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ФОРМАЛЬНО-КИНЕТИЧЕСКИЕ ПОДХОДЫ К ОПИСАНИЮ ТЕРМИЧЕСКОГО РАЗЛОЖЕНИЯ МАТЕРИАЛОВ – ПРОБЛЕМЫ ИДЕНТИФИКАЦИИ ПАРАМЕТРОВ И ИНТЕРПРЕТАЦИИ РЕЗУЛЬТАТОВ: КРАТКИЙ ОБЗОР

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В работе выполнен обзор принципиальных подходов к формально-кинетическому описанию процесса термохимической конверсии материалов. Рассмотрены варианты классификации используемых методов обработки кинетических кривых, а также анализ вариантов включения в расчет аппроксимации температурного интеграла Аррениуса. Выполнена идентификация кинетических параметров на основе анализа результатов термического разложения модельного материала в неизотермических условиях несколькими известными методами, не предполагающими вычисление температурного интеграла. Показано, что проведение обратного расчета в рамках любого из используемых методов с целью прогнозирования величины степени разложения дает адекватные результаты. Задача сравнения методов между собой не ставилась, так как расчеты выполнены для модельного материала при очень малом наборе экспериментальных данных. Результаты расчетов используются в качестве иллюстративного материала, подтверждающего возможности идентификации параметров А и Е уравнения Аррениуса указанными методами. В рамках настоящего исследования было также найдено решение двумерной оптимизационной задачи нахождения минимального значения среднеквадратического отклонения расчетных данных от экспериментальных. Указанная задача была решена методом перебора параметров для определения локального оптимума комбинации А и Е при численном нахождении температурного интеграла. Показано что, несмотря на большой объем вычислительных операций, при таком подходе может быть получено сочетание А и Е, обеспечивающих минимальное при заданной точности вычислений расхождение между экспериментальными и прогнозируемыми значениями.

Ключевые слова: термохимическая конверсия, формальная кинетика, термогравиметрический анализ, закон Аррениуса, порядок реакции, скорость подъема температуры, температурный интеграл

FORMAL KINETIC APPROACHES TO THE DESCRIPTION OF THERMAL DECOMPOSITION OF MATERIALS - PROBLEMS OF PARAMETER IDENTIFICATION AND RESULTS INTERPRETATION: A BRIEF REVIEW

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The paper provides an overview of the principal approaches to the formal kinetic description of the process of thermochemical conversion of materials. The variants of classification of the methods used for description of kinetic curves are observed, as well as the analysis of options for including the approximation of the Arrhenius temperature integral in the calculation. The kinetic parameters were identified based on the analysis of the results of thermal decomposition of the model material under non-isothermal conditions by several well-known methods that do not involve the calculation of the temperature integral. It is shown that performing a reverse calculation within the framework of any of the methods used in order to predict the conversion rate of decomposition gives adequate results. The task of comparing the methods was not set by itself, since the calculations were performed for the model material with a very small set of experimental data. The calculation results are used as illustrative material confirming the possibility of identifying the parameters A and E of the Arrhenius equation by these methods. Within the framework of this study, a solution was also found to the two-dimensional optimization problem of finding the minimum value of the standard deviation

of the calculated data from the experimental ones. This problem was solved by iterating over the parameters to determine the local optimum of the combination of A and E when numerically finding the temperature integral. It is shown that, despite the large volume of computational operations with this approach, a combination of A and E can be obtained, providing the minimum discrepancy between experimental and predicted values for a given accuracy of calculations.

Key words: thermochemical conversion, formal kinetic, thermogravimetric analysis, Arrhenius law, reaction order, temperature growth rate, temperature integral

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INTRODUCTION

In the past decades, thermo-chemical treatment of biomass has been the subject of increasing attention [1-4]. However, thermal decomposition of such solids, which occurs when chemical compounds are heated, is very complex chemical process for deterministic modeling, and therefore formal kinetic approaches are widely used [5-7]. Therefore, kinetic analysis of solid-state decompositions is usually based on consideration of a single step kinetic equation [6-7]. In the past decades, a wide range of simplified methods have been proposed and accepted for modeling of biomass reaction kinetics [5-9]. A common basis for classifying the analytical methods is to divide them into model-fitting and model-free once. A more detailed scheme [5, 10] is presented in fig.1.

