НОВЫЙ МЕТОД АНАЛИЗА ТЕРМОГРАВИМЕТРИЧЕСКИХ ДАННЫХ

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Целью данного исследования является проверка корреляционного метода Коутса - Редферна и разработка нового метода анализа кинетических характеристик для брутто процесса термического разложения пиролизной смолы при неизотермических условиях. Указанный процесс термического преобразования был исследован экспериментально методом термогравиметрического анализа. Существует несколько кинетических моделей, чтобы анализировать механизм пиролиза в терминах формальных реакций. В рамках этого подхода кинетические параметры процесса пиролиза могут быть оценены по данным полной потери массы в процессе нагрева (термогравиметрический анализ – ТГА). Процедура термогравиметрического анализа может проводиться как в изотермических, так и в неизотермических условиях, но всегда экспериментальные данные, полученные в ее процессе, должны быть преобразованы в подходящие корреляционные соотношения. Полученные результаты показали, что реакция пиролиза протекает в диапазоне температур от 540 К до 700, К и индукционный период процесса составляет примерно 224 мин. Кинетические параметры были установлены традиционным методом Коутса –Редферна. Для снижения трудоемкости идентификационных процедур по сравнению с методом Коутса–Редферна и учета наличия индукционного периода реакции был предложен новый метод расчета кинетических параметров. В результате исследования было показано, что по сравнению с методом Коутса –Редферна предложенный способ дает более достоверную зависимость для расчета кинетических параметров. Предложенный метод использует алгоритм Коутса–Редферна для оценки механизма реакции, но величина постоянной скорости реакции определяется непосредственно из получаемых экспериментальных данных о скорости термического превращения.

Ключевые слова: пиролиз, формальная кинетика, термогравиметрический анализ, пиролизные смолы, закон Аррениуса, порядок реакции, скорость подъема температуры, поддерживающая кривая

AN INNOVATE METHOD OF THERMOGRAVIMETRIC DATA ANALYSIS

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The objective of the study is to examine the Coats-Redfern approximation and to propose an innovative kinetic calculation method for the complex process of the heavy tar thermal decomposition under non-isothermal process. The thermal decomposition process was examined using the thermogravimetric analysis. There are several kinetic models proposed to analyze pyrolysis mechanism in terms of the formal reaction. In this manner, the kinetic parameters of the pyrolysis process can be evaluated based on total mass loss (thermogravimetric analysis –TGA). The TGA procedures can be conducted with isothermal or non-isothermal conditions, but the experimental data obtained according to this procedure have to be transformed into appropriate correlation. The obtained results have shown that the reaction takes place within temperature range of 540 K to 700 K and the inductive period of the process is about 224 min. Kinetic parameters were estimated with using of the conventional Coats-Redfern method. A new kinetic calculation method has been designed to provide a less laboriousness of identifications procedures compared with Coats-Redfern approximation and to take into account an induction time of the process. As the outcome of this study, it was shown that the kinetic parameters estimated with using of the proposed model-fitted method gives the more appropriate correlation in comparison with the conventional Coats-Redfern method. The proposed method uses the Coats-Redfern algorithm for evaluation of the reaction mechanism, but the value of the constant rate is defined directly from experimental data on the conversion rate.

Key words: pyrolysis, formal kinetic, thermogravimetric analysis, tar, Arrhenius law, reaction order, temperature growth rate, fitting curve

INTRODUCTION

The new realities and the world challenges require using renewable biomass for energy production with much higher efficiencies than obtained in their actual utilization [1]. Thermo-chemical treatment of biomass has been the subject of increasing attention, but it has been emphasized [1-4] that many theoretical and experimental efforts are required for finding a possible and effective technology for utilization of biomass. It is undeniable that any industrial biomass processing is connected with choosing of an apparatus and its operation parameters. The complexity of these tasks brought about a broad variety of approaches to simulating of the processes. The comparative analysis of the

