ISSN 0361-5219, Solid Fuel Chemistry, 2016, Vol. 50, No. 5, pp. 300–305. © Allerton Press, Inc., 2016.
Original Russian Text © M.I. Baikenov, A.V. Ivannikova, G.G. Baikenova, Z.S. Khalikova, E.V. Kochegina, N.Zh. Rakhimzhanova, A.B. Karimova, A.T. Kezdikbaeva, 2016, published in Khimiya Tverdogo Topliva, 2016, No. 5, pp. 27–33.

Effect of Iron Additives on the Thermal Degradation of Coal from the Shubarkol Deposit

M. I. Baikenov*, A. V. Ivannikova, G. G. Baikenova, Z. S. Khalikova, E. V. Kochegina, N. Zh. Rakhimzhanova , A. B. Karimova, and A. T. Kezdikbaeva
Buketov State University, Karaganda, 100028 Kazakhstan
** e-mail: Murzabek_b@mail.ru*

Received September 11, 2015

Abstract—The kinetic parameters of the thermal degradation of coal in a temperature range of 32–458°C without additives and in the presence of nanosized iron powder as a catalyst were calculated based on thermogravimetric analysis data. The rate constants and activation energies of the first and second steps of thermal degradation processes were determined. The influence of the catalytic additive on the value of activation energy was found. The results of the thermogravimetric analysis can be used in a study of thermocatalytic modification processes for the hydrogenation of fossil coals.

DOI: 10.3103/S0361521916050037

Recently, the development of coal conversion for the production of synthetic liquid fuel by destructive hydrogenation has been widely used.

Thermal degradation is a step of destructive hydrogenation processes, and the yield and quality of the products depend on its conditions. Thermal analysis gives useful information on the thermal degradation of low-rank coals utilized for hydrogenation. A study of the thermal decomposition of coals with catalytic additives in a temperature range close to hydrogenation conditions is of interest for explaining the mechanism of hydrogenation of the organic matter of coal and determining their structure peculiarities.

The aim of this work was to study the effect of catalytic additives on the kinetic parameters of the thermal degradation of coal.

EXPERIMENTAL

Brown coal from the Shubarkol deposit with the following physicochemical characteristics (wt %) was used in this study: W^a, 1.9; A^d, 5.0; S^{daf}, 0.40; N^{daf}, 1.36; O^{daf}, 15.85; V^{daf}, 43.4; C^{daf}, 76.99; and H^{daf}, 5.4. The test coal had following petrographic composition (%): vitrinite, 90; liptinite, 1; seminite, 2; and fusinite, 7. The chemical composition of the mineral matter of coal was as follows (wt %): SiO_2, 59.9; Al_2O_3, 18.3; Fe_2O_3, 12.3; CaO, 0.9; MgO, 1.7; TiO_2, 1.0; P_2O_5, 0.14; and SO_3, 1.7.

The nanosized iron powder obtained by electrochemical synthesis using a combination of direct current electrolysis with high-voltage pulsed discharge followed by treatment with a dilute solution of sulfuric acid (0.02%) for the removal of partially formed oxides was used as a catalytic additive. The powder was stabilized with 0.1–0.5% solutions of surfactants. To prevent the oxidation of powders, filtration and drying were performed in a flow of an inert gas (argon). The iron content of the powder was 99.7%. The particle sizes of the iron powder varied from 41.46 to 88.67 nm.

Thermogravimetric analysis was carried out on a LabsysEvoSetaram derivatograph (France) in two identical Al_2O_3 crucibles, the construction of which made it possible to perform temperature measurements directly in a test sample. A weighed portion of prepared coal (analytical crushing) without a catalyst or in the presence of the catalytic additive (1, 3, or 5% on an organic matter of coal (OMC) basis) was loaded in one of the crucibles, and the other was empty. Both of the crucibles were placed in an electric furnace of the instrument and heated under the conditions of a linear increase in the temperature from 32 to 458°C at a constant heating rate of 10 K/min; in this case, weight changes were measured. Upon reaching a certain sample temperature, a group of reactions came into play, whose rates became noticeable at this temperature.

The experiments were conducted away from oxygen in order to exclude oxidation reactions. Nitrogen was used as an inert atmosphere.

