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Steady-state equation of thermal explosion in a distributed activation energy medium: numerical solution and approximations

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Abstract. This work presents a mathematical model of thermal explosion in a medium described by a Gaussian distribution of reactivity, along with the determination of critical values for model parameters and their dependence on the distribution dispersion. The numerical solution of boundary value problems for steady-state temperature distribution in a reaction medium (a sweep method along with the iterative refinement of a source function, a half-interval method to find the critical value of the Frank-Kamenetskii parameter) was used. The grid convergence was investigated for the used difference scheme; the first order of accuracy was observed as a result of numerical evaluation of the critical value of the Frank-Kamenetskii parameter. Calculations were carried out with accuracy to three decimal places. Numerical methods were implemented as programs in the MATLAB environment. Numerical approximations were obtained for solutions of the thermal explosion equation characterised by distributed activation energy in the quasi-steady-state approximation. It was shown that the critical value of the Frank-Kamenetskii parameter is associated with the dispersion of the distribution and the Arrhenius parameter by a simple approximate analytical formula, confirmed by comparing with numerical estimates. Since the dependence of the critical value of the Frank-Kamenetskii parameter on the dispersion is described by a Gaussian function, the reaction medium becomes thermally unstable even at small values of the distribution dispersion. Calculations showed that a significant dispersion of reactivity (on the order of tenths of the average) can be observed only for chemical reactions characterised by low sensitivity to temperature (i.e. a small heat effect or low activation energy). Approximate formulas for critical conditions were also obtained for asymmetrical distribution functions. The analysis allows the proposed mathematical model to be used for assessing the thermal stability of reactive media having distributed reactivity (for example, natural materials, polymers, heterogeneous catalytic systems, etc.).
Keywords**:** thermal explosion, distributed activation energy, critical conditions
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ЭНЕРГЕТИКА

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Стационарное уравнение теплового взрыва в среде с распределенной энергией активации: численное решение и приближения

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Резюме. Цель работы – анализ математической модели теплового взрыва в среде с гауссовым распределением реакционной способности; определение критических значений параметров модели и их зависимости от дисперсии распределения. В работе использовалось численное решение краевых задач для стационарного распределения температуры в реакционной среде (метод прогонки с итерационным уточнением функции-источника, метод половинного деления для нахождения критического значения параметра Франк-Каменецкого). Для использованной разностной схемы исследована сеточная сходимость, показан первый порядок точности при численной оценке критического значения параметра Франк-Каменецкого. Расчеты проводились с точностью до третьей значащей цифры. Численные методы реализованы в виде программ в среде MATLAB. Получены численные приближения для решений уравнения теплового взрыва с распределенной энергией активации в квазистационарном приближении. Показано, что критическое значение параметра Франк-Каменецкого связано с дисперсией распределения и параметром Аррениуса простой приближенной аналитической формулой, которая подтверждается путем сравнения с численными оценками. Зависимость критического значения параметра Франк-Каменецкого от дисперсии оказывается гауссовой, поэтому уже при малых значениях дисперсии распределения реакционная среда становится термически неустойчивой. Расчеты показали, что значительная дисперсия реакционной способности (порядка десятых долей от среднего) может наблюдаться только для химических реакций с низкой чувствительностью к температуре (т.е. с малым тепловым эффектом или с низкой энергией активации). Для несимметричных функций распределения также получены приближенные формулы для критических условий. Проведенный анализ позволяет применять предложенную математическую модель для реагирующих сред с распределенной реакционной способностью (например, природных материалов, полимеров, гетерогенных каталитических систем и т.д.) для оценки их тепловой устойчивости.

Ключевые слова: тепловой взрыв, распределенная энергия активации, критические условия

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INTRODUCTION

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

$$\lambda \frac{d^2T}{dx^2} + Q\rho k_0 \exp\left(-\frac{E}{RT}\right) = 0. \qquad (1)$$

Here T is temperature, λ is thermal conductivity, x is spatial coordinate, Q is reaction heat, ρ is reagent density, k_0 is preexponential (frequency) factor, E is activation energy, R is universal gas constant. Boundary conditions for the symmetry axis and boundaries are written as follows:

$$\left.\frac{dT}{dx}\right|_{x=0} = 0,\ T(L) = T_0. \qquad (2)$$

Here L is characteristic length (half-width). Using dimensionless variables, we obtain an equation with boundary conditions:

$$\frac{d^2\theta}{d\xi^2} + Fk \exp\left(\frac{\theta}{1+Ar\theta}\right) = 0, \qquad (3)$$

$$\left.\frac{d\theta}{d\xi}\right|_{\xi=0} = 0,\ \theta(1) = 0. \qquad (4)$$

Here the dimensionless parameters are defined as follows:

$$\xi = \frac{x}{L},\ \theta = \frac{E}{RT_0^2}(T - T_0),\ Ar = \frac{RT_0}{E},$$

$$Fk = \frac{Q\rho E k_0}{\lambda L R T_0^2} \exp\left(-\frac{E}{RT_0}\right).$$

The parameter Ar is usually small; therefore, in most cases, 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^0 equal to 0.88 was obtained by Frank-Kamenetskii [1]. The thermal explosion equation is used to predict the conditions of ignition, for example, during storage of fuels and heat treatment of materials [2–5]. Modified problems, for example, taking into account burnout, sample geometry, special boundary conditions, thermal explosion in systems with parallel reactions, thermal explosion in medium with the thermal conductivity coefficient depending on temperature, were considered in [6–13]. Non-stationary equations of thermal explosion were numerically solved in [14–18], where the classification of solutions is

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given and the problem parameters are estimated at which transitions between classes occur. Variational formulations for thermal explosion problems were considered in [7, 19, 20].