approaches can be found in [5-6]. It should be noted here that there are several approaches, which allows giving a detailed and accurate results of the process simulations. The Eulerian or hybrid Euler-Lagrange [6], the Markov Chains [7] or other different stochastic approaches [8-11] can be mention here as examples of suitable instruments for engineering practice. One of these models can be used to predict reactions of the industrial process only if values of operating material constant are available. The accessibility and determination accuracy of the process constants is essential part of the parametric identification of any model. Particularly the rate at which chemical structure transforms into other forms defined by chemical kinetics. It is necessary to know the kinetic parameters of the

chemical process such as an order of the reaction, an activation energy and pre-exponential factor of Arrhenius equation. In some cases, it is possible to determine a dominant reaction and its kinetic parameters. For example [12], it is true for a thermal decomposition of clean inorganic materials. However the thermal degradation of biomass solids do not obey the idealized single-step kinetic pattern but are included of consecutive or concurrent reaction steps [13-14]. Thus, the thermal decomposition of the biomass solids behavior can be correlated with their chemical evolution in terms of formal kinetic. The formal kinetic approach allows replacing set of reactions with a single gross formal reaction. There are several kinetic models proposed to analyze pyrolysis mechanism in terms of the formal reaction. In this manner, the kinetic parameters of the pyrolysis process can be evaluated based on total mass loss (thermogravimetric analysis – TGA). The TGA procedures can be conducted with isothermal or non-isothermal conditions [14], but the experimental data obtained according to this procedure have to be transformed into appropriate correlation. There are several model-free and model-fitting methods (appropriate review can be found in [15]) for evaluating kinetics parameters. The most widely used model-fitting method is Coats-Redfern correlation [16]. This method allows evaluating a kinetic triplet from thermo-analytical date, but accuracy of this scheme is iffy [13-15, 17].

The core issue of the present study is to examine the Coats-Redfern approximation and to propose an innovative kinetic calculation method for the complex process of wood tar thermal degradation under non-isothermal conditions. The investigation was conducted by thermogravimetric analysis of wood tar degradation. The proposed kinetic calculation method was designed to provide a less laboriousness of identifications procedures compared with Coats-Redfern approximation and to take into account an induction time of the process.

<div align="center">THEORY</div>

<div align="center">*Traditional approach*</div>

The complex process of a wood sample thermal degradation is considered here as a single gross reaction. The following equation represents the reaction kinetics:

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

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 $(m–m_\infty)$ 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 [14-17]:

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty}, \quad (2)$$

or in the other form as

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

where m_0 is the initial sample mass.

The following differential equation is normally used to describe the process kinetics [14-17]:

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

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 [13-19]:

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

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

The following kinetic relationship [14-17] comes from Eqs. (4)-(5)

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

The more explicit kinetic relationship for non-isothermal heating conditions can be obtained from Eq.(6) by introducing the new parameter β for heating rate (β = dT/dt) and separation of variables. If we multiply both sides of (6) by β≠0, we get [14-17]

$$\frac{d\alpha}{dt}\frac{dt}{dT} = \frac{A}{\beta} exp\left(-\frac{E}{RT}\right) f(\alpha). \quad (7)$$

Thus, the variables separation gives the following expression [14-17]:

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} exp\left(-\frac{E}{RT}\right) dT. \quad (8)$$

When the left hand part of Eq. (8) is integrated up to the conversion α and the right hand part of it is integrated over a time dependent temperature range, one obtains [17,19]

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T exp\left(-\frac{E}{RT}\right) dT. \quad (9)$$

Introducing the new variable x = E/(RT) allows transforming Eq.(9) to the following form [17, 19]:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{AE}{\beta R} \int_x^\infty \frac{exp(-x)dx}{x^2}, \quad (10)$$

where g(α) is called the integral conversion function [13-17].

The exponential integral on the right hand part of Eq. (10) has no analytical solution and various methods are employed for its reasonable evaluation by series solutions or other approximations [13-17]. It is possible to classify these solutions into three categories: 1) Series solution; 2) Complex approximations; 3) Simple approximations [17]. These all are discussed in the work [17].

