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COMPARISON OF THE THERMOBITUMINIZATION KINETICS OF BALTIC OIL SHALE IN OPEN RETORTS AND AUTOCLAVES

I. JOHANNES[*], L. TIIKMA, A. ZAIDENTSAL

Tallinn University of Technology
5 Ehitajate Rd., 19086 Tallinn, Estonia

The kinetic models deduced for description of laboratory low-temperature pyrolysis of Baltic oil shale in open retorts and autoclaves are discussed. The apparent activation energies and frequency factors (E_1-E_4 and A_1-A_4) estimated for the two devices are compared approximating the process to the parallel-subsequent thermal decomposition of kerogen into three phases: volatiles, benzene extract and coke. Common for the both devices linearity, $\ln A_i = 2.23 + 0.174\ E_i$, is revealed between the kinetic constants taken from the previous papers. It is shown that E_1 for decomposition of kerogen into thermobitumen and oil (TBO) in autoclaves is lower than at decomposition into thermobitumen (TB) at retorting, whereas the values of E_2 and E_4, characteristic of decomposition of kerogen and TB into volatiles, are lower in open retorts than under pressure in autoclaves, and E_3, characteristic of coke formation from high-molecular TB, is lower than in the case of oil-containing TBO. Time-dependencies of the yields of TBO, gas, solid residue and undecomposed kerogen at various nominal temperatures are predicted for pyrolysis in both devices under equal heating rates using the deduced unified model. It is shown that in the both devices secondary decomposition of TBO into coke and gas begins before the total decomposition of the initial kerogen has been completed, and the current decomposition degree of kerogen and yield of TBO are affected mainly by pyrolysis duration and temperature, whereas the reactor type has only a slight effect.

Introduction

It has been known since the middle of the last century [1, 2] that at semi-coking the organic matter (OM) of Baltic oil shale, kukersite, passes an intermediate stage – thermobituminization. The effect of temperature on the distribution of thermal decomposition products of OM at optimum durations ensuring the maximum yield of the phase soluble in organic solvents is

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[*] Corresponding author: e-mail *ille.johannes@ttu.ee*

shown in Fig. 1. The figure demonstrates that under appropriate conditions under which the coke formation has not started yet, nearly 90% of OM can be extracted and separated from the oil shale mineral part as a mix (TBO) consisting of thermobitumen (TB) and oil**.** Elaboration of a new technology basing on separation and upgrading of TBO would increase notably the oil potential of kukersite and decrease significantly the part of organic matter being wasted with the hazardous semicoke deposed. Reviews concerning up to date experimental results of oil shale low-temperature pyrolysis in retorts and autoclaves were given in the latest publications [3, 4]. The optimum pyrolysis duration at different nominal temperatures and heating rates was recently quantitatively described by mathematical modelling of the oil shale low-temperature pyrolysis kinetics in a Fischer retort [5] and laboratory batch autoclaves [6]. The first-order kinetic model was deduced basing on an approximated parallel-consequent scheme of the phase transformations and experimentally estimated current yields of the three phases: volatiles, benzene extracts of the cubic residues, and insoluble solid residues. As far oil was incorporated into the volatile phase at the open air pyrolysis and into the liquid extract in autoclaves, the direct comparison of the pyrolysis kinetics in the two devices was complicated. Furthermore, the heating rates in the devices were different, too.

The aim of this work was comparison of the effectiveness and kinetics of oil shale thermobituminization in open retorts and autoclaves.

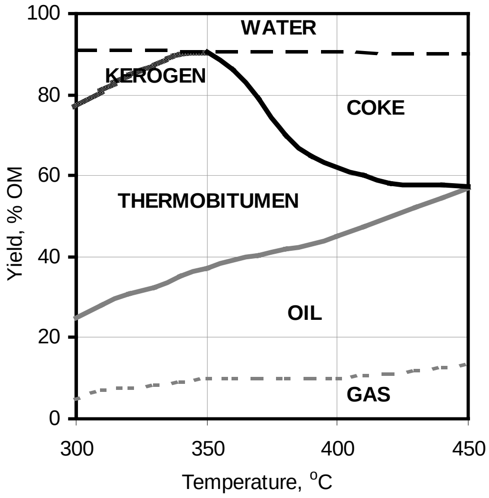

Fig. 1. Distribution of organic matter at pyrolysis of oil shale in open retorts at durations ensuring the maximum yield of TBO [1, 2].