Model-fitting and model-free approaches both have some advantages and disadvantages over each other [25-27]. Over the past two decades, a significant increase in popularity of model-free approaches can be found [25]. Partially, this is because many of the simpler model-free methods are easy for programming and realization, whereas the model-fitting methods usually require specialized software [25-26]. The most significant difference between model-free and model-fitting methods is that using model-fitting scheme the entire kinetic triplet (the activation energy, preexponential factor, and reaction model) can be found through a single computational step. Model-free methods to evaluate the kinetic triplet need several computational steps [25-26].

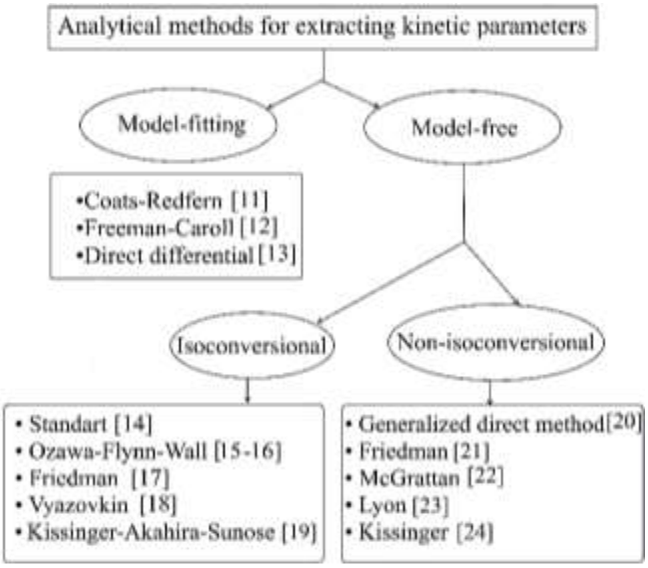

Fig. 1. Analytical methods for evaluating the kinetic parameters from experiments with thermal transformation of materials [5, 10]
Рис. 1. Аналитические методы оценки кинетических параметров из экспериментов с термопреобразованием материалов [5, 10]

Another way to classify the same schemes will be to divide them into two types, namely, the allocation of integral and differential methods [28]. The essence of the methods will be clarified in the next section of the paper; here we will only give some integral and differential approaches to illustrate the classification on this basis (Fig. 2).

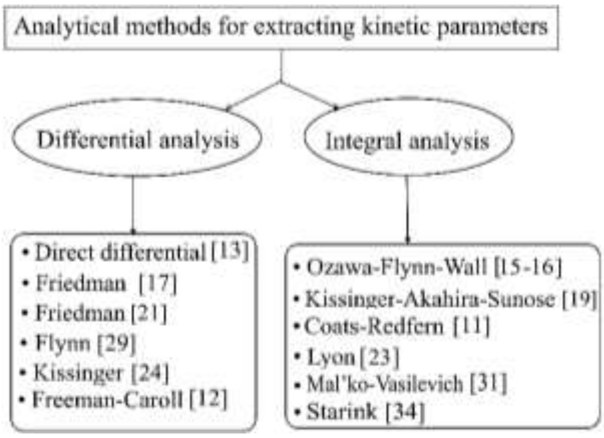

Fig. 2. Some integral and differential approaches for evaluating the kinetic parameters from experiments with thermal transformation of materials
Рис. 2. Некоторые интегральные и дифференциальные подходы для оценки кинетических параметров из экспериментов с термопреобразованием материалов

THEORETICAL BACKGROUND

The essence of the differential methods

First consider the differential method following Flynn [29]. The complex process of thermo-chemical treatment of a biomass sample is considered here as a single gross reaction. The following equation represents the reaction kinetics:

$$\frac{dm}{dt} = -k \cdot (m - m_\infty)^2, \tag{1}$$

where m is the current value of the sample mass, t is the reaction time, m_∞ is the terminal value of the sample mass (corresponded to the highest possible value of mass loss), k is the temperature-dependent reaction rate constant, n is the order of the reaction. The term m_∞ can be defined as a «ballast», while the term (m–m_∞) denotes the mass of a reactant m_r.

