KINETICS OF LOW-TEMPERATURE RETORTING OF KUKERSITE OIL SHALE

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A step-by-step mathematical model was deduced for description of the co-effect of time, temperature and heating rate at low-temperature (370–410 °C) on the yield of kukersite oil shale pyrolysis products in a laboratory retort. According to the scheme applied, the parallel formation of thermobitumen and volatiles from kukersite, and parallel-consequent formation of volatiles and coke from the thermobitumen formed were approximated to the first order kinetic reactions. The algorithms for estimation of the corresponding rate coefficients (k_1–k_4) were proposed. The values of apparent activation energy (E_1-E_4) and frequency factor (A_1-A_4) were calculated using the temperature dependencies of the rate coefficients estimated on the basis of experimental results obtained at isothermal retorting. A kinetic compensation effect was revealed between the bulk of kinetic constants found: $lnA = 0.176(\pm0.009)E – 2.59(\pm2.29)$. The share factors and their temperature dependencies for distribution of malthenes and asphaltenes in thermobitumen, and gas and oil in volatiles were found from the experimental results of kukersite low-temperature retorting. The effect of time on the yield of the products predicted introducing the constants found into the model deduced agreed satisfactory with the experimental results obtained at retorting of kukersite under non-linear increase of temperature up to 370–410 °C and keeping 20–60 minutes under the nominal temperature.

Introduction

The retorting technologies of kukersite oil shale being in use for industrial production of shale oil lose more than one third of the kukersite organic matter with semicoke and gas. A possibility for separation about 90% of kukersite organic matter from its mineral part in the form of volatiles and soluble in organic solvents thermobitumen (TB) intrigues in ecological and economical

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aspects. TB, the main product of low-temperature (350–410 °C) pyrolysis of kukersite is a high-molecular non-volatile intermediate product of kerogen pyrolysis.

Formation of TB studied intensively in the middle of the last century [1–15] is of interest again [16, 17]. A review [16] about previous works concerning formation of TB was compiled. In the work [17] the yields of gas, soluble in benzene fraction and solid residue formed at pyrolysis of oil shale in an autoclave under the ranges of nominal temperature 340–380 °C and reaction time 10–1200 minutes were estimated. The optimum time for the maximum yield of the benzene soluble fraction consisting of TB and oil (TBO) was established for every nominal temperature. In the paper [18] a first order kinetic model was proposed for description of the co-effect of time and temperature on the yield of products at autoclavic pyrolysis of kukersite in the range 420–500 °C. The apparent kinetic constants for parallel formation of TBO and gas from kerogen, and parallel-consequent formation of gas and coke from TBO formed were estimated.

The aim of this study was creation of a mathematical model enabling prediction of the current yields of gas, oil, thermobitumen, malthenes, asphaltenes, solid residue, kerogen not decomposed and coke in the latter at low-temperature retorting of kukersite under any heating rate and nominal temperature, and to establish the conditions for the maximum total yield of TB and oil.

For modelling of oil shale thermobituminization a simplified scheme (Fig. 1) was used where the process was assumed to consist of parallel formation of TB and volatiles from kerogen, and of the simultaneous consequent decomposition of TB into volatiles and coke. The contribution of malthenes and asphaltenes in TB, and oil and gas in volatiles were described by parallel reactions introducing the corresponding temperature depending share factors.
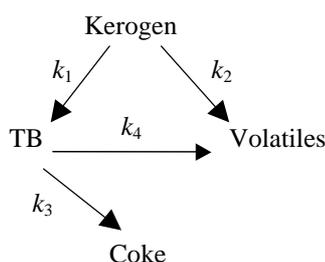

Fig. 1. Scheme of pyrolysis kinetics.

Experimental part

The initial material applied was dry powdered kukersite with kerogen content 32.3% and the oil yield in Fischer assay – 24%.