Equation (1) describes the temperature distribution during a chemical reaction with a given value of the activation energy. However, in some systems (for example, for reactions in the condensed phase or at the interface, catalytic processes, oxidation of polymers or natural materials), the activation energy 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 [21–26] for coals, biomass and artificial polymers.

For such systems, the heat balance can be described in the form of the following integro-differential equation:

$$\lambda \frac{d^2T}{dx^2} + Q\rho k_0 \int \exp\left(-\frac{E+\varepsilon}{RT}\right) g(\varepsilon) d\varepsilon = 0. \quad (5)$$

Here ε is the deviation of the activation energy, and $g(\varepsilon)$ is the distribution function of this value (with a mean value equal to 0). Using dimensionless parameters and splitting exponent in integrand of equation (5), one can rewrite it the following form:

$$\frac{d^2\theta}{d\xi^2} + Fk \exp\left(\frac{\theta}{1+Ar\theta}\right) \times \int \exp\left(-\frac{\varepsilon}{RT}\right) g(\varepsilon) d\varepsilon = 0. \quad (6)$$

Introducing the variable $s = \varepsilon/E$, we rewrite the equation as:

$$\frac{d^2\theta}{d\xi^2} + Fk \exp\left(\frac{\theta}{1+Ar\theta}\right) \int \exp\left(-\frac{s}{Ar}\right) \exp\left(\frac{s\theta}{1+Ar\theta}\right) f(s) ds = 0. \quad (7)$$

One of the features of equation (7) is the impossibility of neglecting the parameter *Ar*: in the integrand, *Ar* is in the denominator of the exponent. This factor takes into account the reaction rate at temperature T_0.

It can be seen that for $f(s) = \delta(s)$ Eq. (7) turns into Eq. (3). In this paper, we will consider the Gaussian distribution function:

$$f(s) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{s^2}{2\sigma^2}\right). \quad (8)$$

Here σ is the variance. For a Gaussian distribution function, a shift in the mean value occurs:

$$\exp\left(-\frac{s}{Ar}\right) \exp\left(\frac{s\theta}{1+Ar\theta}\right) \exp\left(-\frac{s^2}{2\sigma^2}\right) = \exp\left[s\left(\frac{\theta}{1+Ar\theta} - \frac{1}{Ar}\right) - \frac{s^2}{2\sigma^2}\right]. \quad (9)$$

Thus the product of two exponential functions gives a new Gaussian function, but with a different factor and mean value: the extremum will be observed at *s* about $-\sigma^2/Ar$ (since usually the critical value θ is of the order of unity, deviations from the maximum will be of the order of σ^2). The integral of this function can be found analytically. Equation (7) can then be rewritten as:

$$\frac{d^2\theta}{d\xi^2} + Fk \exp\left[\frac{\theta}{1+Ar\theta}\right] \times \exp\left[\frac{\sigma^2}{2}\left(\frac{\theta}{1+Ar\theta} - \frac{1}{Ar}\right)^2\right] = 0. \quad (10)$$

The boundary conditions remain the same as for the classical problem. It can be seen that, as σ tends to zero, Eq. (10) transforms into Eq. (3). Now we can formulate a question: how the parameters σ and *Ar* will affect the critical conditions of a thermal explosion, i.e. the existence of a bounded solution to equation (10)?

NUMERICAL METHOD

To solve stated problem, numerical calculations were carried out. The parameters σ and *Ar* are, generally speaking, independent. Therefore, the calculations were carried out with the simultaneous variation of both parameters.

Equation (10) is nonlinear, and even if we use the usual approximation $Ar\theta << 1$, the result leads to cumbersome quadratures. Therefore, instead of an exact solution, we seek an approximate numerical solution using a grid. Let there be *k*-th approximation Y^k for the function θ. Then the next approximation can be estimated using the scheme with splitting into physical processes [27]. The source term is calculated using an explicit formula:

$$S_i = Fk \exp\left(\frac{Y_i^k}{1+ArY_i^k}\right)\times \times\exp\left[\frac{\sigma^2}{2}\left(\frac{Y_i^k}{1+ArY_i^k}-\frac{1}{Ar}\right)^2\right]. \quad (11)$$

Here *i* counts grid points. Then the problem of thermal conductivity is solved with a given distribution of heat sources:

$$Y_{i-1}^{k+1} + Y_{i+1}^{k+1} - 2Y_i^{k+1} = -h^2 S_i. \quad (12)$$

Here *h* is the spatial grid step ($h = 1/N$). Boundary conditions (4) in difference form are written as follows:

$$Y_1^{k+1} - Y_2^{k+1} = 0,\ Y_N^{k+1} = 0. \quad (13)$$

The solution of a system of linear equations (12, 13) is found by the tridiagonal matrix algorithm. The resulting approximation is refined again until the differences between the approximations Y^k and Y^{k+1} become less than the specified error (10^{-3}). Since all the variables in the problem are dimensionless, the calculation accuracy will not depend on their absolute values. 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: calculations are carried out for a deliberately large value of Fk_{max} and a deliberately small value of Fk_{min} (for the first iteration, they are equal to 10 and 0, respectively), then the new value is determined as $Fk_{i+1} = (Fk_{max} + Fk_{min})/2$. If the new value leads to the solution blow-up, it becomes the upper limit of the range; if at this value the numerical solution converges, then it becomes the lower boundary of the range. The general scheme of the algorithm is shown in fig. 1. Since calculations have shown that the critical value of *Fk* at small values of *Ar* and large values of σ can be much less than unity, the permissible error ΔFk depends on the current value of Fk_{k+1}, which ensures accuracy to the required number of significant digits. In calculations it is assumed $\Delta Fk = 10^{-4}\times Fk_k$, i.e. calculations are carried out up to the third significant digit.