In order to use a kinetic analysis method the mass term is transformed into the conversion term α, which is defined as [25-31]:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}, \tag{2}$$

or, in the other form, as

$$\alpha = \frac{m_0 - (m_r + m_\infty)}{m_0 - m_\infty}, \tag{3}$$

where m_0 is the initial sample mass.

The following differential equation is normally used to describe the process kinetics [25-31]:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha), \qquad (4)$$

where f(α) is the function called a reaction model.

The rate constant k depends only on the process temperature and can be described by Arrhenius equation [25-31]:

$$k = A \cdot \exp\left(-\frac{E}{RT}\right), \qquad (5)$$

where A is the pre-exponential Arrhenius factor (min^{-1}), E is the activation energy (J mol^{-1}) and R is the gas constant (8,314 $JK^{-1}mol^{-1}$). These variables do not depend on the process temperature T (K).

The following kinetic relationship [25-31] comes from Eqs. (4), (5):

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) f(\alpha). \qquad (6)$$

Taking the natural logarithms on both sides of Eq. (6) gives

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln(A \cdot f(\alpha)) - \frac{E}{RT}. \qquad (7)$$

According to [29] the reaction rate at the degree *i* $(d\alpha/dt)_i$ is a function of the current (*i*-th) values of $f(\alpha_i)$ and $T(\alpha_i)$

$$\ln\left(\left(\frac{d\alpha}{dt}\right)_i\right) = \ln(A \cdot f(\alpha_i)) - \frac{E}{R}\frac{1}{T(\alpha_i)}. \qquad (8)$$

By plotting from Eq. (8) a graph ln[(dα/dt)i] against the reciprocal of temperature 1/T(αi), one can determine the kinetic parameters for isothermal thermogravimetric analysis (TGA). If the graph is linear, then the slope defines (-E/R) and the ordinate interception defines ln(A·f(αi)). Thus, for a given form f(α) the slope and the ordinate interception of the plot of ln(dα/dt) against 1/T(α) allows estimating kinetic parameters.

This scheme can also be employed for non-isothermal TGA with a constant heating rate β = dT/dt. In this case Eq. (6) is modified by multiplying both sides of the equation by β ≠ 0 and we get [27-31]

$$\frac{d\alpha}{dt} \cdot \frac{dt}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) f(\alpha). \qquad (9)$$

Thus, the obvious modification gives the following expression [17]:

$$\ln\left(\beta\frac{d\alpha}{dT}\right) = \ln\left(A \cdot f(\alpha)\right) - \frac{E}{RT}. \qquad (10)$$

The isoconversional assumption permits the estimation of the apparent activation energy without the knowledge of reaction model, and for a specific value of α allows to consider ln(A·f(α)) = const. In Friedman's method [17], α indicates the value related to a considered conversion and the subscript «i» refers the heating rate:

$$\ln\left(\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right) = const_{\alpha} - \frac{E}{RT_{\alpha,i}}. \qquad (11)$$

The activation energy at a constant value of α can be estimated from the slope of the plot of the left hand side of the Eq. (11) against the inverse of the temperature [17, 32-33]. The Friedman method has a clearly mathematical basis but creates uncertainties associated with the accuracy of the measurement and the calibration of the analysis equipment [34]. Thus, the Friedman method is characterized by high sensitive to systematic errors from the total heat released with the process, therefore the results can be inaccurate (to 16%) [35].

The essence of the integral methods

The integral methods are based on the integral form of the Eq.(9) when the left hand part of it is integrated up to the conversion α and the right hand part of it is integrated over a time dependent temperature range [25-28]

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)dT. \qquad (12)$$

Introducing the new variable x = E/(RT) allows transforming Eq.(12) to the following form [31]:

$$\int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{AE}{\beta R}\int_x^{\infty}\frac{\exp(-x)dx}{x^2}, \qquad (13)$$

where g(α) is called the integral conversion function [25-31].

Difficulties of the temperature integral estimation

The exponential integral on the right hand part of Eq. (13) has no exact analytical solution and various approaches are used for its reasonable evaluation by series solutions or other approximations [6, 30]. It is possible to classify these solutions into three categories: 1) approximate calculation; 2) series solution; 3) numerical integration [6, 30-31]. Following [30], we will call the integral in the right part of equations (12)-(13) the «temperature integral».