As a rule, a retorting process begins under non-isothermal heating up conditions. In this work, the experiments were conducted in a 500-ml aluminium retort by heating the kerogen up to the nominal temperature according to the pyrolysis standard ASTM D 3904-90: the first 20 minutes – 20 °/min, and then accordingly, 9, 7 and 6 °/min, at ten-minute intervals. The nominal temperatures applied were chosen in the region optimal for formation of TB, 370–410 °C, established earlier [12–15]. The isothermal period was kept for 20 minutes. TB from the solid residue was extracted in Soxhlet with the 1:1 mix of benzene and ethanol. The yield of malthenes was estimated as the hexane soluble fraction of TB. The results of experiments are given in Table 1.

Though simplified, the scheme 1 consisting of parallel-consequent decomposition reactions under non-linear increase of temperature was too complicated for estimation of the rate coefficients. So, in this work the experimental data for estimation of kinetic constants were taken from the thesis of Schulman [15] who had applied a specific device for isothermal retorting. The time dependencies of the yields of volatiles, TB and solid residue obtained in [15] are shown in Fig. 2. One can see that the results give quite similar curves at the two temperatures tested, except the reaction time required at 350 °C exceeds that at 386 °C by an order of magnitude. To handle more experimental points for estimation of kinetic constants, the data for calculations were interpolated from Fig. 2*a* after every 50 minutes and from 2*b* after every 5 minutes (Table 2).

Table 1. **Effect of nominal temperature (°C) and total time (min) on the yield of products (% on kerogen basis) at non-isothermal retorting of kukersite**

| Temperature	Time	Oil	Gas	Thermo-bitumen	Malthenes	Solid residue
370	39	8.85	2.29	30.65	13.42	58.20
	92	23.07	6.07	55.11	24.95	15.76
380	50	19.26	4.71	55.29	n.d.*	20.74
	60	22.38	5.29	57.99	n.d.	14.33
390	52	23.10	5.42	61.61	24.82	9.88
	62	27.86	6.19	57.00	n.d.	8.95
	92	32.51	9.01	46.01	18.77	12.48
400	53	24.15	5.73	56.04	n.d.	14.09
	63	29.63	7.06	53.50	n.d.	9.81
410	55	30.12	5.98	53.90	n.d.	10.00
	65	31.73	7.12	51.70	n.d.	9.44
	95	33.68	8.20	47.99	n.d.	5.82

n.d.* – not determined
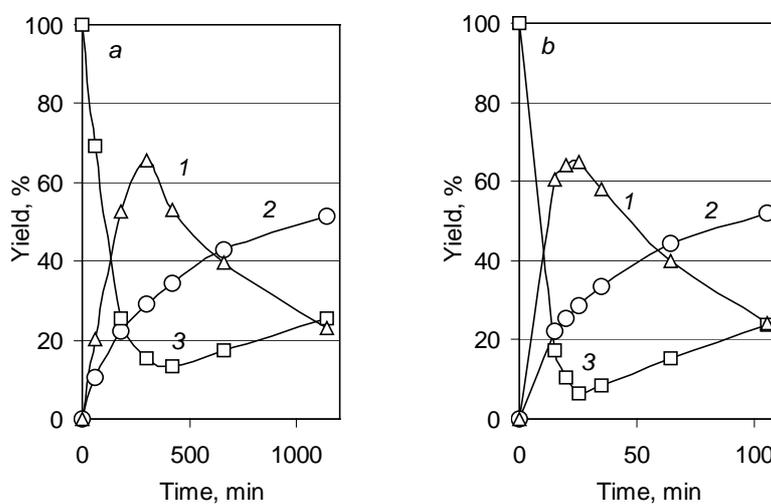
Fig. 2. Effect of retorting time on the yield of thermobitumen (*1*), volatiles (*2*) and solid residue (*3*) at isothermal retorting temperatures 350 °C *(a)* and 386 °C *(b)* by Schulman [15].