Probably the best-known method was first described in [16]. This approach is called Coats-Redfern model-fitting method and it is widely used for evaluating the kinetics parameters [13-14]. This method usually derives kinetic parameters from a single heating rate; however, it can be transformed into iso-conversional approach. In this case, it involves series of experiments at different heating rates [18-19]. The key equation of the method is as follows [16]:

$$ln\left(\frac{g(\alpha)}{T^2}\right) = ln\left(\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right) - \frac{E}{RT}. \quad (11)$$

Taking into account that the (2RT/E)<<1, Eq. (11) can be rearranged in the next form [20-21]:

$$ln\left(\frac{g(\alpha)}{T^2}\right) = ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}. \quad (12)$$

If the condition for Eq. (12) is met, it can be seen that, in the regression Eq. (12), 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. (12)). In other words, under conditions of absolute convergence between experimental data and predictions by Eq. (12), 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.

Table

Differential, f(α), and integral, g(α), kinetic functions for various solid-state reaction models [19, 21]
Таблица. **Дифференциальные, f(α), и интегральные, g(α), кинетические функции, соответствующие различным механизмам химических реакций в твердом теле [19, 21]**

№	Reaction model	Code	f(α)	g(α)
1	Power law	P_1	$4 \cdot \alpha^{3/4}$	α
2	Power law	$P_{3/2}$	$(2/3) \cdot \alpha^{-1/2}$	$\alpha^{2/3}$
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_2	$2 \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
7	Avrami-Erofe'ev	A_3	$3 \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$
8	Avrami-Erofe'ev	A_4	$4 \cdot (1 - \alpha) \cdot [-\ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$
9	Prout-Tompkins	B_1	$\alpha \cdot (1 - \alpha)$	$\ln[\alpha \cdot (1 - \alpha)] + e^{\alpha}$
10	Contracting area	R_2	$2 \cdot (1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
11	Contracting volume	R_3	$3 \cdot (1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	1-D Diffusion	D_1	$1/(2 \cdot \alpha)$	α^2
13	2-D Diffusion	D_2	$[-\ln(1 - \alpha)]^{-1}$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
14	3-D Diffusion	D_3	$\dfrac{3 \cdot (1 - \alpha)^{2/3}}{2 \cdot (1 - (1 - \alpha)^{1/3})}$	$\left(1 - (1 - \alpha)^{1/3}\right)^2$
15	Reaction order: first order,	F_1	$(1 - \alpha)$	$-\ln(1 - \alpha)$
16	Reaction order: n-th order	F_n	$(1 - \alpha)^n$	$[1 - (1 - \alpha)^{1-n}]/(1 - n)$

The proposed approach

In order to obtain the more accurate description of thermal decomposition of the wood tar, an innovative kinetic calculation method is proposed and examined in the present study.

The looping of the possible variants of the kinetic models is still required in the proposed approach and it is connected with the conventional Coats – Redfern method. However, the pre-exponential Arrhenius factor and the activation energy are evaluated using the new method described below. It is supposed that the reaction model is known. It means the reaction rate constant k can be obtained directly from the experimental data according to the following relationship:

$$k_j = \frac{g(\alpha_j^{exp})}{t_j^{exp}}, \quad (13)$$

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_{ind}. This can be expressed as follows:

$$t_j^{exp} = t_j - t_{ind}. \quad (14)$$

The inductive period of the reaction t_{ind} can be evaluated by using the following procedure. The accepted reaction model g(α) is expressed as a function $\alpha^{calc} = f(k, t, t_{ind})$. In particular, this relationship for the

third order reaction has the form (see the line 16 in Table 1 with n = 3):

$$\alpha_j^{calc} = 1 - \sqrt{\frac{1}{1+2k_j^{exp}(t_j-t_{ind})}}. \quad (15)$$

The calculated values of α^{calc} with various values of t_{ind} 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

$$\sigma_i = \frac{1}{N}\sum_{j=1}^{N}\left(\frac{\alpha_j^{exp}-\alpha_{j,i}^{calc}}{\alpha_j^{exp}}\right)^2, \quad (16)$$

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

Eqs. (15), (16) 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 (13) is evaluated, the values of the kinetic parameters can be determined through analysis of the $ln(k_j)$ as a function of inverse absolute temperature $(1/T_j)$. This linearization plot allows determining the values of the activation energies and pre-exponential factor.

