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INVESTIGATION OF THE KINETICS OF THE COAL PYROLYSIS PROCESS

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The study of the processes occurring in the temperature range of the main decomposition of the organic mass of coal (OMC) makes it possible to understand both the general patterns and the specifics of the decomposition of solid fuels. This temperature interval is used to calculate the kinetic parameters of the process, which carry important information both about the nature of the structural-chemical transformations and about the structure and direction of thermal destruction of OMC. In this article, to study the kinetics of pyrolysis of coal, the method of thermogravimetric analysis was used, in which heating of coal samples was carried out in ceramic crucibles in the temperature range of 25-900 °C at different heating rates (5-25 deg/min) in nitrogen and oxygen media. Coal from the Kenderlyk deposit was chosen as the object of study. Based on the constructed differential DTG curves (dependence of the sample mass change rate on time) at different heating rates, the kinetic parameters of pyrolysis of coal were calculated using the equations of non-isothermal formal kinetics. The effect of the rate and temperature of coal heating on the kinetic parameters of pyrolysis of coal has been studied. The main stages of OMC decomposition are revealed. It has been found that the heating rate of coal samples significantly affects the temperature and process rate corresponding to the main decomposition maxima on the differential DTG curves. The dependence between the kinetic parameters of pyrolysis of coal in the temperature range of the main decomposition of OMC on the rate and temperature of heating, as well as between the kinetic parameters at different stages of the main decomposition of coal, is analyzed.

Keywords: thermogravimetric analysis, coal, pyrolysis, DTG curves, kinetic parameters, decomposition stages, heating rate.

ИССЛЕДОВАНИЕ КИНЕТИКИ ПРОЦЕССА ПИРОЛИЗА УГЛЯ

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Изучение процессов, протекающих в температурном интервале основного разложения органической массы угля (ОМУ), позволяет понять как общие закономерности, так и специфику разложения твердых топлив. Этот температурный интервал используется для расчета кинетических параметров процесса, которые несут важную информацию как о характере структурно-химических превращений, так и о структуре и направлении термодеструкции ОМУ. В данной статье для исследования кинетики пиролиза угля использовали метод термогравиметрического анализа, в котором нагрев образцов угля проводили в керамических тиглях в интервале температур 25-900°С при разных скоростях нагрева (5-25 град/мин) в средах азота и кислорода. В качестве объекта исследования выбран уголь месторождения Кендерлык. На основе построенных дифференциальных кривых DTG (зависимость скорости изменения массы образца от времени) при разных

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скоростях нагрева рассчитаны кинетические параметры пиролиза угля, с использованием уравнений неизотермической формальной кинетики. Изучено влияние скорости и температуры нагрева угля на кинетические параметры пиролиза угля. Выявлены основные стадии разложения ОМУ. Установлено, что скорость нагрева образцов угля заметно влияет на значения температуры и скорости процесса, соответствующие максимумам основного разложения на дифференциальных кривых DTG. Проанализирована зависимость между кинетическими параметрами пиролиза угля в интервале температур основного разложения ОМУ от скорости и температуры нагрева, а также между кинетическими параметрами на разных стадиях основного разложения угля.

Ключевые слова: термогравиметрический анализ, уголь, пиролиз, кривые DTG, кинетические параметры, стадии разложения, скорость нагрева.