Table 2. **Yield of pyrolysis products, % on kerogen basis, extrapolated from Fig. 2**

350 °C				386 °C			
Time, min	Solid residue	Thermo-bitumen	Volatiles	Time, min	Solid residue	Thermo-bitumen	Volatiles
0	100	0	0	0	100	0	0
50	69	17.5	9	5	72	22	7.5
100	48	32.5	15	10	43	42	15
150	31	47.5	20	15	17.5	60	22
200	20	54.5	23	20	10	64	25
250	14.0	56	27	25	7	65	29
300	12.3	56.5	29	30	7.5	62	31
350	12.9	56	32	35	8.5	58	34
400	13.5	54	34	40	10	55	35.5
450	14	50	36	45	11	51.5	38
500	14.5	48	38	50	12	48	40
550	15	45	39.5	55	13	45	42
600	16	42.5	41.5	60	14.5	42	43.5
650	17	40	42.5	65	15.5	39.5	45
700	18	38	43.5	70	17	37.5	46
800	20	34	45	75	18	35	47
900	22	31	47	80	19	33.5	48
1000	23	27.5	49.5	85	20	32	49

Results and discussion

Estimation of rate coefficients and kinetic constants

Admitting that the complicated thermal decomposition reactions presented schematically in Fig. 1 can be approximately described analogously to the autoclavic pyrolysis of oil shale [19] by the first order kinetic equation, the current concentration of the initial kerogen insoluble in organic solvents (y) should decrease with time as follows:

$$-dy/dt = (k_1 + k_2)y = k_y\,y, \qquad (1)$$

and the total decomposition rate coefficient of kerogen (k_y) can be found from the slope of the integrated form of Eq. (1) as follows:

$$\ln y = \ln y_0 - k_y\,t. \qquad (2)$$

Before coke formation has begun, the current values of y can be estimated experimentally by the percentages of solid residue. So, under isothermal conditions there should be a time interval where Eq. (2) would express a straight line whose slope is equal to k_y. The experimental results in Table 2 depicted in Fig. 3 in the form of Eq. (2) show a linear decrease of the logarithm from the solid residue percentage during the first period of the pyrolysis. In the second period the yield of solid residue increases due to coke formation. The values of k_y corresponding to the slopes in Fig. 3 are brought in the first column of Table 3.
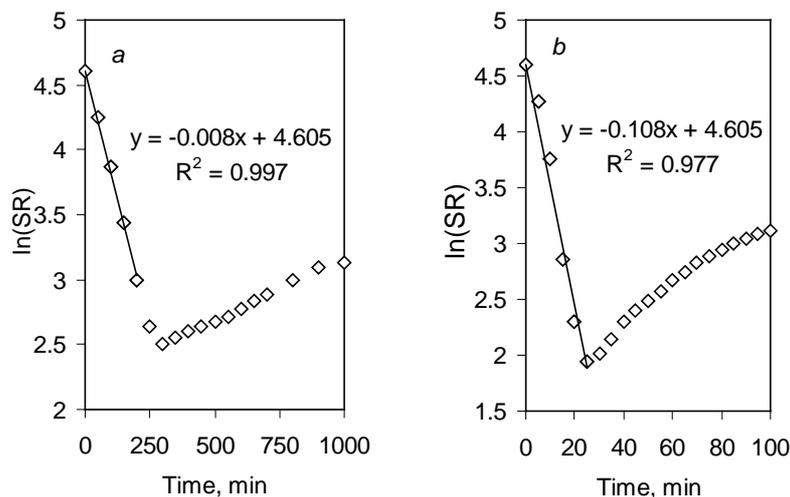

Fig. 3. Plot of logarithm from the yield of solid residue versus time at retorting temperatures 350 *(a)* and 386 °C *(b).*

Table 3. **Rate coefficients for low-temperature retorting of kukersite, 1/min**

Temperature, °C	k_y	k_1	k_2	k_3	k_4	k_{TB}
350	7.85E–03	4.740E–03	2.606E–03	6.610E–04	4.870E–04	1.148E–03
386	0.1081	0.09120	0.03150	5.395E–03	5.665E–03	0.01106