RESULTS AND DISCUSSION

As a result of thermogravimetric analysis, the curves of the thermal degradation of coal without a catalyst and in the presence of the iron nanopowder additive (1, 3, or 5% on an OMC basis) were obtained; they exhibited two macro stages of the process.

The first stage was related to the evaporation of water and the release of oxygen-containing gases due to the decomposition of the lateral groups of macromolecules (because the carbon–oxygen bonds are least thermally stable). At this stage, the cleavage of bonds between the basic structural units and the removal and partial disintegration of side chains predominantly occurred; O_2, N_2, and S were partially moved away [1]. The yield of volatile substances in this region was small. At the second stage, an increase in the intensity of the group of thermal synthesis reactions was observed because of an increase in the reactivity of the heated OMC substances. In this case, the decomposition of hydroxyaromatic and heterocyclic fragments, the thermochemical transformations of humic substances, the synthesis of new more thermally stable compounds on their basis, and an increase in the number of unsaturated bonds can occur; in this case, the rate of formation of volatile substances increased [2]. The reactions of aromatization and polycyclization (with the release of gaseous products, predominantly, H_2 and CH_4, CO, and N_2 in smaller amounts) were intensified on a further increase in the temperature, and the formation of higher molecular weight polycyclic systems with a network structure occurred [3].

Each of the stages was represented by an *S*-shaped line. This shape is explained by the fact that the rate of reaction initially increased due to an increase in the rate constant according to the Arrhenius equation; then, the rate of destruction decreased because of the decomposition of the reagent.

For treating the curves obtained, let us represent the process of the thermal degradation of coal as follows [4]: parent substance A is consecutively decomposed to form intermediate solid product B and volatile product P_1. Then, B is converted into intermediate product C with the release of volatile product P_2:

$$A \xrightarrow{k_1} B + P_1\uparrow \xrightarrow{k_2} C + P_2\uparrow \xrightarrow{k_3} \ldots.$$

The thermal degradation process as a whole is described by a scheme of sequential first-order reactions. The rate of the process was monitored based on the accumulation of total volatile substances; that is, their weight was measured over a certain time interval. In this case, the weight of the released volatile substances was equal to the weight loss of the solid sample.

As a rule, the rates of the release of volatile substances at each stage can be described by a first-order reaction equation with the subsequent determination of the rate constants of stages.

The weights of the volatile substances released at each stage are different, and the number of moles that participate in the reaction is unknown. In connection with this, we tentatively consider that the same number of reagent moles equal to the number of moles of the parent substance $n_{A,0}$ is decomposed at each stage. The maximum number of moles of volatile products that can be isolated at each stage is also $n_{A,0} = n_{P1\max} = n_{P2\max}$.

The rate of the release of volatile substances at a certain stage of decomposition is determined by the weight m_i of the volatile substances released at this stage. Then, the system of equations that describes the two-stage process of the thermal degradation of coal can be represented in the form

$$\begin{gathered}\frac{dm_1}{d\tau} = k_1 m_{\max}\left(1 - \frac{m_1}{m_{1\max}}\right) = k_1(m_{1\max} - m_1),\\ \frac{dm_2}{d\tau} = k_2 m_{2\max}\left(\frac{m_1}{m_{1\max}} - \frac{m_2}{m_{2\max}}\right).\end{gathered} \tag{1}$$

Because, in our case, the stages of decomposition were far separated in time, the release of volatile substances according to the first equation ceased at the beginning of the second stage, and $m_1 = m_{1\max}$. Then, the system of equations obtained became simplified:

$$\begin{gathered}\frac{dm_1}{d\tau} = k_1(m_{1\max} - m_1),\\ \frac{dm_2}{d\tau} = k_2(m_{2\max} - m_2).\end{gathered} \tag{2}$$

In this case, the first equation remained without changes, and the second was obtained by conversion:

$$\begin{aligned}\frac{dm_2}{d\tau} &= k_2 m_{2\max}\left(\frac{m_{1\max}}{m_{1\max}} - \frac{m_2}{m_{2\max}}\right) =\\ &= k_2\left(m_{2\max} - m_{2\max}\frac{m_2}{m_{2\max}}\right).\end{aligned} \tag{3}$$

The total weight loss of the parent substance and the rate of the release of volatile substances are

$$m = \sum_i m_i \quad \text{and} \quad \frac{dm}{d\tau} = \sum_i \frac{dm_i}{d\tau}, \tag{4}$$

in particular, in the consideration of a case of two stages of degradation,

$$m = m_1 + m_2; \qquad \frac{dm}{d\tau} = \frac{dm_1}{d\tau} + \frac{dm_2}{d\tau}. \tag{5}$$

Because the test processes in our case proceeded under nonisothermic conditions, the rate constants k_1 and k_2 changed in the course of an experiment in accordance with the Arrhenius equation. The processes were carried out under the conditions of a linear increase in the temperature

$$T = T_0 + \beta\tau, \tag{6}$$

where T_0 is the initial temperature, K, and β is the rate of heating, K/min.