The Doyle method can be used as the example of approximate calculation method for right hand part of Eq. (13) [36]. Following this method and introducing a new notation p(x) for right hand part integral in Eq. (13) it can be obtained:

$$g(\alpha) = \frac{AE}{\beta R}p(x). \qquad (14)$$

Doyle established [36] that the function p(x) is linear with respect to x over a short range of x values, and hence

$$\ln(p(x)) \approx -a - b \cdot x. \qquad (15)$$

Using the first three terms of the Schlemilch series expansion in Eq.(15) for the x values in the range for the degree of transformation 28 – 50 Doyle estimated the parameters of this equation [36]:

$$\ln(p(x)) \approx -2.315 - 0.457 \cdot x\,. \qquad (16)$$

Ozawa [15] and Flynn&Wall [16] independently developed a method for calculating non-isothermal kinetics. They suggested taking the logarithm of Eq. (14) to obtain the following form:

$$\ln(g(\alpha)) = \ln\frac{AE}{\beta R} + \ln(p(x))\,. \qquad (17)$$

Then, solving the exponential integral p(x) by using the Doyle's approximation (Eq. (16)) for the temperature integral, they obtained the following result [15-16, 37]:

$$\ln(g(\alpha)) = \ln\frac{AE}{\beta R} - 2.315 - 0.457\cdot\frac{E}{RT}\,. \qquad (18)$$

One way to avoid involvement of the temperature integral in the analysis is to perform the analysis directly upon the differential TGA curve. There are some methods to do this [30].

As an example of avoidance of the temperature integral, we consider the integral method proposed in the paper [31]. The proposed method is initially assumes following the algorithm of Coats-Redfern model-fitting method [11].

The key equation of the method is as follows [11]:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\left(1 - \frac{2RT_m}{E}\right)\right) - \frac{E}{RT}\,, \qquad (19)$$

where T_m is average reaction temperature.

Taking into account that the (2RT/E)<<1, Eq. (19) can be written in the following form [31,38-39]:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}\,. \qquad (20)$$

It can be seen that, in the regression Eq. (20) the term $\ln(g(\alpha)/T^2)$ increases linearly as the function of (1/T) with the slope (-E/R). The activation energies, reaction model, and pre-exponential factor can be determined through analysis of this function (the clip part of the Y-axis allows to evaluate the reaction model, and the activation energy can be determined from the fitted value of the logarithm in the right hand part of Eq. (20)). In other words, under conditions of absolute convergence between experimental data and predictions by Eq. (20), we have to obtain the coefficient of total determination R^2 equal to 1. Thus, the sequence of the Coats-Redfern method implementation consists of looping through the possible variants of the kinetic models. The variants of the kinetic models are presented in the Table 1.

Table 1

Differential, f(α), and integral, g(α), kinetic functions for various solid-state reaction models [6-7, 38]

***Таблица 1*. Дифференциальные, f(α), и интегральные, g(α), кинетические функции, соответствующие различным механизмам химических реакций твердого тела [6-7, 38]**

№	Reaction model	Code	f(α)	g(α)
1	Power law	P_1	1	α
2	Power law	$P_{3/2}$	$(2/3)\cdot\alpha^{-1/2}$	$\alpha^{3/2}$
3	Power law	P_2	$2\cdot\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	P_3	$3\cdot\alpha^{2/3}$	$\alpha^{1/3}$
5	Power law	P_4	$4\cdot\alpha^{3/4}$	$\alpha^{1/4}$
6	Avrami-Erofe'ev	$A_{3/2}$	$(3/2)\cdot(1-\alpha)\cdot[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
7	Avrami-Erofe'ev	A_2	$2\cdot(1-\alpha)\cdot[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
8	Avrami-Erofe'ev	A_3	$3\cdot(1-\alpha)\cdot[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami-Erofe'ev	A_4	$4\cdot(1-\alpha)\cdot[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
10	Prout-Tompkins	B_1	$\alpha\,(1-\alpha)$	$\ln[\alpha\cdot(1-\alpha)]+e^{\alpha}$
11	Contracting area	R_2	$2\cdot(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
12	Contracting volume	R_3	$3\cdot(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
13	1-D Diffusion	D_1	$1/(2\cdot\alpha)$	α^2
14	2-D Diffusion	D_2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
15	3-D Diffusion	D_3	$\dfrac{3\cdot(1-\alpha)^{2/3}}{2\cdot\left(1-(1-\alpha)^{1/3}\right)}$	$\left(1-(1-\alpha)^{1/3}\right)^2$
16	Reaction order: first order,	F_1	$(1-\alpha)$	$-\ln(1-\alpha)$
17	Reaction order: n-th order	F_n	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}]/(1-n)$