According to the scheme 1, concentration of TB (x_1), volatiles (x_2) and coke (x_3) change with time as follows:

$$dx_1/dt = k_1 y - (k_3 + k_4)\, x_1 = k_1 y - k_{TB}\, x_1 \tag{3}$$

$$dx_2/dt = k_2\, y + k_4\, x_1 \tag{4}$$

$$dx_3/dt = k_3\, x_1 \tag{5}$$

Dividing Eqs (3), (4) and (5) with Eq. (1) and thereafter multiplying with k_y linear relationships (Y_i) are obtained between the ratio of changes in the concentration of any product and initial kerogen *versus* the current ratio of the concentrations of TB and kerogen

$$Y_i = -k_y dx_i/dy = a + bx_1/y, \tag{6}$$

where when $i = 1$: $a = k_1$ and $b = k_{TB}$, and when $i = 2$: $a = k_2$ and $b = k_4$.

The real percentage of the kerogen not decomposed (y) in the total solid residue was calculated for Eq. (6) by means of the rate coefficient k_y from Table 3 using the exponential form of Eq. (2)

$$y = 100/\exp(k_y t). \tag{7}$$

The coefficient k_3 was found from the difference

$$k_3 = k_{TB} - k_4. \tag{8}$$

Introducing the data series from Table 2 into Eq. (6) gives satisfactory linear plots of Y_i versus x_1/y (Fig. 4). The rate coefficients, equal to the corresponding regression constants, at the two temperatures applied are presented in Table 3.

In this work, the kinetic constants (E_i and A_i) in the Arrhenius relationship

$$k_i = A_i \exp(-E_i/RT) \tag{9}$$

were calculated using the data given in Table 3 as follows:

$$E_i = [R(T_1 T_2)\, \ln(k_{i1}/k_{i2})]/(T_2 - T_1) \tag{10}$$

$$A_i = k_i \exp(E_i/RT). \tag{11}$$

The kinetic constants found are presented in Table 4. The apparent activation energies for parallel formation of TB and volatiles, 280 and 236 kJ/mol, are comparable with that for total semicoking, 260 kJ/mol, estimated by Aarna and Kollerov [6, 7].
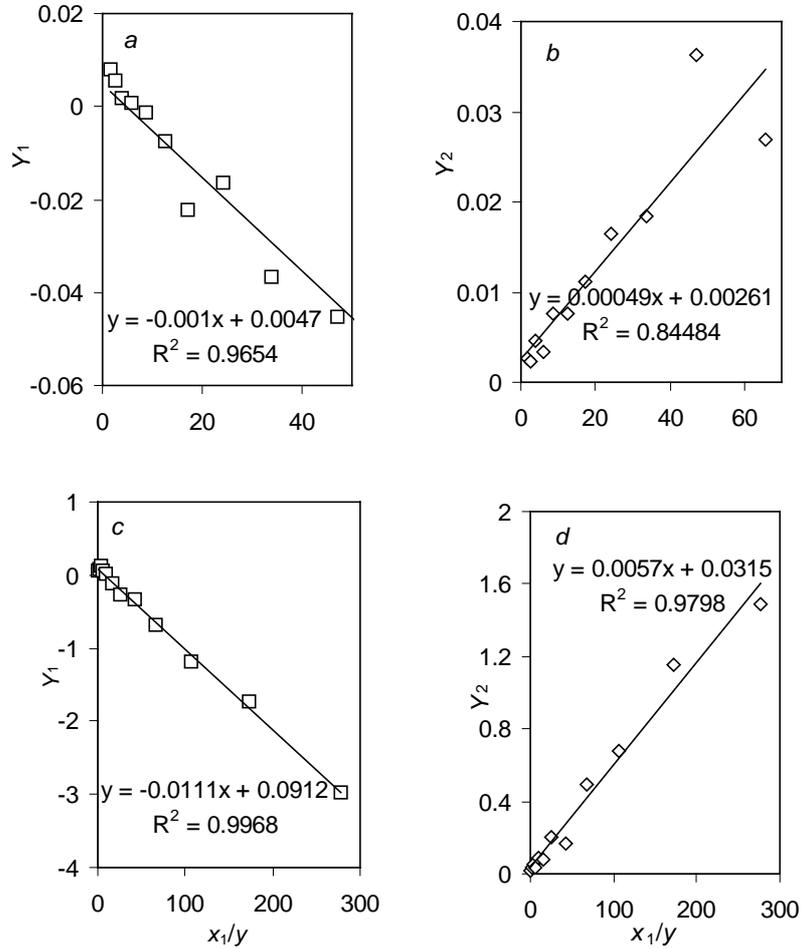
Fig. 4. Depiction of Equation (6) for estimation of k_1 and k_{TB} (*a* and *c*), and k_2 and k_4 (*b* and *c*) at temperatures 350 (*a* and *b*) and 386 °C (*c* and *d*).