On this basis, we write the Arrhenius equation for constants at the *i*th stage as

$$k_i = k_{0i} e^{-\frac{E_i}{R(T_0 + \beta\tau)}}, \tag{7}$$

and the rate equation of the *i*th stage of first-order reaction

Table 1. Results of the processing of kinetic curves for the thermal degradation of coal without a catalyst and in the presence of an additive

Entry	Time, min	m, mg	$m_{i\max} - m_i$, mg	r_i, mg/min	$-\ln[r_i/(m_{i\max} - m_i)]$	t, °C	$10^3/T$, K^{-1}
				Coal			
1	–	0	–	–	–	32	3.28
2	7.7	0.006	1.116	0.056	2.987	90	2.75
3	8.6	0.102	1.019	0.131	2.049	100	2.68
4	10.9	0.523	0.599	0.195	1.120	125	2.51
5	13.2	0.874	0.248	0.114	0.777	150	2.36
6	15.5	1.047	0.075	0.046	0.489	175	2.23
7	17.7	1.121	–	–	–	200	2.11
8	20.0	1.149	2.963	0.055	3.983	225	2.01
9	22.4	1.211	2.901	0.014	5.368	250	1.91
10	24.7	1.250	2.862	0.026	4.712	275	1.82
11	27.0	1.333	2.779	0.039	4.278	300	1.75
12	29.4	1.421	2.692	0.043	4.136	325	1.67
13	31.7	1.529	2.584	0.055	3.850	350	1.61
14	34.1	1.722	2.390	0.102	3.152	375	1.54
15	36.5	2.056	2.056	0.205	2.308	400	1.49
16	38.8	2.698	1.414	0.348	1.401	425	1.43
17	41.3	3.763	0.350	0.501	–	450	1.38
18	42.0	4.112	–	–	–	458	1.37
				Coal + 1% Fe			
1	0	0	–	–	–	32	3.28
2	8.6	0.094	1.567	0.141	2.407	100	2.68
3	10.9	0.617	1.044	0.287	1.293	125	2.51
4	13.2	1.218	0.443	0.206	0.766	150	2.36
5	15.5	1.529	0.133	0.081	0.496	175	2.23
6	17.7	1.661	–	–	–	200	2.11
7	20.1	1.747	4.010	0.009	6.073	225	2.01
8	22.4	1.827	3.930	0.040	4.593	250	1.91
9	24.7	1.910	3.847	0.047	4.406	275	1.82
10	27.0	2.011	3.746	0.046	4.391	300	1.75
11	29.4	2.136	3.621	0.054	4.212	325	1.67
12	31.7	2.319	3.438	0.083	3.727	350	1.61
13	34.1	2.563	3.194	0.151	3.053	375	1.54
14	36.5	3.015	2.742	0.271	2.314	400	1.49
15	38.9	3.901	1.856	0.457	1.402	425	1.43
16	41.3	5.304	0.453	–	–	450	1.38
17	42.0	5.757	–	–	–	458	1.37
				Coal + 3% Fe			
1	–	–	–	–	–	32	3.28
2	8.6	0.099	1.513	0.133	2.434	100	2.68
3	10.9	0.629	0.982	0.284	1.242	125	2.51
4	13.2	1.214	0.397	0.199	0.692	150	2.36
5	15.5	1.496	0.116	0.066	0.567	175	2.23

Table 1. (Contd.)