КӨМІР ПИРОЛИЗІ ПРОЦЕСІНІҢ КИНЕТИКАСЫН ЗЕРТТЕУ

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Көмірдің органикалық массасының (КОМ) негізгі ыдырауының температуралық интервалында жүретін процестерді зерттеу қатты отындардың ыдырауының жалпы заңдылықтарын да, ерекшеліктерін де түсінуге мүмкіндік береді. Бұл температура аралығы құрылымдық-химиялық түрлендірулердің сипаты туралы да, КОМ-ның термодеструкциясының құрылымымен бағыты туралыда маңызды ақпаратты беретін процестің кинетикалық параметрлерін есептеу үшін қолданылады. Бұл мақала да көмір пиролизінің термиялық деструкциясының кинетикасын зерттеу үшін термогравиметриялық талдау әдісі қолданылды, онда көмір үлгілерін қыздыру керамикалық тигельдерде азотпен оттегі орталарында әртүрлі (5-25 градус/мин) қыздыру жылдамдығында 25-900 °С температурада жүргізілді. Зерттеу объектісі ретінде Кендірлік кен орнының көмірі таңдалды. Салынған DTG (үлгі массасының өзгеру жылдамдығының уақытқа тәуелділігі) дифференциалдық қисықтар негізінде әртүрлі қыздыру жылдамдықтарында көмір пиролизінің кинетикалық параметрлері изотермиялық емес формальды кинетика теңдеулерін қолдана отырып есептелді. Көмірді қыздыру жылдамдығымен температурасының пиролиз процесінің кинетикалық параметрлеріне әсері зерттелді. КОМ-ның ыдырауының негізгі кезеңдері анықталды. Көмір үлгілерінің қыздыру жылдамдығы DTG дифференциалдық қисықтарындағы негізгі ыдырау максимумдарына сәйкес келетін температурамен процесс жылдамдығының мәндеріне айтарлықтай әсер ететіні анықталды. Көмір пиролизінің кинетикалық параметрлері арасындағы тәуелсіздік, КОМ-нің негізгі ыдырау температураларының аралығындағы қыздыру жылдамдығымен температурасына, сондай-ақ көмірдің негізгі ыдырауының әртүрлі кезеңдеріндегі кинетикалық параметрлер арасындағы байланыс талданады.

Түйін сөздер:термогравиметриялық талдау, көмір, пиролиз, DTG қисықтары, кинетикалық параметрлер, ыдырау кезеңдері, қыздыру жылдамдығы.

Introduction. When studying the kinetics of thermal decomposition of solid fuels, the thermogravimetric analysis (TGA) method is widely used, both in isothermal and dynamic modes [1-4]. The express method of dynamic thermogravimetry has become widely used. The proposed methods for determining the kinetic parameters of non isothermal pyrolysis can be divided into model (model fitting) and model-free, or isoconversion (model-free) [5]. When applying

the model method, it is sufficient to carry out one thermoanalytical measurement. In the general case, the problem of determining the constants is reduced to the selection and "fitting" of a mathematical model for the reaction rate to the experimentally obtained kinetic curve or its individual sections [6]. At the same time, kinetic analysis using non-isoconversion methods does not allow one to evaluate the dynamics of coal pyrolysis at different stages, since the resulting total value of the

apparent activation energy is a complex function of the reactions occurring at individual stages.

Non-isothermal methods make it possible to obtain in a relatively short time a great deal of information about the nature of the decomposition process with registration of all transformation stages in a wide temperature range. At the same time, the study of the processes occurring in the temperature range of the main decomposition of the organic mass of coal (OMC) makes it possible to understand both the general patterns and the specifics of the decomposition of solid fuels. This temperature interval is used to calculate the kinetic parameters of the process, which carry important information both on the nature of structural chemical transformations and on the structure and direction of OMC thermal destruction [7]. At the same time, the composition and properties of coal thermal processing products depend not only on their structural and chemical characteristics, the nature of various chemical additives, temperature, pressure, medium composition, but also on the size of coal particles and the nature of heating (slow, high-speed) [8].

Mathematical models that are used to determine the kinetic parameters of thermal degradation of coal cause certain difficulties due to their complex structure, the variety of types of chemical bonds and simultaneously occurring reactions [9,10]. Therefore, the choice of an adequate kinetic model of thermal destruction is an important research problem.

The purpose of this work is to study the kinetics of the pyrolysis of coal using the TGA method. Coal from the Kenderlyk deposit (Kazakhstan) was chosen as the object of study. The objectives of the study are to determine the main stages of OMC decomposition, to study the influence of the rate and temperature of coal heating on the kinetics of pyrolysis of coal.

Materials and methods. The experiments were carried out on a TGA4000 thermogravimetric analyzer. Standard test methods for the analysis of coal according to ASTM D7582-12 "Standard Test Methods for Proximate Analysis of Coal and Coke by Macro Thermogravimetric Analysis" was used. Coal samples were heated in ceramic crucibles in the temperature range of 25-900°C at different heating rates (5-25 deg/min) in the presence of nitrogen and oxygen. The sample weight was 1 gram. The experiments were carried out in two stages. At the 1st stage, the temperature was raised from room temperature 25°C to 40°C and kept at this temperature for 15 minutes to stabilize the temperature. At the second stage, the test sample in crucibles with a closed lid was heated

from 40°C to 915±3°C. The heating rate in different experiments was set at 5, 10, 15, 20, 25 °C/min. When the furnace is heated, the TGA device weighs the closed crucibles at certain intervals and records the data in a special program.