Table 4. **Apparent kinetic constants for low-temperature retorting of kukersite**

	k_1	k_2	k_3	k_4
A, 1/min	1.53E+21	1.69E+17	1.38E+12	2.05E+17
E, kJ/mol	280	236	183	246

Kinetic compensation effect

A kinetic compensation effect (KCE), a linear interdependence of Arrhenius parameters according to

$$\ln A = c + bE \tag{12}$$

is evident in Fig. 5. Noteworthy is that the relationship is valid between both the kinetic constants of kerogen thermal decomposition obtained using an open retort in this work and those obtained under pressure in autoclaves in the work [19]. No explanation has yet been generally accepted for the wide-spread occurrence of KCE [20]. At low-temperature pyrolysis of kukersite the values of the coefficients are as follows: $c = -2.59(\pm 2.29)$ and $b = 0.176$ (± 0.009).
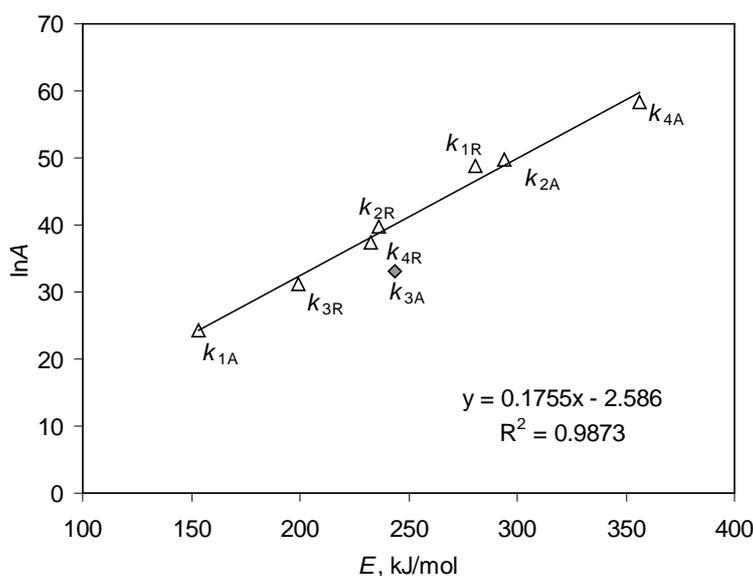

Fig. 5. Plot of ln$A$ versus E for the rate coefficients k_i at low-temperature pyrolysis of kukersite in the laboratory autoclave (index A) and retort (index R).

Estimation of share factors of malthenes and asphaltenes in TB, and oil and gas in volatiles

Admitting the parallel formation of malthenes and asphaltenes in the bulk of TB, as well as of gas and oil in the bulk of volatiles, the changes in their yields should be proportional, and can be characterized by the share factor

$$B_i = \mathrm{d}x_{ij}/\mathrm{d}x_i. \tag{13}$$

Understandably, the share of the second component is $1 - B_i$.