The influence of the grid step was carried out using the example of solving problem (3), since its critical value *Fk* is known for $Ar = 0$. The dependence of the critical value *Fk* on the number of grid points is shown in fig. 2. Influence of the grid step on the calculation error shown in fig. 3: it can be seen that the numerical scheme has an order of accuracy close to one (in relation to critical value of *Fk* parameter). The calculation results become insensitive to the grid step already at the number of nodes equal to 1000. This value was used further in the numerical solution of equation (10).

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}–10^{-2} (at larger values, features of degeneration of the thermal explosion are observed [28]). The parameter σ, 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 on the value of σ is 0.3.

NUMERICAL RESULTS

The calculation results for the critical value of *Fk* are shown in fig. 4. It can be seen that with a decrease in *Ar* and with an increase in σ, the curves sharply fall down: the critical value of *Fk* decreases to negligible values, i.e., with other things being equal, an increase in the activation

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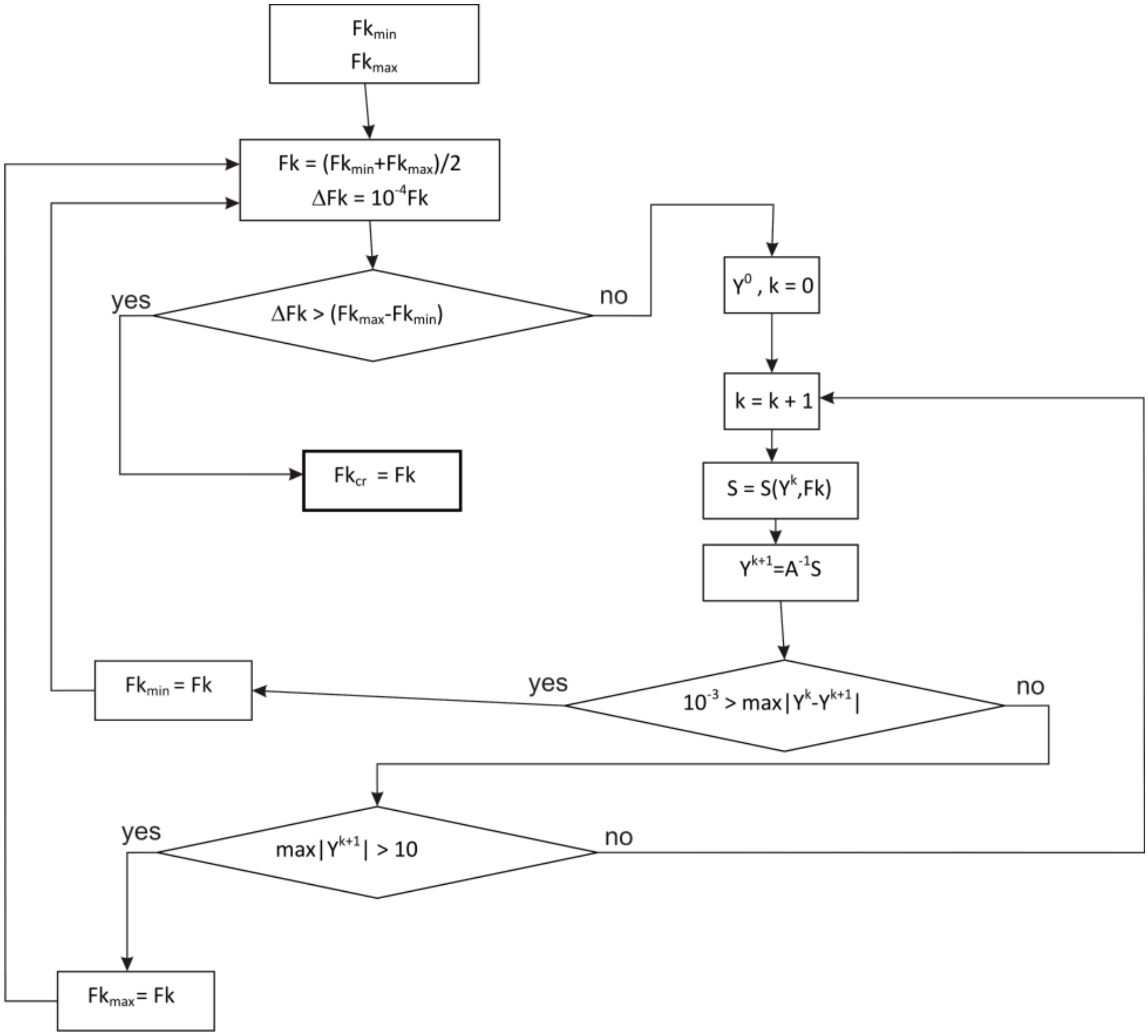