MATERIALS AND METHODS

Materials: characterization of chemical and thermal properties

The heavy tar used in this work came from the pyrolysis process of wood particulate solids (sawdust). A description of the tar producing process is presented in details in the previous study [22]. The overall view of the apparatus is presented in Fig. 1a. The main unit of the apparatus is the reactor 1 equipped with an electrical heater. The reactor is a metallic cylindrical tank with outer wall forming an insulated outer jacket. The resistive heating element is placed as a spiral on the surface of the internal tank wall. Produced tar is cooled down to ambient temperature by the cooling system 2 before discharging into the container 3.

Fig. 1b shows a sample of the tar. The standard testing was carried out to obtain an accurate characterization of chemical and thermal properties of the tar. The tar density was 0.9 g·sm^{-3} and it was measured by weighting. The tar viscosity was determined with rotational viscometer Brookfield DV2T. The obtained value was in the range 395±4 Pa·s (at the temperature 17 °C). The calorific value of the tar (28.8 MJ/kg) was found using the calorimeter systems B-08MA«K». The flash point was determined using the closed cup test by the automatic device TVZ-LAB-11. The estimated value was 190 °C.

Analysis method

The thermal decomposition experiments were performed using the thermogravimetric analyzer «Thermoscan-2». This device records the mass loss as a function of time with the accuracy 0.001 mg. The experiments were carried out under continuous increase of heating intense with the rate 1 °C per min (from 20 °C to 700 °C). The experimental test was performed in triplicate. The sample mass placed into the analyzer was initially 0.4 g for each test. The thermal decomposition analysis, kinetic modeling, and statistical parameters (R^2) were estimated using the software Microsoft Office Excel 2013.
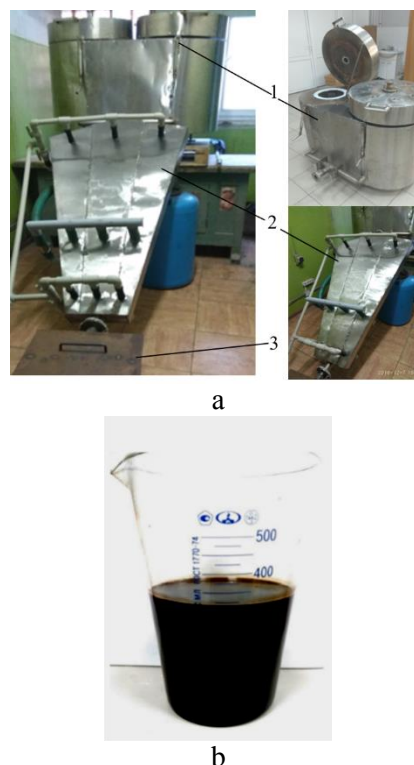

a

b

Fig.1. a – photograph of the experimental set up (left) and its main units (right): 1– the reactor, 2 – the cooling system, 3 – the receiving hopper for the obtained tar; b – photograph of the tar sample
Рис.1. a – фотография экспериментальной установки (слева) и ее основных элементов (справа): 1– реактор, 2 – система охлаждения, 3 – приемный бункер для получаемой смолы; b – фотография образца смолы

RESULTS AND DISCUSSIONS

Fig. 2a illustrates the mass loss of the sample due to the thermal decomposition. As it can be seen from the plot, the pyrolysis process begins at about 540 K. The conversion rate growths rapidly with the temperature increase until about 700 K. These facts indicates that the main pyrolysis process occurs in the range from approximately 540 K to 700 K, and then the weight loss decreases slowly to the terminal temperature of about 750 K.