The experimental data in Table 1 evidence that under the studied conditions the share factor of malthenes in TB (B_{1m}) decreases, and that of oil in total volatiles (B_{2o}) increases with an increase in temperature. These effects can be approximated to a linear relationship

$$B_i = a_B + b_B \mathrm{t} \tag{14}$$

shown in Fig. 6. When the temperature t is expressed in °C, the values of a_B and b_B for malthenes in TB are 1.106 and 0.550, and for oil in volatiles – 0.00179 and 6.66E-04. The effect of pyrolysis time on the values of B_i was irregular and less than the experimental errors.
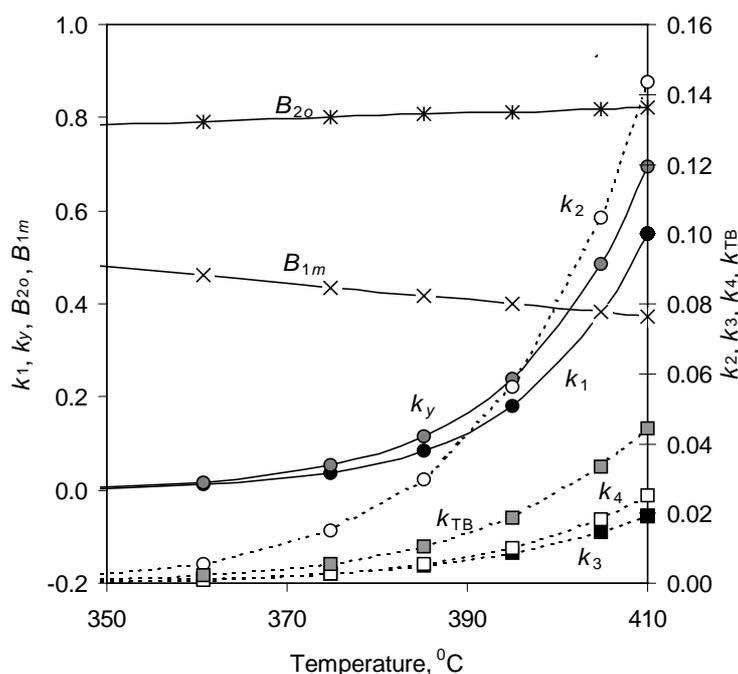

Fig. 6. Effect of temperature on the rate coefficients, 1/min, and on the share factors of malthenes in thermobitumen, B_{1m}, and of oil in volatiles, B_{2o}, formed.

Prediction of current concentrations of the pyrolysis products

As described above, thermal decomposition of kukersite in Fischer retort is conducted under the non-linear increase of temperature. The simplest way to describe such a process is to handle it as consisting of short isothermal subsequent steps under the mean temperature of the steps.

As an example, prediction of current yields of the pyrolysis products at nominal temperatures 370 and 410 °C is described.

At first, the current rate coefficients and share factors were calculated. The results are depicted in Fig. 6 where for better understanding the plain curves belong to the left axis and the dotted curves to the right one. For calculation the coefficients

- the current temperatures after every 2 minutes intervals and the mean temperatures of the steps were calculated according to the heating regime applied;

- for every mean temperature the values of (i) the rate coefficients (k_i) were calculated by Eq. (9) using the corresponding apparent kinetic constants from Table 4, and (ii) the share factors (B_i) were calculated by Eq. (14).

The results obtained evidence that at the low-temperature region formation of TB from kerogen is preferred, and the rate coefficient for formation of volatiles from the initial kukersite (k_2) overcomes that from TB. The share of oil in volatiles increases a little with temperature in the studied region, whereas the share of malthenes in TB decreases, presumably, just because of oil formation from malthenes.