The initial data for calculating the kinetic parameters of the process under study were taken from the data of a special program (on a computer), which displays the values of the masses of coal samples (mg), heating rate (°C/min), time (sec), temperatures (°C). These parameters are fixed at certain intervals during the entire period of programmed heating.

To characterize the process of pyrolysis of OMC, the following indicators were chosen: mass loss of samples in various temperature ranges; temperature T_{max} , velocity v_{max} , rate constant k_{max} corresponding to the highest rate of mass loss (i.e., the maxima of the main decomposition on the DTG curves at the inflection points); pre-exponential factor k_0 and activation energy E_{act} related to the stages of the main thermal decomposition of coal. Due to the diversity and complexity of physicochemical transformations, these kinetic parameters describe not certain reactions, but the overall processes of pyrolysis of OMC, therefore they are considered as "effective parameters" of formal kinetics [11].

The kinetic parameters of the main thermal decomposition of OMC were determined based on the equations of non-isothermal formal kinetics [12]. The Arrhenius law is used as the initial equation, which describes the dependence of the reaction rate constant (k) on temperature:

$$k = k_0 e^{-E/RT} \tag{1}$$

where k_0 – pre-exponential factor; E – activation energy; – absolute temperature.

Equation (1) can be represented in the differential form:

$$v = d\alpha/dt = f(\alpha)k_0e^{-E/RT}$$
 (2)

where v – process speed, α – OMC conversion rate, $f(\alpha)$ – conversion function.

According to experimental data [11], the processes of the main thermal decomposition of coal proceed in the first order, so the function $f(\alpha)=1-\alpha$. Then, using the logarithm, equation (2) is transformed to the form:

$$\ln\left[\frac{1}{1-\alpha} \cdot \frac{d\alpha}{d\tau}\right] = \ln k_o - \frac{E}{RT} \tag{3}$$

Equation (3) is a linear equation $y=b+a\cdot x$, in which $y=\ln\left[\frac{1}{1-\alpha}\cdot\frac{d\alpha}{dt}\right]$, $b=lnk_0, =-E, x=1/RT$, which makes it possible to lay the experimental points on a straight line, from the tangent of the angle of

inclination of which to the abscissa axis, the activation energy of the process can be calculated, and from the segment cut off along the ordinate axis, the preexponential.

To obtain reliable results, experimental data are calculated using the least squares method, according to which the coefficients a and b are equal:

$$a = \frac{n\sum_{i=1}^{n} x_i y_i - \sum_{i=1}^{n} x_i \sum_{i=1}^{n} y_i}{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}, \ b = \frac{\sum_{i=1}^{n} \left(y_i - a\sum_{i=1}^{n} x_i\right)}{n}$$
(4)

The root-mean-square errors of determining a and b (and hence the activation energy and pre-exponential) are calculated as:

$$S_{a} = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{i} - ax_{i} - b\right)^{2}}{\left(n - 2\right)\sum_{i=1}^{n} \left(x_{i} - x_{\mathrm{cp}}\right)^{2}}}, \ S_{b} = \sqrt{\left(\frac{\sum_{i=1}^{n} \left(y_{i} - ax_{i} - b\right)^{2}}{n - 2}\right)\left(\frac{1}{n} + \frac{x_{\mathrm{cp}}^{2}}{\sum_{i=1}^{n} \left(x_{i} - x_{\mathrm{cp}}\right)^{2}}\right)} \tag{5}$$

Based on (4), the activation energy and the pre-exponential are determined:

$$E = \frac{\sum_{i=1}^{n} \ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{d\tau}\right) \cdot \sum_{i=1}^{n} \left(\frac{1}{RT}\right) - n \sum_{i=1}^{n} \ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{d\tau}\right) \cdot \frac{1}{RT}}{n \sum_{i=1}^{n} \left(\frac{1}{RT}\right)^{2} - \left(\sum_{i=1}^{n} \frac{1}{RT}\right)^{2}}$$
(6)

$$k_0 = \exp\left[\frac{\sum_{i=1}^n \left(\ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{d\tau}\right) - a\sum_{i=1}^n \ln\frac{1}{RT}\right)}{n}\right]$$
(7)