According the method [31] the search of suitable variant from the possible kinetic models is still required and this procedure is accompanied with the conventional Coats-Redfern method. However, the pre-exponential Arrhenius factor and the activation energy can be evaluated by using of the following approach.

For the selected reaction model, the reaction rate constant k is obtained directly from the experimental data according to the following relationship:

$$k_j = \frac{g(\alpha_j^{exp})}{t_j^{exp}}, \qquad (21)$$

where j is the measurement number, g is the accepted integral model. The experimental time t^{exp} indicates the time during which the α^{exp} changes sufficiently. In other words, it is the process time excluding the inductive period of the reaction t_0. This can be expressed as follows:

$$t_j^{exp} = t_j - t_0. \qquad (22)$$

The inductive period of the reaction t_0 can be evaluated by using the following procedure. The accepted reaction model g(α) is expressed as a function $\alpha^{calc} = f(k,t,t_0)$. In particular, this relationship for the third order reaction has the form (see the line 17 in Table 1 for n = 3) [31]:

$$\alpha_j^{calc} = 1 - \sqrt{\frac{1}{1+2k_j^{exp}\left(t_j - t_0\right)}}. \qquad (23)$$

The calculated values of α^{calc} with various values of t_0 are compared to the corresponding values of experimental α^{exp}, and t_{min} is determined as the value that minimizes the average deviation σ, which is defined as follows:

$$\sigma_i = \frac{1}{N}\sum_{j=1}^{N}\left(\frac{\alpha_j^{exp} - \alpha_{j,i}^{calc}}{\alpha_j^{exp}}\right)^2, \qquad (24)$$

where N is the number of experimental points, j is the number of testing value of the induction time.

Eqs. (23)-(24) are introduced here to show the formalized procedures of evaluation of inductive period of the reaction. These procedures allow determine its values clearly. When the empirical relationship (21) is evaluated, the values of the kinetic parameters can be determined through analysis of the $\ln(k_j)$ as a function of the inverse absolute temperature ($1/T_j$). This linearization plot allows determining the values of the activation energies and pre-exponential factor [31]. The method, described in the paper [31], can serve as an example of avoidance the calculation of the temperature integral. These methods are widely used for kinetic studies of wood and derivatives of plant materials [28, 38-45].

Actually, it follows from Eq. (12) that we have to use the following forms for second-order reactions:

$$g(\alpha) = (1-\alpha)^{-1} - 1 = \frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)dT, \qquad (25)$$

where T_0 is the temperature at the end of the induction period.

Then, instead of Eq. (23), we have to use the more strict following relationship:

$$\alpha_j^{calc} = 1 - \frac{1}{1+\frac{A}{\beta}\int_{T_0}^{T_j}\exp\left(-\frac{E}{RT}\right)dT}. \qquad (26)$$

However, this way makes it very difficult to identify kinetic parameters, although the mathematical formalization of identification procedures is increasing (A and E).

RESULTS AND DISCUSSIONS

In this section, we will set some model data on the thermal decomposition of the model material. In fact, we take a very limited set of kinetic data from our previous study [31]. We don’t set the task to compare the accuracy of various methods, but only want to perform several calculations as an illustration of some inaccuracies that will be discussed further. To clarify the model situation, we will assume that the value of the conversion rate does not change in the initial period equal to 224 min (respectively before reaching T_0 = 530 K). The temperature increased linearly during the process with rate β = 2.37 K·min^{-1}. Thermal transformation of the model material is considered to be of second order reaction model (F_2).