Entry	Time, min	m, mg	$m_{i\max} - m_i$, mg	r_i, mg/min	$-\ln[r_i/(m_{i\max} - m_i)]$	t, °C	$10^3/T$, K^{-1}
6	17.8	1.611	–	–	–	200	2.11
7	20.1	1.687	4.006	0.029	4.944	225	2.01
8	22.4	1.762	3.932	0.033	4.766	250	1.91
9	24.7	1.849	3.845	0.042	4.509	275	1.82
10	27.0	1.949	3.745	0.049	4.336	300	1.75
11	29.4	2.074	3.620	0.059	4.122	325	1.67
12	31.7	2.246	3.448	0.083	3.722	350	1.61
13	34.1	2.505	3.189	0.144	3.097	375	1.54
14	36.5	2.967	2.727	0.262	2.344	400	1.49
15	38.9	3.825	1.869	0.456	1.411	425	1.43
16	41.3	5.236	0.458	–	–	450	1.38
17	42.0	5.693	–	–	–	458	1.37
Coal + 5% Fe							
1	–	–	–	–	–	32	3.28
2	8.7	0.084	1.565	0.153	2.324	100	2.68
3	11.0	0.641	1.009	0.295	1.229	125	2.51
4	13.2	1.236	0.413	0.205	0.699	150	2.36
5	15.5	1.531	0.118	0.068	0.553	175	2.23
6	17.8	1.649	–	–	–	200	2.11
7	20.1	1.729	4.056	0.044	4.527	225	2.01
8	22.4	1.794	3.992	0.030	4.903	250	1.91
9	24.7	1.881	3.904	0.032	4.815	275	1.82
10	27.1	1.973	3.812	0.050	4.332	300	1.75
11	29.4	2.099	3.686	0.065	4.031	325	1.67
12	31.8	2.266	3.519	0.083	3.751	350	1.61
13	34.1	2.522	3.263	0.134	3.191	375	1.54
14	36.5	2.986	2.799	0.271	2.335	400	1.49
15	38.9	3.868	1.917	0.495	1.353	425	1.43
16	41.3	5.341	0.444	0.675	–	450	1.38
17	42.0	5.786	–	–	–	457	1.37

Table 2. Calculated rate constants and activation energies of the thermal degradation of coal without a catalyst and in the presence of an additive

Catalyst concentration, %	E, kJ/mol		k, min^{-1}	
	stage 1	stage 2	stage 1	stage 2
0	37.41	62.36	$5.55 \cdot 10^{-5}$	$1.67 \cdot 10^{-4}$
1	34.92	54.87	$1.12 \cdot 10^{-4}$	$6.11 \cdot 10^{-4}$
3	34.92	46.56	$1.23 \cdot 10^{-4}$	$3.03 \cdot 10^{-3}$
5	33.26	44.90	$2.04 \cdot 10^{-4}$	$4.5 \cdot 10^{-3}$

$$r_i = \frac{dm_i}{d\tau} = \exp\left(a_i - \frac{b_i}{T_0 + \beta\tau}\right)(m_{i\,\max} - m_i), \qquad (8)$$

where $a_{\mathrm{i}} = \ln k_{0i}$, and $b_i = E_i/R$.

Thus, to find the kinetic parameters of the thermal degradation of coal without a catalyst and in the presence of the additive, we obtained the weights of released volatile substances based on each particular curve. We plotted the time dependences of the weights of released volatile substances. We found the values of $m_{i\max}$ from the horizontal sections of the curves. We drew tangents to the curves at selected points and found the rates of sample weight changes r_i from their slopes. Table 1 summarizes the results of the process-