The current yields of the products were calculated as follows:

- the current percentage of the not decomposed (insoluble in benzene) kerogen per its initial content during the non-isothermal stage was calculated using Eq. (1) integrated in the ranges of time t_{n-1} and t_n

$$y_n = y_{n-1}/\exp[(k_1 + k_2)(t_n - t_{n-1})] \tag{15}$$

    where at $t_{n-1} = 0$ min, $y_{n-1} = 100\%$;

- after the nominal temperature was attained, the concentrations of the initial kerogen at time t were calculated basing on the not decomposed kerogen concentration (y_{nom}) at time t_{nom} as follows

$$y = y_{nom}/\exp[k_y(t - t_{nom})] \tag{16}$$

- the current yield of TB was calculated using the relationship deduced from Eq. (6)

$$x_{1,n} = x_{1,n-1} + [(y_{n-1} - y_n)k_1/(k_1 + k_2)][k_1 + (k_3 + k_4)x_{1,n-1}/y_{n-1}], \tag{17}$$

    where at $t = 0$ min, $x_{1,n} = 0\%$;

- the current yield of volatiles was calculated analogously as follows:

$$x_{2,n} = x_{2,n-1} + [(y_{n-1} - y_n)k_2/[(k_1 + k_2)][k_2 + k_4 x_{1,n-1}/y_{n-1}], \tag{18}$$

    where at $t = 0$ min, $x_{2,n} = 0\%$;

- the current coke yield was calculated as the difference

$$x_{3,n} = 100 - (y_n + x_{1,n} + x_{2,n}) \tag{19}$$

- the total yield of the total solid residue at time t was calculated as the sum of current y and x_3;

- the current yields of malthenes and oil were found using the corresponding values of B_i given in Fig. 6 as follows:

$$x_{1m,n} = x_{1m,n-1} + B_1(x_{1,n-1} - x_{1,n}) \tag{20}$$

$$x_{2o,n} = x_{2o,n-1} + B_2(x_{2,n-1} - x_{2,n}) \tag{21}$$

- the yields of asphaltenes and gas were calculated as corresponding differences between the concentrations of TB and malthenes, and volatiles and oil.

The yields predicted by Eqs (15)–(21) for the two limit nominal temperatures tested in this work are presented in Fig. 7*a* and 7*b*. In the figure, for better understanding, the dotted curves and grey points express the total yield of two products (marked as white and black): target product (oil + TB),
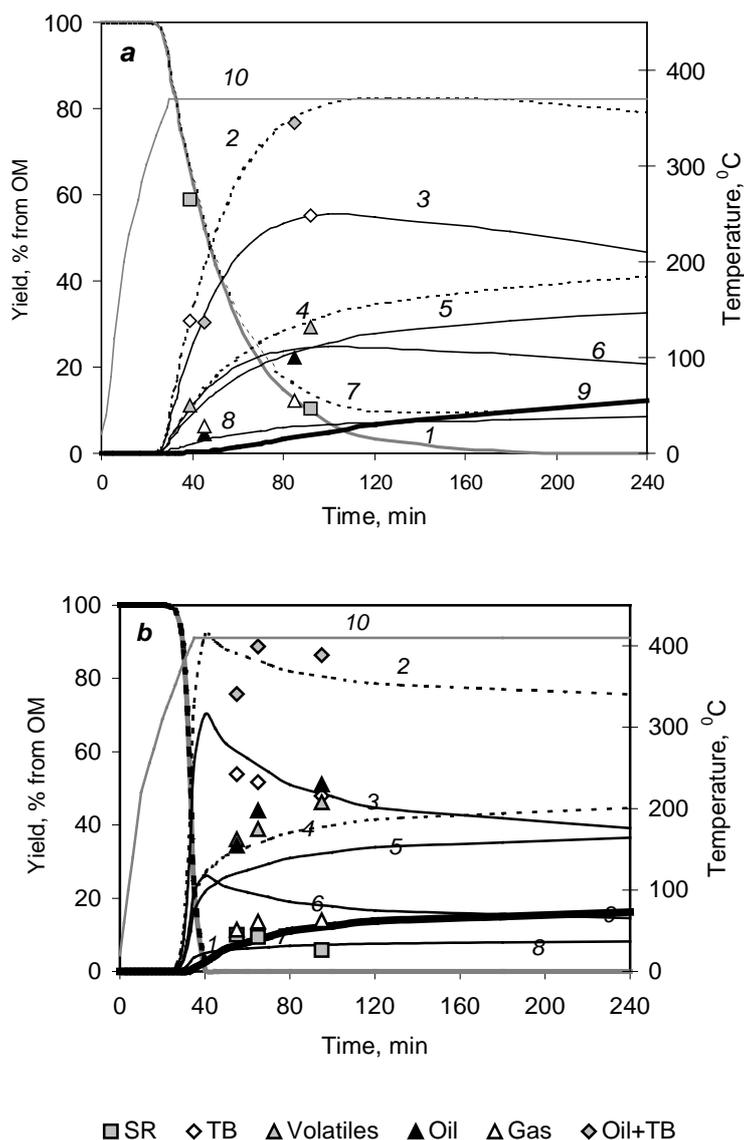