Fig. 1. Algorithm for determining the critical value of the parameter Fk for the given values of Ar and σ
Рис. 1. Алгоритм определения критического значения параметра Fk для заданных значений Ar и σ

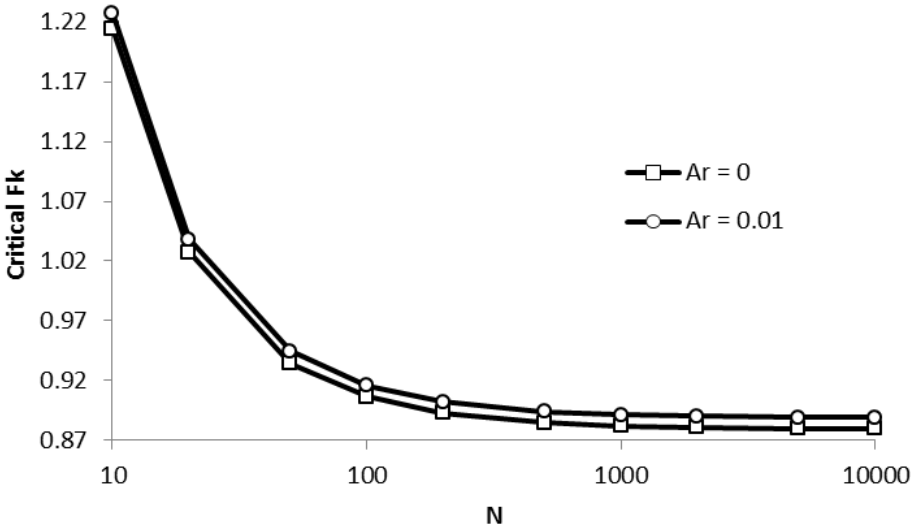


Fig. 2. Grid size influence on the critical value of the parameter Fk from the equation (3)
Рис. 2. Влияние размера сетки на критическое значение параметра Fk из уравнения (3)

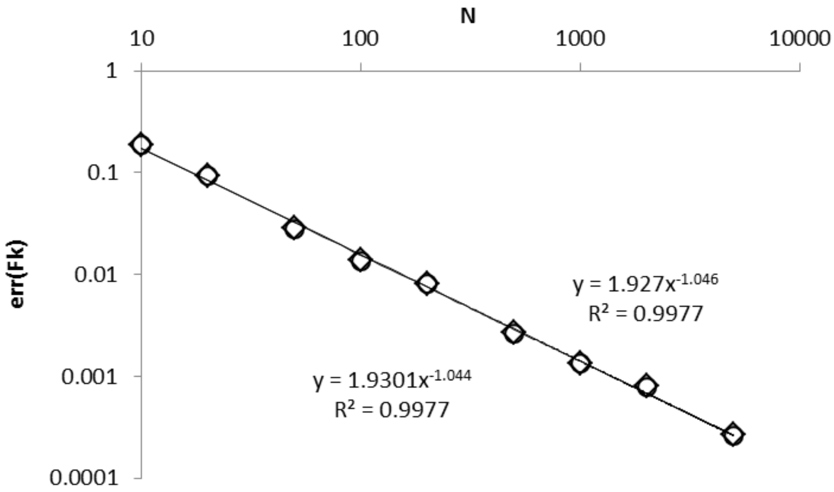


Fig. 3. Dependence of the calculation error of the calculated critical parameter Fk value on the grid size
Рис. 3. Зависимость погрешности вычисления расчетного значения критического параметра Fk от размера сетки

energy of the combustion reaction and an increase in the variance of the activation energy make the reaction system less stable. An increase in variance leads to an increase in the fraction of reaction centers that are involved in chemical reaction with a lower activation energy. The main contribution is concerned with the left side of the distribution, in which (E + ε) <E. A decrease in Ar, in turn, increases the sensitivity of the reaction rate to temperature, and therefore, even at small σ, the critical value of the parameter Fk becomes small. Note that the parameter Ar, generally speaking, is included in Fk; therefore, for fixed properties of the reacting material, the parameter Fk is mainly determined by the size of the sample (or reaction vessel).

The calculated critical values of the parameter Fk turn out to be so small that their determination leads to computational difficulties associated with the multiplication of very small and very large numbers: such numerical procedures are known to be a source of errors. Therefore, the calculations were carried out not for the entire range of σ, but only up to those values at which the critical value of Fk is of the order of 10^{-12}. Obviously, such small values no longer correspond to any physical picture of the phenomenon: from a practical point of view, in such systems it is impossible to choose suitable parameters for the quasi-steady reaction (in our calculations, deviations from the mean of other quantities affecting the reactivity, such as the preexponential factor and the concentration of the reagent, was not considered at all).