The results obtained from thermogravimetric analysis were elaborated according to the model-fitting methods discussed above for estimating of the reaction kinetic parameters.
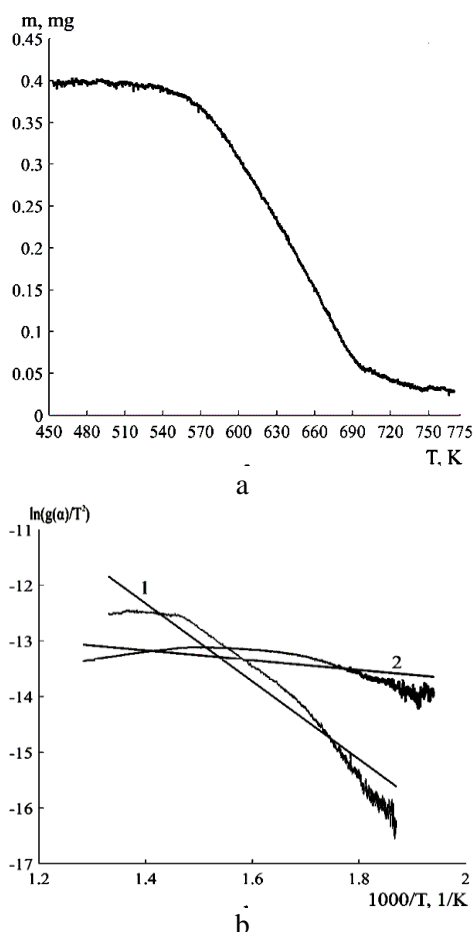
Fig. 2. a – the sample mass versus temperature in the experimental study; b – some examples of linearization plots (y=ln(g(α)/T²), x=1000/T) obtained using the Coats-Redfern method (line 1: y=-6.9951·x-2.5294 obtained for first order model F_1 (R^2=0.924); line 2: y=-0.8784·x-11.9392 obtained for power law P_3 (R^2=0.485); dotted lines are experimental data obtained with a readability of 0.001 mg)

Рис. 2. a – график экспериментальной температурной зависимости массы образца; b – некоторые примеры графиков линеаризации (y=ln(g(α)/T²), x=1000/T) при использовании метода Коутса-Редферна (линия 1 – y=-6,9951·x-2,5294 получена для модели реакции первого порядка F_1 (R^2=0,924); линия 2 – y=-0,8784·x-11,9392 получена для степенного закона P_3 (R^2=0,485); точечные линии – показания экспериментального прибора с чувствительностью 0,001 мг)

The kinetic parameters were first estimated using the Coats-Redfern method for the all-possible kinetic approaches, which are presented in Table 1 (n = 1, 2, 3 were examined for the n-th order model).

The calculated squares of the correlation coefficients (R^2) concern the linear fittings. They were higher for all cases of n-th order model ($R^2 = 0.995$ for n = 3, $R^2 = 0.988$ for n = 2, and $R^2 = 0.924$ for n = 1). In general, the power law series gave the worse values of R^2 (for example, $R^2 = 0.571$ for P_4 and $R^2 = 0.485$ and 0.491 for the models P_3 and P_2 respectively). The other models provided intermediate results (in most cases the obtained values of R^2 were in the range from 0.60 to 0.75).

It may be stated that the most appropriate outcome from using the Coats-Redfern method for analysis of the tar was achieved for the third order reaction model ($R^2 = 0.995$). The linearization plot obtained for this case is shown in Fig. 3a. The regression equation was defined in the following form:

$$y = -13.732 \cdot x_T + 9.3178 \qquad (17)$$

where $y = \ln(g(\alpha)/T^2)$ and $x_T = 1000/T$.