The calculation of the kinetic parameters of the pyrolysis of OMC using the above equations (1-7) was carried out using the computer program MathCAD, in which the initial data are: arrays of mass values (weights of undecomposed coal), time, temperature, as well as

the values of the serial numbers of the start and end points decomposition stages on the DTG kinetic curves and the number of these points.

Results and discussion. The characteristics of the coal from the Kenderlyk deposit are shown in Table 1.

Table 1 - Characteristics of coal from the Kenderlyk deposit

Composition of coal, %									heat of combustion, (kcal/kg)	
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10.43	9.62	41.37	74.41	18.82	4.79	1.57	0.41	6203	5752	

Figure 1 shows the DTG curves of coal in a nitrogen atmosphere at heating rates of 10-25 deg/min. When analyzing the curves, three stages of the main decomposition of the organic mass of coal of the

Kenderlyk deposit were revealed on the differential DTG curves, where peaks with maxima of the mass loss rate (inflection points) are observed.

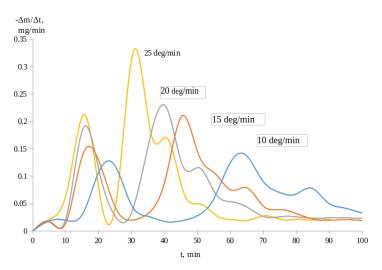


Figure 1 - DTG curves of coal in nitrogen environment

The first stage with a maximum at temperatures T_{max} is mainly associated with the release of oxygencontaining gases due to the decomposition of side groups of macromolecules (because carbon-oxygen bonds are the least thermally stable). At this stage, the bonds between the main structural units are predominantly broken, side chains are cleaved and partially decomposed, O_2 , N, S are partially removed. The yield of volatile substances in this temperature range is low. In the 2nd stagea peak is observed with a maximum, which is responsible for the increase in the intensity of the group of thermosynthesis reactions due to an increase in the reactivity of the substances heated by the OMC. In this case, decomposition reactions of hydroxyaromatic and heterocyclic fragments can occur, as well as thermochemical transformations of humic substances and the synthesis of new, more thermally stable compounds based on them, an increase in the number of unsaturated bonds, and the rate of formation of volatile substances increases [13]. At the third stage the thermal decomposition reactions

of the most thermally stable organomineral complexes develop, by the end of this stage, the release of the bulk of the resin and gaseous hydrocarbons is observed, the process ends with the formation of semi-coke. With a further increase in temperature, the aromatization and polycyclization reactions are intensified (with the elimination of gaseous products, mainly H_2 , and in a smaller amount, CH_4 , CO, N_2), and the formation of higher molecular polycyclic systems of a network structure occurs.

At the 3rd stage of OMC decomposition at heating rates β from 10 to 25 deg/min, peaks with a maximum mass loss rate are weakly pronounced (decreasing with increasing β), which is associated with the superposition of several processes and the impossibility of their separate estimates for the calculation of kinetic parameters (Figure 1).

Tables 2-5 show the results of calculating the kinetic parameters of the pyrolysis of coal from the Kenderlyk deposit using the above method.

Table 2 - Values of mass loss of coal samples and temperature T_{max} at various stages of decomposition in a
nitrogen environment

Speed of	Speed of Mass loss from sample, %						Tmax, °C		
heating,	30-300°C	300-600°C	600-900°C	30-900°C	Stages of decomposition				
°C /min	30-300 C	300-000 C	000-900 C	30-900 C	1	2	3		
5	11.28	18.74	10.82	40.84	135	347	461		
10	10.27	17.91	9.71	37.89	161	389	513		
15	9.95	17.23	09.02	36.20	173	402	547		
20	9.52	16.98	8.94	35.44	192	429	582		
25	09.08	16.15	8.47	33.70	217	443	621		

Table 3 - Values of mass loss of coal samples and temperature T_{max} at various stages of decomposition in an oxygen environment