Experimental

Low-temperature retorting and pyrolysis in autoclaves

The detailed description of the retorting experiments and their results is published in [5] and autoclavic experiments in [6].

Briefly, the initial material applied in retorting experiments was dry powdered kukersite with kerogen content 32.3%, and the oil yield in Fischer assay – 24%. The pyrolysis was 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 °C/min, and then 9, 7 and 6 °C/min, at ten-minute intervals, accordingly. The nominal temperatures applied were between 370–410 °C. The isothermal period was kept for 20 minutes. TB from the solid residues was extracted in Soxhlet with the 1:1 mix of benzene and ethanol. The yields of water, oil, TB after evaporation of the solvent mix, and solid residue were estimated by weight, the gas yield and losses – by difference.

At autoclavic pyrolysis 4.0 grams of dry powdered kukersite with kerogen content 50.5% was heated in 20-cm^3 micro-autoclaves being placed in a muffle oven at five nominal temperatures in the range of 340–380 °C. After definite residence times between 45–1200 minutes the autoclaves were cooled and opened at room temperature. The mass of gas formed was determined by the weight loss after discharging. The liquid product (water + TB + oil) was removed from the solid residue in a Soxhlet extractor with benzene. Mass of the solid residues was weighted after drying the extraction cake at 105–110 °C. The percentage of the organic matter remained in the solid residues was estimated by the mass burning out from the acid-treated and dried residues at 800–850 °C. The solvent benzene was removed from TBO using a vacuum rotation evaporator at 60–70 °C, and after that keeping the flask during an hour in a drying oven at 80 °C.

Theoretical approach

Algorithms for estimation of kinetic constants

For an unified approach, the complicated thermal decomposition of oil shale both in open retorts and autoclaves can be approximately described by the rate factors (k_i) of the following common first order parallel-consequent phase transformations (with the corresponding concentration symbols in parenthesis) as follows:

k_1: kerogen (y) → extract (x_1),

k_2: kerogen (y) → volatiles (x_2),

k_3: extract (x_1) → coke (x_3),

k_4: extract (x_1) → volatiles (x_2).

The differential equations for the kinetic scheme proposed for the both devices are expressed as follows:

$$-\mathrm{d}y/\mathrm{d}t = (k_1 + k_2)y = k_y y, \tag{1}$$

$$\mathrm{d}x_1/\mathrm{d}t = k_1 y - (k_3 + k_4)\, x_1 = k_1 y - k_{\mathrm{TB}}\, x_1, \tag{2}$$

$$\mathrm{d}x_2/\mathrm{d}t = k_2 y + k_4 x_1, \tag{3}$$

$$\mathrm{d}x_3/\mathrm{d}t = k_3 x_1. \tag{4}$$

For estimation of the rate factors, the following linear relationships can be deduced from Eqs. (1)–(4):

$$\ln y = \ln y_0 - k_y t, \tag{5}$$

$$k_y(\mathrm{d}x_1/\mathrm{d}y) = k_1 + k_{\mathrm{TB}}(x_1/y), \tag{6}$$

$$k_y(\mathrm{d}x_2/\mathrm{d}y) = k_2 + k_4(x_1/y), \tag{7}$$

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

In the second stage where the initial kerogen is practically exhausted, Eq. (2) is simpler, and k_{TB} can be found from the slope of its integrated form

$$-\mathrm{d}x_1/\mathrm{d}t = (k_3 + k_4)x_1 = k_{\mathrm{TB}} x_1, \tag{9}$$

$$\ln x_1 = \ln x_{1,0} - k_{\mathrm{TB}}(t - t_0), \tag{10}$$

where t_0 and $x_{1,0}$ belong to the beginning of the second stage, corresponding to the minimum value of y.