The activation energy was obtained by multiplying of x_T by R. This operation gave the value $E_a = 114.2$ kJ/mol. Using of the combination of the equations (12) and (17) allowed calculating the pre-exponential Arrhenius factor and obtained value was $A = 1.70 \cdot 10^8$ min⁻¹. Thus, the using of Coats-Redfern method for analysis of the tar thermal decomposition allowed establishing the rate constant k (min⁻¹) for the third order reaction model as follows:

$$k = 1.70 \cdot 10^8 exp\left(-\frac{114.2 \cdot 10^3}{RT}\right). \qquad (18)$$

The following example calculations are given in Fig. 3 to examine the obtained semi-empirical equation (18). The computation results were obtained with using the calculating scheme in more details below. The general expression for g(α) in the case of the third order reaction model is given as $0,5[1-(1-\alpha)^{-2}]$ and can be presented as:

$$\alpha = 1 - \sqrt{\frac{1}{1+2kt}}. \qquad (19)$$

The calculating results obtained with using of the equations (17)-(19) were compared with experimental data.

This comparison is shown in Fig. 3b. It can be seen that the obtained experimental and calculated values at some points are differed more than doubled.

The proposed innovative kinetic calculation method is examined in this part of the paper. The Coats – Redfern algorithm is still required to evaluation of the reaction mechanism. However, the value of the constant rate is defined using of the equations (13)-(16) with the inductive period $t_{ind} = 224$ min (obtained using equations (15)-(16)). The results obtained through this isoconversional method are presented in Fig. 4. The linearization plot provided by this method considers logarithm of the constant rate as a function from the inverse temperature. This linearization is illustrated by Fig. 4a and the equation obtained using this method is expressed in the following form:

$$y = -11.645 x_T + 13.784, \qquad (20)$$

where $y = \ln(k)$ and $x_T = 1000/T$.

Eq. (20) leads to the kinetic constant in the following regression form:

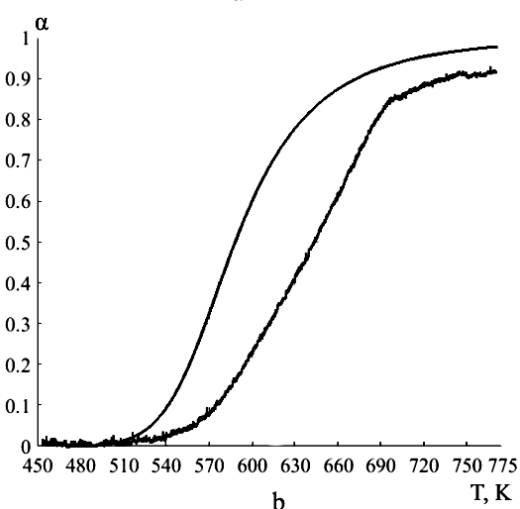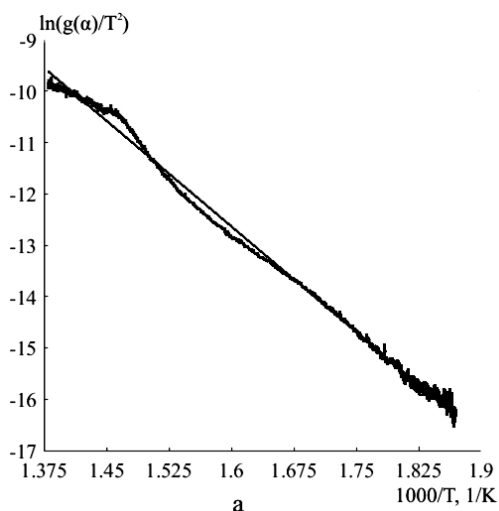$$k = 9.69 \cdot 10^5 exp\left(-\frac{96.8 \cdot 10^3}{RT}\right). \qquad (21)$$

Fig. 3. a – linearization plot ln(g(α)/T²)=f(1/T) for Coats-Redfern method (solid line is Eq. (17), dotted line is the experimental data obtained with the readability of 0.001 mg); b – the tar conversion rate versus temperature: dotted line – the experimental data obtained with a readability of 0.001 mg, solid line – calculation with Eqs.(17)-(19))