Speed of	Mass loss from sample, %					Tmax, °C		
heating,	30-300°C	300-600°C	600-900°C	30-900°C	Stages of decomposition			
°C/min					1	2	3	
5	14.87	23.72	14.09	52.68	143	364	467	
10	13.92	22.81	13.26	49.99	170	383	515	
15	12.81	21.79	12.13	46.73	181	420	532	
20	11.59	20.45	11.27	43.31	208	448	558	
25	11.18	19.43	10.83	41.44	232	462	581	

Table 4 - Kinetic parameters of thermal destruction of OMC in a nitrogen environment

Speed of	Basic decomposition stages							
heating,	1st stage			2nd stage				
°C/min	k _{max} , 10 ⁻³ c ⁻¹	k ₀ , 10 ² c ⁻¹	E _{act} , kJ/mol	k _{max} , 10 ⁻³ c ⁻¹	k ₀ , 10 ⁴ c ⁻¹	E _{act} , kJ/mol		
5	2.75	4.92±0.16	72.45±2.84	2.46	3.72±0.12	97.29±3.82		
10	1.82	6.27±0.19	68.29±2.73	1.59	2.93±0.08	92.16±3.57		
15	3.47	6.71±0.15	65.07±2.26	2.84	2.14±0.16	84.53±3.19		
20	2.61	5.62±0.18	58.38±2.47	1.95	2.51±0.09	79.84±2.85		
25	4.28	3.84±0.13	56.92±2.39	03.01	3.68±0.14	76.82±2.63		

Table 5 - Kinetic parameters of thermal destruction of OMC in an oxygen environment

Speed of	Basic decomposition stages							
heating,	1st stage			2nd stage				
°C/min	k _{max} ,	k ₀ ,	E _{ac} ,	k _{max} ,	k0,	E _{act} , kJ/mol		
	10 ⁻³ c ⁻¹	$10^2 c^{-1}$	kJ/mol	10 ⁻³ c ⁻¹	$10^4 c^{-1}$	Lact, KJ/IIIOI		
5	2.28	3.46±0.10	68.93±2.71	2.91	4.29±0.38	94.72±3.81		
10	1.97	2.18±0.13	65.17±2.39	3.28	3.78±0.19	88.41±3.49		
15	2.91	2.93±0.21	60.52±2.27	1.94	2.27±0.17	82.37±3.47		
20	3.84	3.07±0.18	54.83±2.16	2.61	1.75±0.13	75.83±3.49		
25	2.37	3.92±0.08	50.64±1.92	3.74	3.14±0.17	72.68±3.23		

As can be seen from Tables 2 and 3, the values of mass loss of coal samples (for nitrogen - up to 40.84 %, for oxygen – 52.68 %) indicate a low thermal stability, and hence a low stage of metamorphism, due to the content of a large amount of oxygen in coal in the form of functional, ether groups and other forms, as well as low values of ash content and moisture (table 1).

The analysis of the obtained data showed that for all coal samples in the temperature range of 300-600 °C (the second and third maxima) the greatest mass loss of OMC is observed (Tables 2, 3), since the main degradation reactions occur in this area. This means an increase in the rate of formation of

volatile substances due to an increase in the reactivity of substances heated by OMC, most of which is converted into condensable hydrocarbons: resins and pyrolysis gas with the simultaneous formation of pyrogenetic water vapor. These mass losses of coal significantly exceed the losses in other intervals of 30-300 °C and 600-900 °C, the values of which are approximately the same.

An increase in the heating rate of coal leads to a noticeable decrease in the total mass loss of OMC – 40.84-33.70 % and 52.68-41.44 % for nitrogen and oxygen, respectively. The latter indicator shows the degree of influence of the residence time of coal particles during thermolysis. This is more clearly seen

in Figure 2, which also shows that the oxidative effect of oxygen contributes to a more significant increase in the loss of OMC mass with an increase in the heating rate compared to the effect of a neutral medium (nitrogen), and this difference is more noticeable especially at low heating rates of 5 deg/min and 10 deg/min.