The procedure for estimation of the rate factors has been described in detail in [5] and [6] as well as that for estimation of the kinetic constants, activation energies (E_i) and freaquency factors (A_i) from the temperature dependencies of the rate factors according to Arrhenius relationship

$$\ln k_{\mathrm{i}} = \ln A_i - E_i/RT. \tag{11}$$

Algorithms for estimation of the distribution factor of oil in volatiles at retorting

As said above, the main difference between the phases obtained by retorting and autoclavic pyrolysis is whether the oil incorporates the volatile phase or extract. For comparison, the both target products were expressed as TBO. To predict the oil yield basing on the pyrolysis scheme proposed, the distribution factor of oil in volatiles B_{o} was applied. Admitting the parallel formation of gas and oil in the bulk of volatiles, the changes in their yields should be proportional, and an increase in the oil yield ($x_{2\mathrm{o}}$) from the total increase of volatiles (x_2) can be characterized by the share factor B_{o} as follows:

$$\mathrm{d}x_{2\mathrm{o}} = B_{\mathrm{o}}\mathrm{d}x_2. \tag{12}$$

The share factor of the second component of the volatiles, gas, is $1 - B_{\mathrm{o}}$.

The experimental data obtained at retorting and published in [5] proved proportionality between the increase in the yields of oil and volatiles and revealed that in the case of the studied temperature interval the share factor of oil in total volatiles (B_o) increases with an increase in temperature, (T, expressed here in °C), according to the linear relationship

$$B_o = -000179 + 6.66\times10^{-4}\, T. \tag{13}$$

The effect of pyrolysis time on the values of B_o was irregular and less than experimental errors.

Algorithms for prediction of current concentrations of the pyrolysis products

Thermal decomposition of kukersite in both devices is conducted under non-linear increase of temperature that can be handled consisting of short isothermal subsequent steps (n) under the mean temperature of the steps, and the current yields of the products can be calculated as follows:

$$y_n = y_{n-1}/\exp[(k_1 + k_2)(t_n - t_{n-1})], \tag{14}$$

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

$$x_{1,n} = x_{1,n-1} + [(y_{n-1} - y_n)k_1/(k_1 + k_2)][k_1 + (k_3 + k_4)x_{1,\,n-1}/y_{n-1}], \tag{15}$$

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

$$x_{2,n} = x_{2,n-1} + [(y_{n-1} - y_n)k_2/[(k_1 + k_2)][k_2 + k_4\, x_{1,\,n-1}/y_{n-1}], \tag{16}$$

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

$$x_{3,n} = 100 - (y_n + x_{1,n} + x_{2,n}), \tag{17}$$

$$x_{2o,n} = x_{2o,n-1} + B_o(x_{2,n-1} - \mathrm{x}_{2,n}). \tag{18}$$

Results and discussion

Compensation effect between the kinetic constants

The kinetic constants found according to the Eqs. (6)–(11) for the both devices are presented in Table 1.

Table. 1. **Apparent kinetic constants**

Rate factor, 1/min	Retort [5]		Autoclave [6]	
	E_i, kJ/mol	A_i, 1/min	E_i, kJ/mol	A_i, 1/min
k_1	280	1.53E+21	153	9.62E+10
k_2	236	1.69E+17	294	3.73E+21
k_3	183	1.38E+12	244	3.70E+16
k_4	246	2.05E+17	356	2.22E+25

Noteworthy is that a common linear relationship

$$\ln A = 2.23(\pm 2.29) + 0.174\ (\pm 0.009)E \qquad (19)$$

with correlation coefficient R = 0.99 is kept between the values of ln*A* and *E* found for low-temperature pyrolysis of oil shale in open retorts and autoclaves (Fig. 2).