Let us interpret the small critical values of the parameter Fk in terms of changes in the effective activation energy. To this end, consider the ratio of the parameters Fk for two reacting systems, in one of which the reaction proceeds with lower activation energy (for example, due to the presence of a catalyst):

$$\frac{Fk_1}{Fk_2} = \frac{\left(Q\rho E_2 k_0\right)/\left(\lambda LRT_0^2\right)\exp\left[-E_2/\left(RT_0\right)\right]}{\left(Q\rho E_1 k_0\right)/\left(\lambda LRT_0^2\right)\exp\left[-E_1/\left(RT_0\right)\right]} = \frac{E_2}{E_1}\exp\left(-\frac{E_2-E_1}{RT_0}\right). \quad (14)$$

If we use modified activation energy $E_2 = E_1 + \Delta\varepsilon$, and variable $\Delta s = \Delta\varepsilon/E_1$, then we can write:

$$\frac{Fk_1}{Fk_2} = \frac{E_1+\Delta\varepsilon}{E_1}\exp\left(-\frac{\Delta\varepsilon}{RT_0}\right) = \left(1+\Delta s\right)\exp\left(-\frac{\Delta s}{Ar}\right). \quad (15)$$

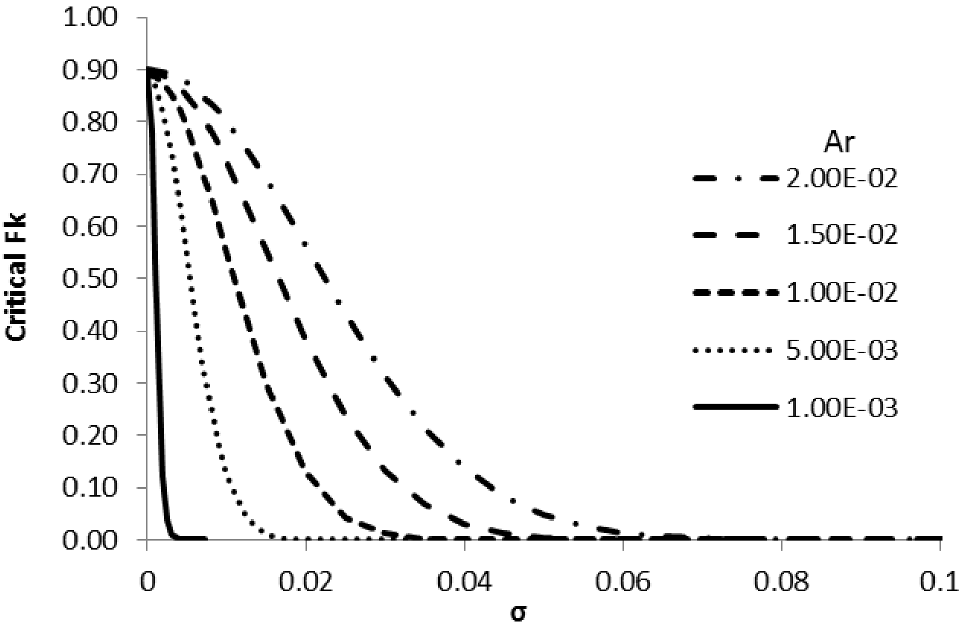


Fig. 4. Calculated dependence of the critical value of the parameter Fk on the parameters σ and Ar
Рис. 4. Расчетная зависимость критического значения параметра Fk от параметров σ и Ar

With small values Δ*s*, the main contribution to the decrease in the ratio Fk_2/Fk_1 will come from the second factor, therefore Δ*s* can be neglected in the first factor, and then we obtain the final formula:

$$\Delta s \approx Ar \ln\left(\frac{Fk_2}{Fk_1}\right). \quad (16)$$

This formula gives the relative change in the average activation energy of the combustion reaction, i.e. the deviation for which the critical value of *Fk* will agree with the classical theory. The dependence of Δ*s* on the parameters *Ar* and σ is shown in fig. 5: this curve is everywhere non-positive, i.e. the effective activation energy of the combustion reaction decreases in all cases. This decrease, however, is much more sensitive to *Ar* than to σ. Note that at σ = 0 the sensitivity of the critical value of *Fk* with respect to *Ar* is small, and a sharp dependence appears only for the distributed reactivity.

APPROXIMATE ANALYTICAL SOLUTION

As mentioned above, equation (10) contains exponential factors, in the exponents of which there are significantly different terms. For example, using estimate *Ar*θ << 1, equation (11) can be simplified as follows:

$$\frac{d^2\theta}{d\xi^2} + Fk \exp\left(\frac{\sigma^2}{2Ar^2}\right)\exp(\theta) = 0. \quad (17)$$

That is, in a fairly good approximation, the critical value of *Fk* in equation (17) differs from the value of *Fk* for the classical problem (3) by a single factor. Therefore, the curves in fig. 4 look like the shoulders of Gaussian curves with variance equal to *Ar*, and the curves in fig. 5 look as branches of a parabola. Indeed, a comparison of the calculated critical values of *Fk* with the factor in the second term in (17) shows good agreement (fig. 7). The deviations grow with increasing *Ar*. This may be one of the marks of the thermal explosion degeneration. Then the expression for the effective activation energy (16) can be rewritten as follows:

$$\Delta s = \frac{\sigma^2}{2Ar}. \quad (18)$$

The results obtained can be used to predict the conditions of thermal explosion in reaction systems, in which the reaction rate has more