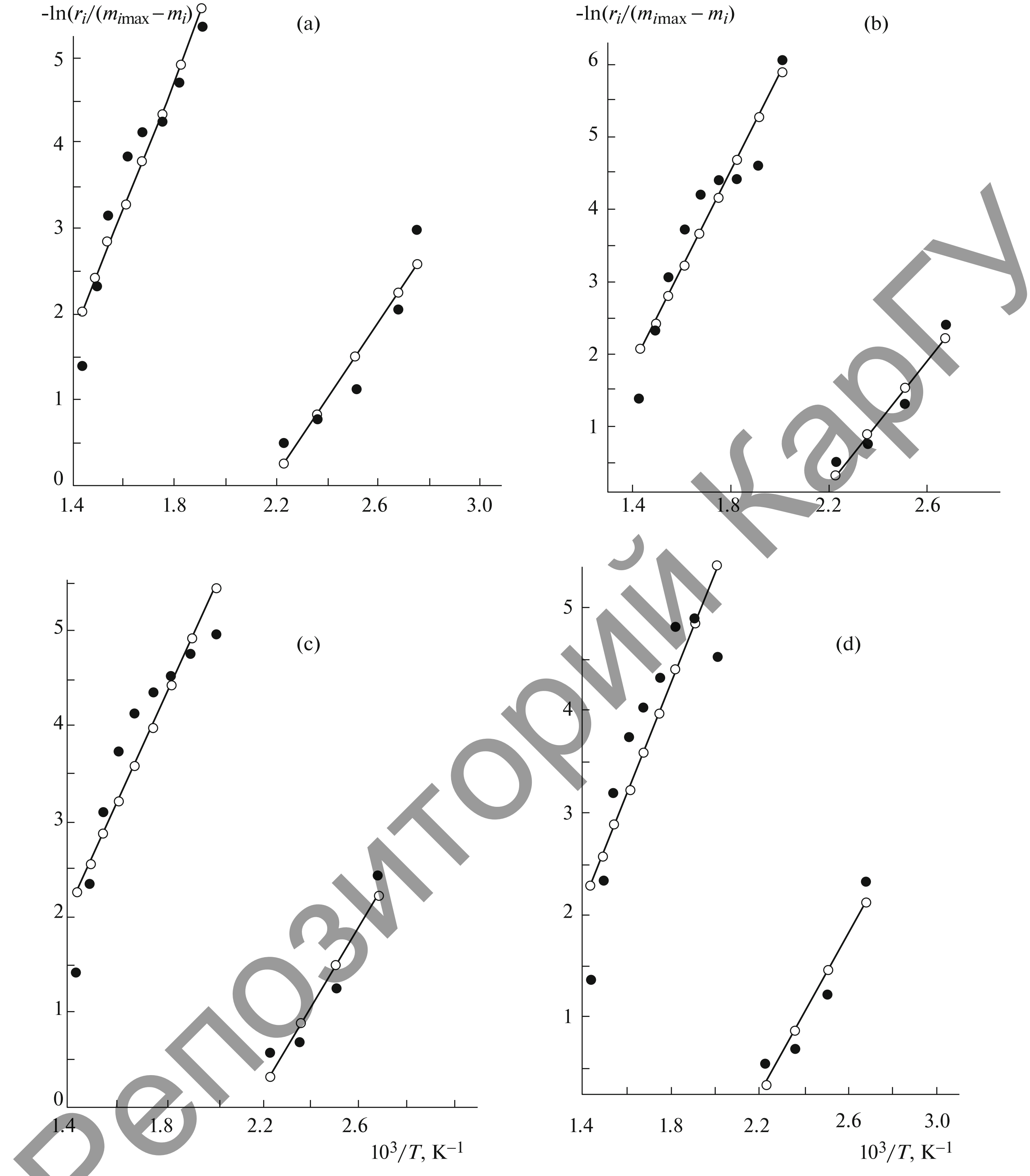

Fig. 1. Linearization of the temperature dependences of the rates of thermal destruction of (a) coal, (b) coal + 1% Fe, (c) coal + 3% Fe, and (d) coal + 5% Fe.

ing of the curves of the thermal degradation of coal with and without a catalytic additive.

The parameters ai = lnk0i and bi = Ei/R were chosen by the linearization of the rate equation of the corresponding stage:

$$\ln \frac{r_i}{m_{i\,\max} - m_i} = a_i - \frac{b_i}{T_0 + \beta\tau}. \tag{9}$$

This equation is the standard description of a straight line ($y = bx + a$); therefore, based on the data given in Table 2, we plotted the dependence of –