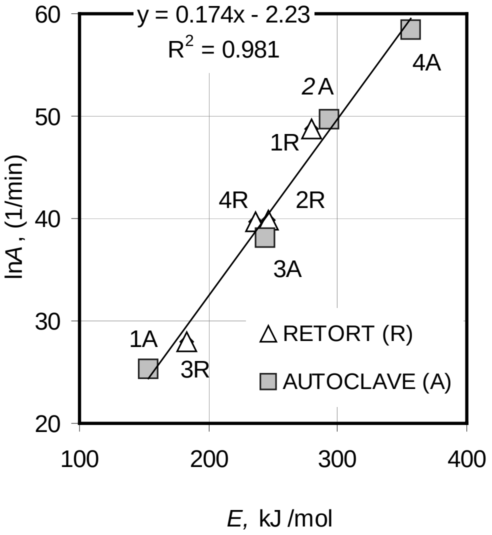

Fig. 2. Relationship between the low-temperature pyrolysis apparent kinetic constants in two devices.

The differences between corresponding activation energies obtained using the two devices (A – autoclave, R – retort) being resulted from the diverse composition of the products help to understand and compare the processes as follows:

- $E_{1A} < E_{1R}$ – decomposition of kerogen into TBO is advanced in the environment of oil not leaving the autoclave;
- $E_{2R} < E_{2A}$ and $E_{4R} < E_{4A}$ – formation of volatiles from kerogen and from TB is advanced in open retorts in comparison with gas formation under pressure in autoclaves;
- $E_{3R} < E_{3A}$ – coke formation from high-molecular TB is superior to that from the oil containing TBO;
- $E_{2R} \approx E_{4R}$ whereas $E_{2A} < E_{4A}$ – in open retorts there is no kinetic difference between formation of volatiles from kukersite or TB, whereas in autoclaves the secondary gas formation from TBO is depressed in comparison with that from kukersite.

Prediction and comparison of the current yields of the pyrolysis products in open retorts and autoclaves

One of the defining factors of pyrolysis kinetics is heating rate. Understandably the heating rate applied at retorting of oil shale in 500-cm^3 open retorts does not coincide with that in 20-cm^3 autoclaves placed into an oven preheated to the nominal temperature. In this work, to compare the efficiency of the devices, the current yields of the products were predicted for both devices under the temperature profiles described earlier [6] as characteristic to autoclavic experiments.

The yields of pyrolysis products in both devices were calculated as sums of n ten-minute steps whose temperatures were approximated to the isothermal mean values of the steps. Rate factors for every increasing temperature step were calculated introducing the kinetic constants from Table 1 into Eq. (11). The corresponding yields of phases were found by Eqs. (14)–(17). Thereafter, the yields of the products obtained at retorting were unified with those at autoclavic pyrolysis. For this aim, the oil yields (x_{2o}) being a part of total volatiles (x_2) at retorting were calculated according to Eqs. (13) and (18). The values of the target product, TBO, were found adding the current oil yield to the corresponding extract yield (x_1), and that of the gas yield, subtracting x_{2o} from x_2. The current values of the organic solid residue were found as sums of the corresponding y and x_3.

Examples illustrating predicted current changes during pyrolysis of oil shale in both devices at the nominal temperatures 350 and 370 °C are presented in Fig. 3.

Comparison of the data obtained at low-temperature pyrolysis of oil shale in open air retorts and autoclaves under unified heating conditions and decomposition products reveals the following results:

- The current decomposition degree of kerogen (curve 0) and yield of the target product, TBO (curve 1), are affected mainly by pyrolysis duration and temperature, whereas the reactor type has a minor effect.
- In both devices decomposition of TBO into coke (curve 3) and gas (curve 2) begins before the total decomposition of kerogen (curve 0) has completed. Therefore, it is impossible to obtain a solid residue without any organic matter at low-temperature retorting without solvents.
- In both devices decomposition of kerogen starts at the same temperature and reaches 10% when the temperature attains 350 °C, and the yield of TBO overcomes 80% at an optimum duration depending on the nominal temperature.
- At the nominal temperature 370 °C the decomposition rate of kerogen and formation of TBO practically coincide in the both devices, and the maximum yield of TBO (83-85%) is obtained at the duration interval 130–150 min.