Рис. 3. a – линеаризация зависимости ln(g(α)/T2)=f(1/T) для метода Коутса-Редферна (линия – зави-симость (17), точечные линии – показания экспериментального прибора с чувствительностью 0,001 мг); b – зависимость степени превращения пиролизной смолы от температуры, полученная в экс-перименте (точечные линии – показания экспериментального прибора с чувствительностью 0,001 мг) в сравнении с расчетными результатами (линия получена с использованием зависимостей (17)-(19))

Fig. 4. a – linearization plot ln(k)=f(1/T) for the proposed method (solid line is Eq.(20), dotted line is the experimental data obtained with the readability of 0.001 mg); b – the tar conversion versus temperature: dotted line is the experimental data obtained with the readability of 0.001 mg, solid line – calculation with eqs.(19)-(21))

Рис. 4. a – график зависимости ln(k)=f(1/T) для предлагаемого метода (сплошная линия – зависимость (20), точечная линия – показания экспериментального прибора с чувствительно-стью 0,001 мг); b – зависимость степени превращения пиро-лизной смолы от температуры, полученная в эксперименте (точечная линия – показания экспериментального прибора с чувствительностью 0,001 мг) в сравнении с расчетными ре-зультатами с использованием зависимостей (19)-(21))

The obtained correlation Eq.(21) with the Eq.(19) gives the results, which are shown in Fig. 4b. The deviation between experimental data and predicted values inside the entire temperature interval does not exceed 25%.

CONCLUSIONS

The thermal decomposition of the tar under non-isothermal conditions was examined through the thermogravimetry technique. It was found that the r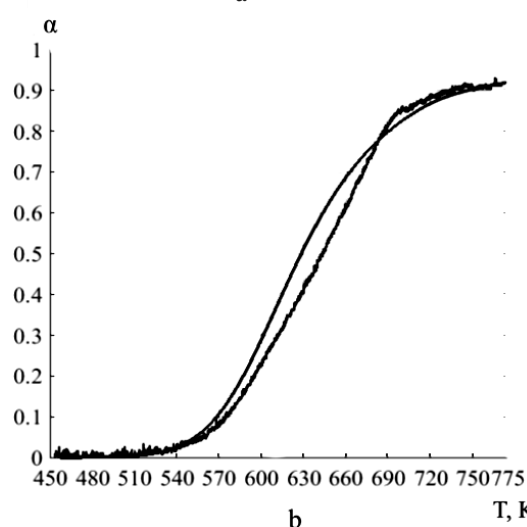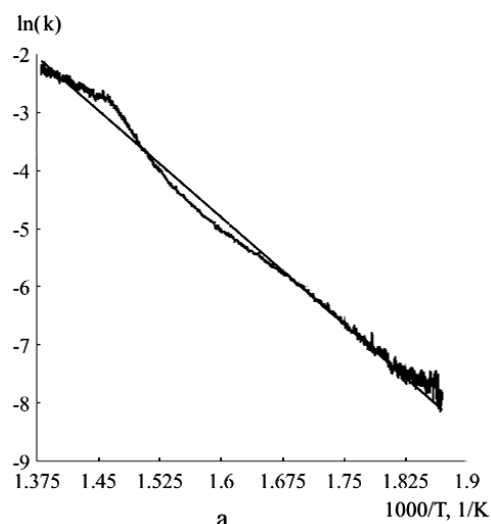eaction takes place within the temperature range from 540 °K to 700 °K. It means that the inductive period of the reaction was about 224 min. Kinetic parameters were estimated using the model-fitted methods. The obtained experimental data were previously analyzed using the conventional Coats – Redfern method, and the proposed kinetic calculation method was designed to provide a less laboriousness identifications procedures compared to the Coats – Redfern approximation and to take into account an induction time of the process. The proposed method uses the Coats – Redfern algorithm for evaluation of the reaction mechanism,

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but the value of the constant rate is defined directly from experimental data on the conversion rate. It is also shown that the kinetic parameters estimated with the proposed method give better correlation with experimental data than the conventional Coats − Redfern method. The obtained results can be effectively combined with theoretical models to describe thermo-physical processes in particulate solids, for instance described in [23-25].

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