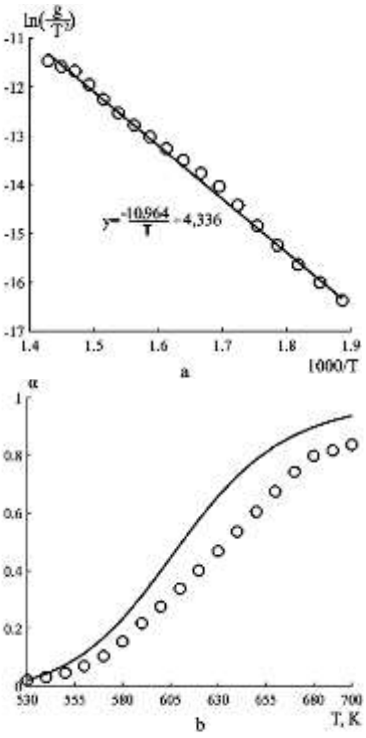

Fig. 3. a – linearization plot $\ln(g(\alpha)/T_2)=y(1/T)$ for Coats-Redfern method [11], markers are experimental data; b – the conversion rate versus temperature: markers – experimental data, line – calculation data

Рис. 3. а – график линеаризации ($y=\ln(g(\alpha)/T_2)$, $x=1000/T$) при использовании метода Коутса-Редферна [11], маркеры – экспериментальные значения; b – зависимость степени превращения от температуры: маркеры – экспериментальные данные, линия – расчетные данные

The kinetic parameters were first estimated by four conventional methods described above: by the Coats-Redfern method [11], by the method proposed Malko et. al. [31], by the differential method [29] and by the Doyle method [36]. The linearization plots obtained for the second order reaction model and the obtained results of the reverse calculation for prediction of α are shown in Fig. 3-6.

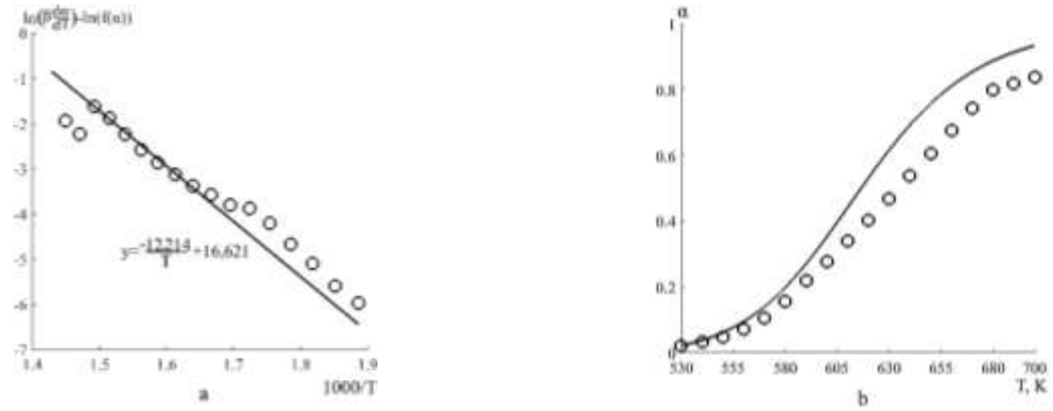

Fig. 4. a – linearization plot ln(βdα/dT)-ln(f(α))=y(1/T) for direct differential method [29], markers are experimental data; b – the conversion rate versus temperature: markers – experimental data, line – calculation data

Рис. 4. a – график линеаризации ln(βdα/dT)-ln(f(α))=y(1/T) при использовании дифференциального метода [29], маркеры – экспериментальные значения; b – зависимость степени превращения от температуры: маркеры – экспериментальные данные, линия – расчетные данные