Fig. 7. Effect of retorting time at nominal temperature 370 °C (*a*) and 410 °C (*b*) on the distribution of kerogen decomposition products: *1* – kerogen, *2* – TB + oil, *3* – TB, *4* – volatiles, *5* – oil, *6* – malthenes, *7* – solid residue, *8* – gas, *9* – coke, and *10* – the current temperature. Curves – calculated, points – experimental.

volatiles (oil + gas) and solid residue (kukersite + coke). The bold black curves belong to coke and grey ones to kukersite. The normal grey curves express the current temperature.

Figure 7 explains essential effect of time and temperature on the yield of the products. One can see that under the heating rate applied, decomposition of the initial kukersite is completed at 370 °C after three hours, but at 410 °C after already 40 minutes. At 370 °C the maximum yield of the target product, TB + oil, has a plain maximum, *ca* 80%, between 100–240 minutes. At 410 °C a sharp elusory maximum of that overcomes 90% between 40 and 45 minutes, and the yield over 80% can be obtained between 40–100 minutes.

Comparison of the yields of the products found experimentally (by the low-temperature non-isothermal retorting) with the data predicted using in Eqs (15)–(21) the kinetic constants found by means of experimental data obtained under the isothermal conditions about fifty years earlier by Schulman [15] shows a more or less satisfactory agreement. Such a harmony is possible only thanks to the invariable composition of Baltic oil shale organic matter all over the mine, and exact consideration of the heating rate of the reaction mix during the experiments.

The mathematical model deduced and constants estimated allow prediction of the co-effects of temperature and time on the different products of low-temperature retorting. The calculated curves presented in Fig. 7 explain that, unlike previous opinions, the coke formation from TB begins before the exhaustion of kerogen is attained. As a result, the optimum time for thermo-bituminization (t_{max}) enabling the maximum the yield of the target product, TBO, should be just after the time corresponding to the equal contents of coke and not decomposed kerogen in the solid residue, the latter constituting about 10% of the initial kerogen. The optimum time and the appropriate time interval for retorting decrease with increase in temperature.

Conclusions

1. A first order parallel-consequent kinetic model was deduced for preliminary description of the co-effect of time, nominal temperature and heating rate on the yield of products at low-temperature pyrolysis of kukersite in laboratory retorts.
2. The rate coefficients for formation of thermobitumen and volatiles from kukersite, and volatiles and coke from thermobitumen, k_1-k_4, were estimated using the experimental results obtained at isothermal retorting by Schulman [15], and the apparent activation energies (E_1-E_4) and frequency factors (A_1-A_4) for the coefficients were calculated.
3. The temperature dependencies for the share factors of malthenes and asphaltenes in thermobitumen, and gas and oil in volatiles were found from the experimental results of kukersite low-temperature retorting.

4. The effect of the retorting time on the yield of thermobitumen, volatiles, solid residue, oil, gas, malthenes, asphaltenes, coke and not decomposed kerogen at various nominal temperatures and heating rates prescribed was predicted introducing the constants found into the model deduced. The calculated and the corresponding experimental results agreed satisfactorily.
5. The maximum total yield of TB and oil from kerogen (91%) was obtained at nominal temperature 410 °C after 40 minutes processing.

Acknowledgement

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