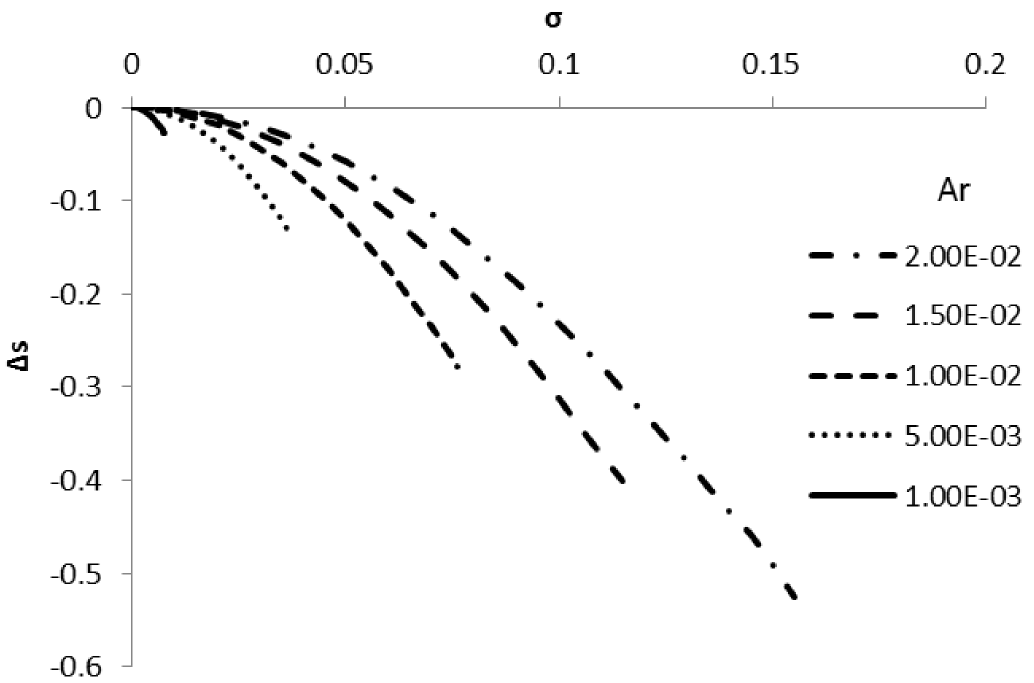


Fig. 5. Relative deviation of the activation energy from the average value for the critical conditions of a thermal explosion
Рис. 5. Относительное отклонение энергии активации от среднего значения для критических условий теплового взрыва

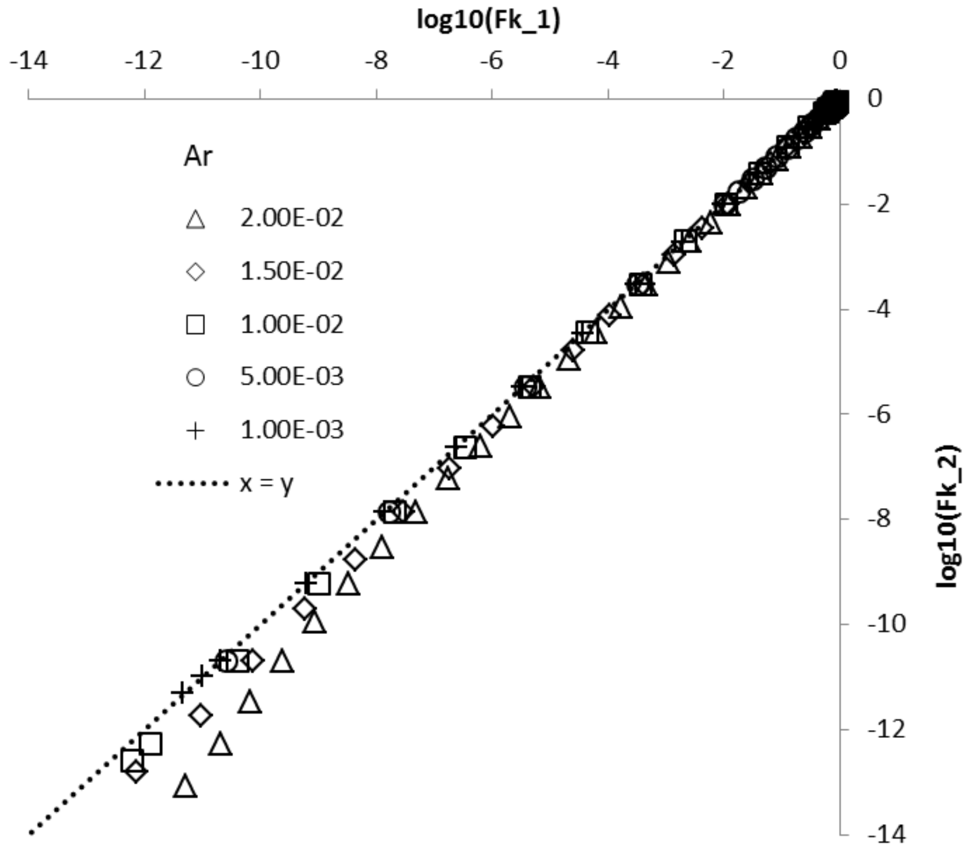


Fig. 6. Comparison of the critical values Fk calculated for the exact problem (Fk1) and for the approximate problem (Fk2)
Рис. 6. Сравнение критических значений Fk, рассчитанных для точной задачи (Fk1) и для приближенной задачи (Fk2)

complex temperature dependence than the traditional Arrhenius formula. This primarily concerns heterogeneous catalytic reactions and low-temperature oxidation of solid fuels such as coal or biomass. For example, if the variance of the activation energy is known from kinetic measurements, it is possible to estimate the critical conditions of a thermal explosion; when carrying out an exothermic reaction with different heating temperatures, the variance of the activation energy can be estimated.