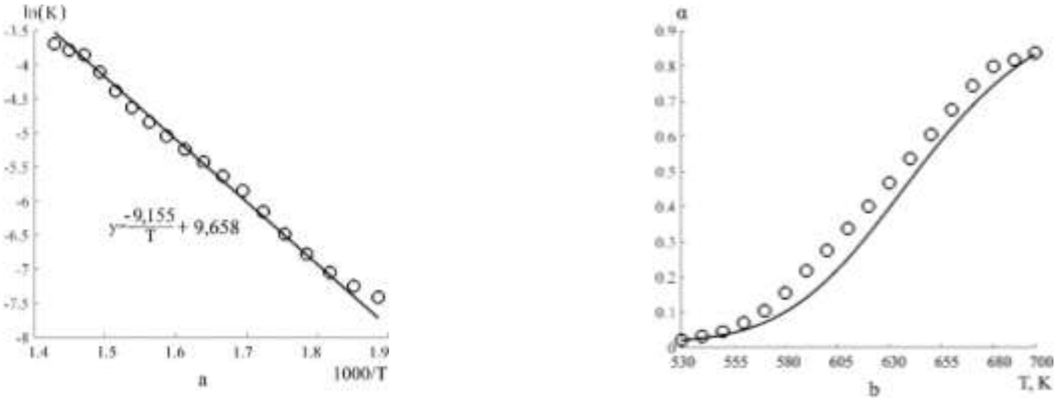

Fig. 5. a – linearization plot ln(k)=y(1/T) for integral method [31], markers are experimental data; b – the conversion rate versus temperature: markers – experimental data, line – calculation data

Рис. 5. a – график линеаризации ln(k)=y(1/T) при использовании интегрального метода [31], маркеры – экспериментальные значения; b – зависимость степени превращения от температуры: маркеры – экспериментальные данные, линия – расчетные данные

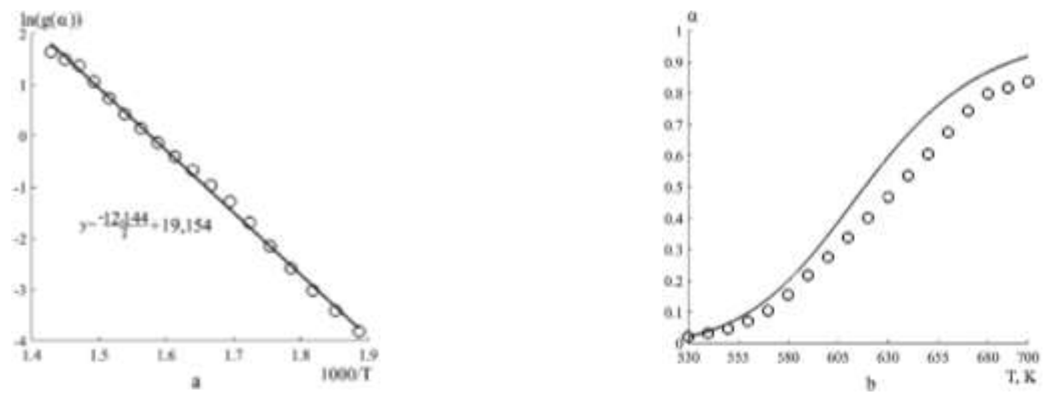

Fig. 6. a – linearization plot ln(g)=y(1/T) for Doyle method [36], markers are experimental data; b – the conversion rate versus temperature: markers – experimental data, line – calculation data

Рис. 6. a – график линеаризации ln(g)=y(1/T) при использовании метода Дойла [36], маркеры – экспериментальные значения; b – зависимость степени превращения от температуры: маркеры – экспериментальные данные, линия – расчетные данные

Within the present study a two-dimensional parametric identification was carried out by iterating through the parameters to determine the local optimum of the combination of A and E (α was determined with using Eq.(26), A was varied within range of 1…10 and E was varied within range 500…80000. The integral was calculated numerically by the trapezoid method with an integration step equal to 0.005 K. The mean square deviation with the inverse sign was considered as an optimization parameter χ:

$$\chi_j = \frac{1}{N}\sum_{j=1}^{N}\left(\alpha_j^{exp} - \alpha_j^{calc}\right)^2 \to \min, \qquad (27)$$

Fig. 7 shows two approximations to the optimal value, namely with a coarse step within wide limits (a) and with a smaller step within mare narrow limits (b). The obtained in this study kinetic parameters are summarized in the Table 2.