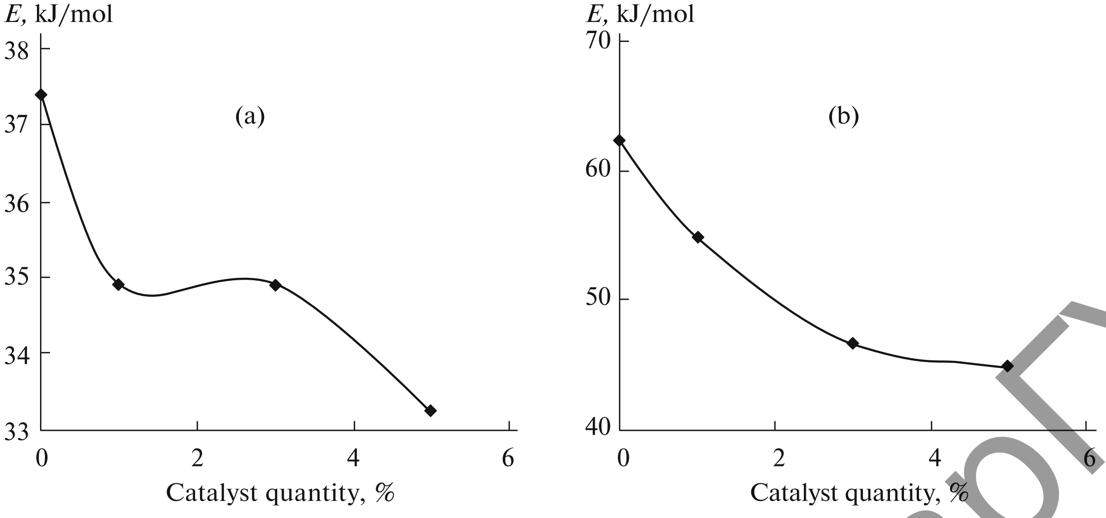

Fig. 2. Dependence of the activation energy (*E*, kJ/mol) on the catalyst quantity (%): (a) at the first stage and (b) at the second stage.

$\ln[r_i/(m_{i\max} - m_i)]$ on $10^3/T$ for each sample (Fig. 1) and treated the resulting curves by a least squares technique.

Table 2 summarizes the calculated values of kinetic parameters; it is evident that the activation energy decreased from 37.41 to 33.26 kJ/mol at the first stage or from 62.36 to 44.90 kJ/mol at the second stage as the catalyst content was increased (Fig. 2). A noticeable increase in the activation energy was detected on going from one stage of basic decomposition to the other with increasing the temperature.

CONCLUSIONS

According to the thermogravimetric analysis data, we calculated the kinetic parameters of the processes of the thermal degradation of coal without a catalyst and in the presence of an additive of iron nanopowder (1, 3, and 5% on an OMC basis) in a temperature range of 32–458°C.

We determined the rate constants and activation energies of the first ($5.55 \cdot 10^{-5}$ min^{-1}, 37.41 kJ/mol; $1.12 \cdot 10^{-4}$ min^{-1}, 34.92 kJ/mol; $1.23 \cdot 10^{-4}$ min^{-1}, 34.92 kJ/mol; $2.04 \cdot 10^{-4}$ min^{-1}, 33.26 kJ/mol) and second stages ($1.67 \cdot 10^{-4}$ min^{-1}, 62.36 kJ/mol; $6.11 \cdot 10^{-4}$ min^{-1}, 54.87 kJ/mol; $3.03 \cdot 10^{-3}$ min^{-1}, 46.56 kJ/mol; $4.5 \cdot 10^{-3}$ min^{-1}, 44.90 kJ/mol) of the thermal degradation processes. We found that, as the catalyst content was increased, the activation energy decreased from 37.41 to 33.26 kJ/mol at the first stage or from 62.36 to 44.90 kJ/mol at the second stage. A noticeable increase in the activation energy was detected upon going from one stage of basic decomposition to the other with increasing the temperature.

Thermogravimetry makes it possible to successfully study the effects of different factors on the thermal decomposition of coals. The process of thermal degradation and the kinetic parameters can be controlled within certain limits by changing the organomineral structure of coals due to catalytic additives.

REFERENCES

1. Sklyar, M.G., *Fiziko-khimicheskie osnovy spekaniya uglei (Physicochemical Fundamentals of Coal Caking)*, Moscow: Metallurgiya, 1984.
2. Falyushin, P.L., Dudarchik, V.M., Kraiko, V.M., et al., *Prirodopol'zovanie*, 2012, p. 305.
3. Alekseev, A.D., *Fizika uglya i gornykh protsessov (The Physics of Coal and Mining Processes)*, Kiev: Naukova Dumka, 2010.
4. Bukvareva, O.F. and Bukharkina, T.V., *Kinetika i termokhimiya protsessov termodestruktsii uglerodsoderzhashchikh veshchestv* (Kinetics and Thermochemistry of the Thermal Degradation of Carbon-Containing Substances), Moscow: RKhTU im. Mendeleeva, 2001.

Translated by V. Makhlyarchuk