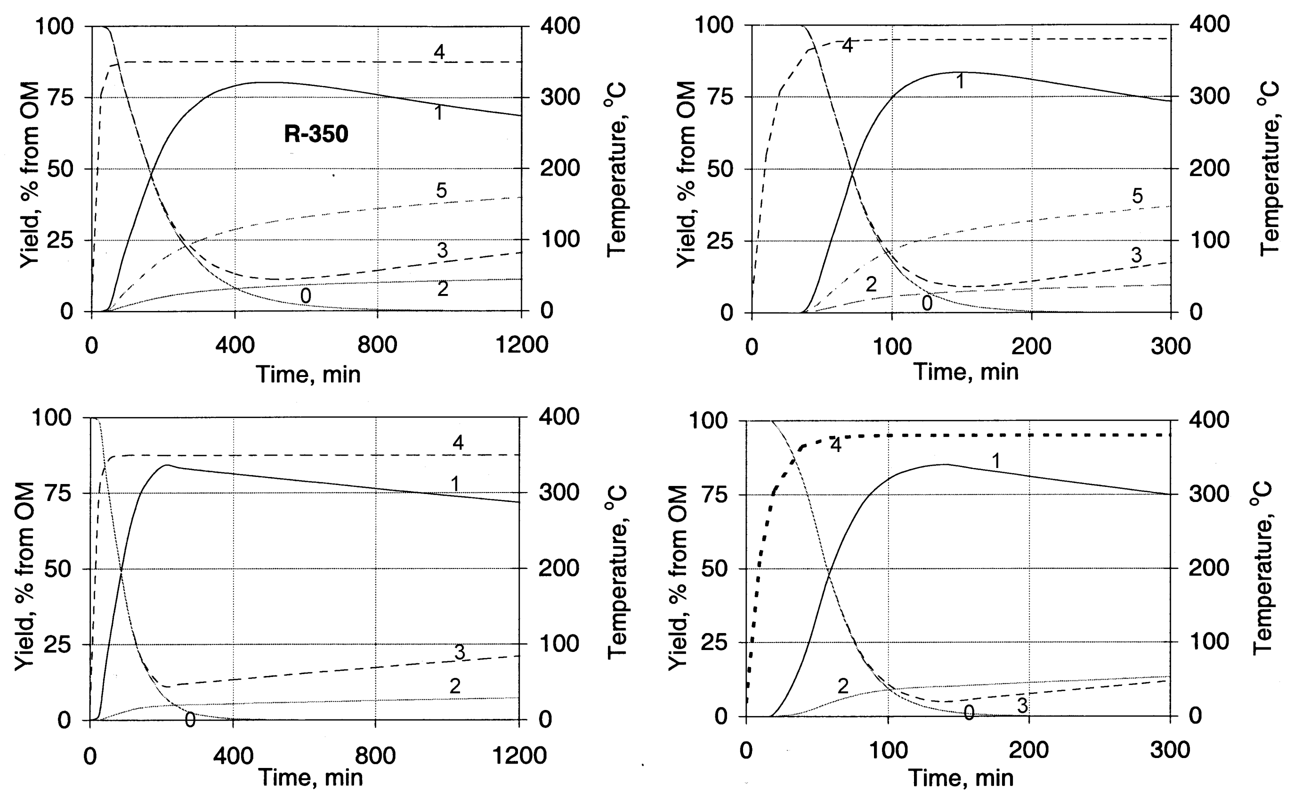

Fig. 3. Effect of pyrolysis duration on the yield of the phases, % from initial kerogen at nominal temperatures 350 and 370 °C in open air retorts (R) and autoclaves (A): 0 – kerogen, 1 – TBO, 2 – gas, 3 – organic solid residue, 4 – temperature, °C.

- At the nominal temperature 350 °C decomposition of kerogen in autoclaves in the environment of oil formed is slightly faster than that at dry retorting in which case the oil fractions with boiling point below 350 °C volatilize. Therefore the maximum yield of TBO (*ca* 80%) is attained in the autoclave after 200 minutes and at retorting only after 400 minutes.

Conclusion

As far there is no significant difference in the pyrolysis kinetics in the both devices, the technically simpler open air retorting followed by the extraction of TB from the cubic residue should be preferred unless an environment of any solution or upgrading reagent is required.

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