Table 2

Estimates of parameters A and E during identification by various methods

***Таблица 2*. Значения параметров А и Е при идентификации различными методами**

№	β, $K{\cdot}min^{-1}$	A, min^{-1}	E, $kJ{\cdot}mol^{-1}$	Algorithm for A and E identification
1	2.37	$2.23{\cdot}10^6$	91.2	Coats-Redfern [11]
2		$2.58{\cdot}10^4$	76.1	Malko et al. [31]
3		$7.27{\cdot}10^6$	102.5	Differential method [29]
4		$4.32{\cdot}10^6$	95.7	Doyle method [36]
5		$1.2{\cdot}10^6$	88.1	optimization with using Eq.(28)

CONCLUSIONS

Various approaches to describe the kinetics of materials thermal decomposition were classified, described and compared from the viewpoint of their parametric identification. The thermal decomposition of the model material under non-isothermal conditions was discussed. The calculation results are used to illustrate the possibility of identifying of the parameters A and E by these methods. Within the framework of this study, a solution to the two-dimensional optimization problem of finding the minimum value of the standard deviation of the calculated data from the experimental ones was also found. This task was solved by iterating over the parameters to determine the local optimum of the combination of A and E when numerically finding the temperature integral. It is shown that, despite the large volume of computational operations with this approach, a combination of A and E can be obtained, providing the minimum discrepancy between experimental and predicted values for a given accuracy of calculations. It is also shown that the combinations of A and E found using "traditional" methods are in a certain range of "comparatively optimal values", the existence of which is due to the nature of the solution of the "temperature integral". It can be concluded that the kinetic parameters obtained using various methods should be taken with caution. High accuracy of the predictions can be reached only when using the methods that were used to identify kinetic parameters.

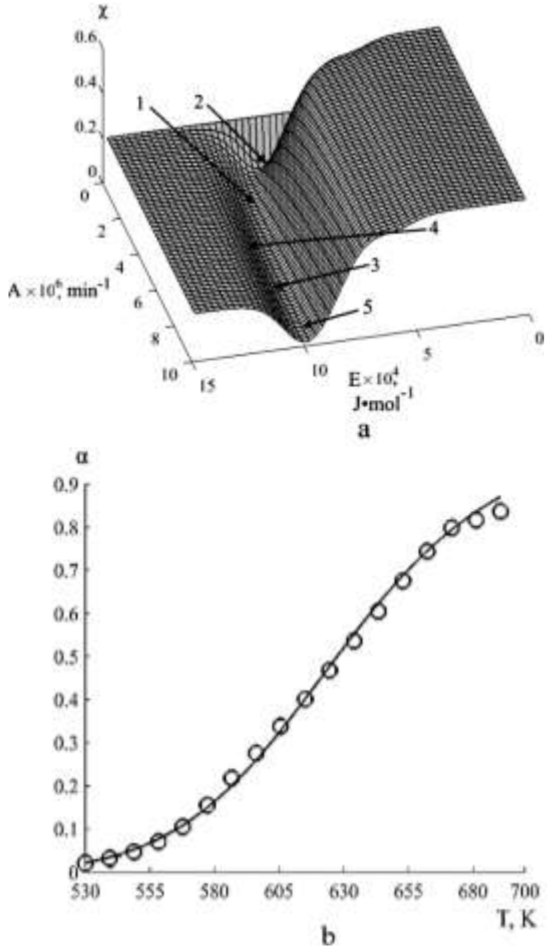

Fig. 7. a – the approximation to the optimal value (a) with a step $2{\cdot}10^5$ for A and $3{\cdot}10^3$ for E (the arrows show the positions of combinations A and E for the methods whose numbers are given in Table 2: 1 – via algorithm Coats-Redfern [11], 2 – with the use of the integral method [31], 3 – via differential method [29], 4 – via Doyle method [36], 5 – via optimization with using Eq.(26); b – the conversion rate versus temperature: markers – experimental data, line – calculation data (via optimization with using Eq.(26))

Рис. 7. а – приближение к оптимальному значению (а) с шагом $2{\cdot}10^5$ для А и $3{\cdot}10^3$ для Е (стрелки показывают позиции комбинаций А и Е для методов, номера которых приведены в таблице 2: 1 – с помощью алгоритма Коутса-Редферна [11], 2 – при использовании интегрального метода [31], 3 – с помощью дифференциального метода [29], 4 – с помощью метода Дойла [36], 5 – поиск оптимальных значений с использованием уравнения (26); b – степень превращения в зависимости от температуры: маркеры – экспериментальные данные, линия – данные расчета (поиск оптимальных значений с использованием уравнения (26))

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The authors declare the absence a conflict of interest warranting disclosure in this article.

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