, Gordopolova I S and Peregudov A N 1987 Fizika Goreniya i Vzryva 23(4) 64 [in Russian]
[6] Merzhanov A G, Ozerkovskaya N I and Shkadinskiy K G 1999 Fizika Goreniya i Vzryva 35(6)
65 [in Russian]

[7] Balakrishnan E, Swift A and Wake G C 1996 Math Comp Model 24(8) 1
[8] Sanchez-Rodriguez D, Farjas J and Roura P 2017 Combust Flame 185 211
[9] Graham-Eagle J G and Wake G C 1985 Proc Royal Soc A 401 195
[10] Zarubin V S, Kuvyrkin G N and Savelyeva I Y 2019 Int J Heat Mass Transf 135 614
[11] Miura K and Maki T 1998 Energy Fuels 12 864
[12] Czajka K, Kisiela A, Moron W, Ferens W and Rybak W 2016 Fuel Proc Tech 142 42
[13] Li M, Jiang L, He J J and Sun J H 2019 Energy 175 1
[14] Wichman I S 1991 Combust Flame 83 240
[15] Donskoy I G 2021 Inform Math Tech Sci Manag 21 54-65