APPROXIMATE SOLUTIONS FOR THE ASYMMETRIC DISTRIBUTION FUNCTION

In the general case, to solve the problem of a thermal explosion in a medium with distributed activation, it is necessary to solve the problem of the heat conduction equation and the equation of chemical kinetics, supplemented by the Fokker-Planck equation (to describe the transition between energy states). The above results refer to the case when the relaxation time to the stationary Gaussian distribution (8) is sufficiently small. However, such relaxation can be rather slow. In the limiting case of large time relaxations, the highly reactive part of the distribution quickly burns out, after which the distribution function becomes asymmetric. Depending on the reaction history, the function may take different forms for which results from a previous section are inapplicable.

Consider a piecewise Gaussian distribution function equal to zero for argument values less than zero:

$$f(s) = \begin{cases} 0, s < 0 \\ C\,exp\left(-\frac{s^2}{2\sigma^2}\right), s \geq 0 \end{cases}. \qquad (19)$$

Substituting it into the thermal explosion equation, we obtain:

$$\frac{d^2\theta}{d\xi^2} + Fk\,exp\left(\frac{\theta}{1+Ar\theta}\right) C \int_0^{\infty} exp\left(-\frac{s}{Ar} + \frac{s\theta}{1+Ar\theta} - \frac{s^2}{2\sigma^2}\right) ds = 0. \qquad (20)$$

After transformations, we arrive at the expression:

$$\frac{d^2\theta}{d\xi^2} + Fk\,exp\left(\frac{\theta}{1+Ar\theta}\right) exp\left[\frac{\sigma^2}{2}\left(\frac{\theta}{1+Ar\theta} - \frac{1}{Ar}\right)^2\right]\left\{1 - \mathrm{erf}\left[\frac{\sigma}{\sqrt{2}}\left(\frac{\theta}{1+Ar\theta} - \frac{1}{Ar}\right)\right]\right\} = 0. \qquad (21)$$

Using the normalization condition and the approximation $Ar\theta << 1$, we obtain:

$$\frac{d^2\theta}{d\xi^2} + Fk\,exp(\theta)\,exp\left(\frac{\sigma^2}{2Ar^2}\right)\left[1 - \mathrm{erf}\left(\frac{\sigma}{Ar\sqrt{2}}\right)\right] = 0. \qquad (22)$$

We assume that the critical value *Fk* is related to Fk^0 by the relation:

$$Fk_{cr}^0 = Fk_{cr}\,exp\left(\frac{\sigma^2}{2Ar^2}\right)\left[1 - \mathrm{erf}\left(\frac{\sigma}{Ar\sqrt{2}}\right)\right]. \qquad (23)$$

The right-hand side of this equation gradually decreases with increasing σ, therefore, to maintain the critical value, Fk_{cr} must grow. That is, the reactive medium becomes more inert, as expected: the proportion of the most reactive part of the distribution decreases with increasing variance.

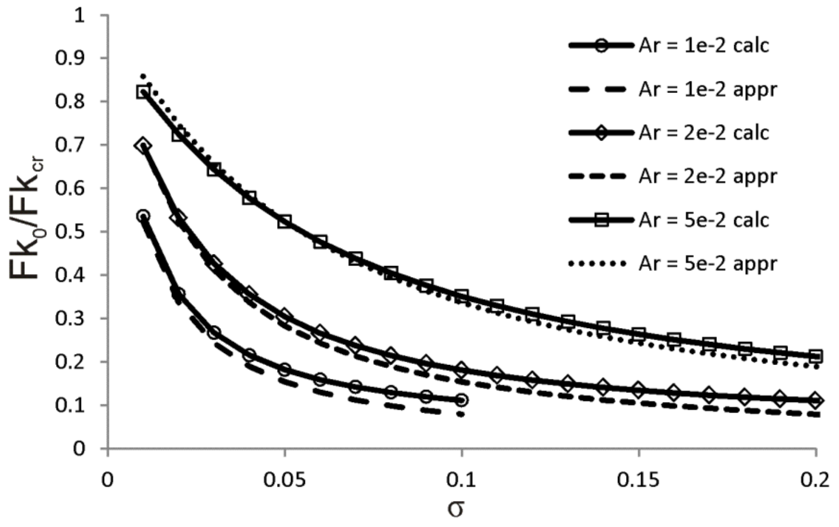
Another option (although less realistic) is a piecewise Gaussian distribution function equal to zero when the argument is greater than zero:

$$f(s) = \begin{cases} 0, s > 0 \\ C\exp\left(-\frac{s^2}{2\sigma^2}\right), s \leq 0 \end{cases}. \qquad (24)$$