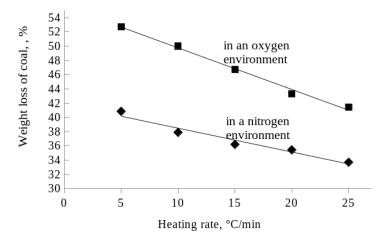


Figure 2 - Values of mass loss of coal samples at heating rates of 5-25 deg / min in nitrogen and oxygen environments

An increase in the heating rate β at all stages of OMC decomposition leads to a shift in the temperature values T_{max} (corresponding to maximum decomposition) towards higher values, which reflects an increase in the thermal stability of coal (Figure 3). So, for a nitrogen environment, an increase in Tmax

for the 1st stage $\Delta T_{max} = 82$ °C, for the 2nd stage $\Delta T_{max} = 96$ °C, for the 3rd stage $\Delta T_{max} = 160$ °C. For the oxygen environment, the increase in T_{max} for the 1st stage $\Delta T_{max} = 89$ °C, the 2nd stage $\Delta T_{max} = 98$ °C, the 3rd stage $\Delta T_{max} = 114$ °C.

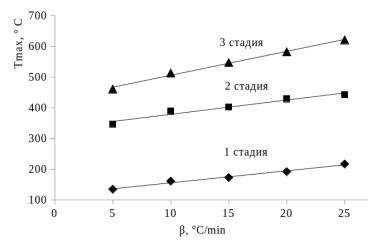


Figure 3 - Dependence of the temperature at the inflection points on the heating rate of coal at various stages of decomposition in a nitrogen environment

An increase in the heating rate β leads to an increase in the rate v_{max} of the OMC destruction process. At the same time, the approximation of points by a straight line

makes it possible to obtain approximate relationships between v_{max} and β (Figure 4). At the same time, the difference between the speed v_{max} at the 1st stage and

the speed v_{max} at the 2nd stage (ie the difference Δv_{max} between the velocities at the inflection points) also increases with increasing $\beta.$ This relationship between

 Δv_{max} and β is described by a similar function close to linear

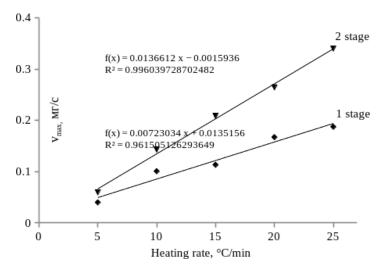


Figure 4 - Dependence of the rate of destruction at the inflection points on the rate of heating of coal at various stages of decomposition in a nitrogen environment

During the transition from one stage of the main decomposition to another with an increase in temperature (over the entire range of β), there is a noticeable increase in E_{act} (Tables 4, 5) and k_0 (by 2 orders of magnitude, i.e. $k_{01} \sim 10^2~s^{-1},\,k_{02} \sim 10^4~s^{-1}),$ i.e. more and more stable molecular structures are involved in the process of OMC destruction. But with an increase in the heating rate β (within each stage of decomposition), the activation energy E_{act} decreases.

The kinetic parameters of thermal destruction of Kenderlyk coal obtained in this work are in good agreement with similar parameters for coals from other Kazakh deposits [14-15]. In these works, the rate constant $k_{max}~(\sim 10^{-3}~s^{-1})$ and the pre-exponential factor $k_0~(\sim 10^2~s^{-1}$ and $\sim 10^4~s^{-1}$, respectively, for the 1^{st} and 2^{nd} stages of the main decomposition of OMC) have comparable values with those for Kenderlyk coal, and the activation energy was in the range of $\approx 30\text{-}100~\text{kJ/mol}$.

Conclusion. Thus, the article reveals the dependence of the kinetic parameters of the coal pyrolysis on the rate and temperature of heating, describes the dependence between the kinetic parameters at different stages of the main decomposition of coal. The kinetic

compensation effect is also established, the equations of linear regression of the activation energy and the pre-exponential factor are derived. The data obtained show that a longer thermolysis time has a more significant effect on the coal degradation process than its heating rate. It should be noted that the process of basic thermal decomposition of OMC itself can be approximately described by the equation of formal kinetics of the 1st order, i.e. the equation of monomolecular transformation, since the exponents of the process under study vary within ≈ 1.0 -1.2 [15]. In general, it can be noted that the calculated values of the activation energy of the stages of the main thermal decomposition of coal are commensurate with the energies of chemical bonds.

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