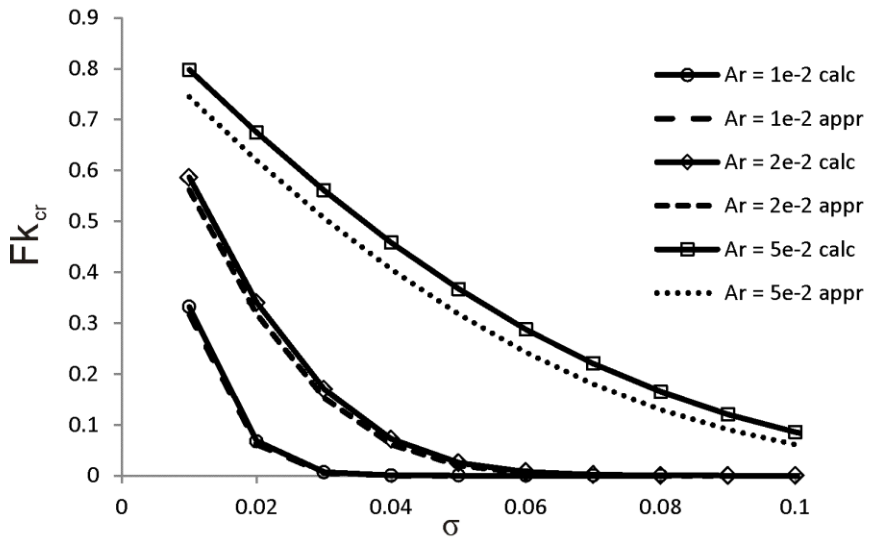
The thermal explosion equation for such a distribution function will be similar to the previous case, but with different integration limits. Therefore, the changes will affect only the multiplier containing the error function. Again using the normalization condition and the high activation energy approximation, we obtain the relation for the critical value of *Fk*:

$$Fk_{cr}^0 = Fk_{cr}\,exp\left(\frac{\sigma^2}{2Ar^2}\right)\left[1 + \mathrm{erf}\left(\frac{\sigma}{Ar\sqrt{2}}\right)\right]. \qquad (25)$$

The right side of the equation is now a growing function of σ. Accordingly, the critical value Fk_{cr} decreases, and the reactive medium is less stable with respect to thermal perturbations.



a



b

Fig. 7. Comparison of the critical values Fk calculated for the exact problem and for the approximate problem with asymmetric distribution of activation energy: a – equation (19); b – equation (24)
Рис. 7. Сравнение критических значений Fk, рассчитанных для точной задачи и для приближенной задачи с асимметричным распределением энергии активации: a – уравнение (19); b – уравнение (24)

Comparison of critical values of *Fk* calculated using numerical procedure and analytical approximations is presented in fig. 7. It can be seen that analytical estimates are fairly good for small values of σ.

Finally, the problem with a continuous different-arm distribution is of additional interest:

$$f(s) = \begin{cases} C\,exp\left(-\frac{s^2}{2\sigma_1^2}\right), s \le 0 \\ C\,exp\left(-\frac{s^2}{2\sigma_2^2}\right), s > 0 \end{cases}. \qquad (26)$$

Combining the previous results, we get:

$$Fk_{cr}^0 = Fk_{cr}C\frac{\sqrt{\pi}}{2}\left\{\sigma_1\,exp\left(\frac{\sigma_1^2}{2Ar^2}\right)\left[1+\mathrm{erf}\left(\frac{\sigma_1}{\sqrt{2}Ar}\right)\right] + \sigma_2\,exp\left(\frac{\sigma_2^2}{2Ar^2}\right)\left[1-\mathrm{erf}\left(\frac{\sigma_2}{\sqrt{2}Ar}\right)\right]\right\}. \qquad (27)$$

Here, the constant *C* depends on the ratio of the variances of different distribution arms. During reaction, the left side of the distribution is depleted faster, that is, we can consider the situation $\sigma_1 < \sigma_2$ (and in the limit $\sigma_1 = 0$) to account for burnout.

Finally, if the symmetry of the distribution is preserved, but there is a shift in the distribution, i.e. the average value of the activation energy is s_μ, then the formula for the critical value of the number *Fk* can be written as:

$$Fk_{cr}^{0} = Fk_{cr}\, exp\left(\frac{\sigma^2}{2Ar^2}\right) exp\left(-\frac{s_\mu}{Ar}\right). \quad (28)$$

As can be seen from this formula, when the average deviation is shifted by $\sigma^2/2Ar$, the critical value of *Fk* does not differ from the standard value (which is similar to Eq. (19)).

CONCLUSIONS

The critical conditions of thermal explosion in a reaction system, the reactivity of which is given by the Gaussian distribution of the activation energy, are investigated. Using numerical methods, the critical values of the parameter *Fk* are obtained for different values of the variance of the activation energy and the parameter $Ar = RT_0/E$. It is shown that the problem of a thermal explosion with a distributed reactivity can be reduced (using realistic approximations) to the classical formulation with an additional factor that takes into account the variance of the distribution and the associated sensitivity of the reaction rate to temperature. Analysis of the approximate equation shows the relationship between the critical value of the parameter *Fk* and the variance of the distribution. The cases of asymmetric distribution function are considered. The results obtained can be applied to study the processes of ignition of materials with distributed reactivity.

Abbreviations:

Ar – Arrhenius parameter
E – average activation energy, J/mol
Fk – Frank-Kamenetskii parameter
f – distribution function of relative activation energy deviation from average value
g – distribution function of activation energy deviation from average value
h – grid step
k_0 – preexponential factor, 1/s
L – characteristic size of rector (sample), m
N – number of grid points
Q – thermal effect of chemical reaction, J/kg
R – gas constant, 8.314 J/mol/K
S_i – source term of i-th grid point
s – relative activation energy deviation from average value
T – temperature, K
x – spatial coordinate, m
Y_i – approximate value of dimensionless temperature in i-th grid point
ε – activation energy deviation from average value
θ – dimensionless temperature
λ – thermal conductivity, W/m/K
ξ – dimensionless spatial coordinate
ρ – reagent mass fraction, kg/m^3
σ – variance of value s

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