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Investigation of Estonian Oil Shale Thermobituminization in Open and Closed System

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

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Termobituumeni moodustumine Eesti põlevkivist avatud ja suletud süsteemis

ALEKSEI ZAIDENTSAL

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INTRODUCTION

The alternative ways of production of synthetic liquid fuels, which are substitutes of petroleum products, are intensively investigated round the world, especially in countries possessing coal, oil shale, and petroleum bitumen deposits.

Oil shales from different deposits vary in chemical composition and technical and technological properties, e.g. in oil yield [1].

Table 1. The oil yield at retorting of oil shales from different deposits, %

Deposit	Oil
Kvarntrop (Sweden)	5.7
Kukersite (Estonia)	22.0
Green River (USA)	10.4
Irati (Brazil)	6.9
Maoming (China)	7.3
El Lajjun (Jordan)	10.1

The Baltic oil shale – kukersite – has got a special place among other oil shales of the world because of its nature, properties and behavior under thermal treatment. Baltic oil shale contains middling 32-35% of organic matter and 68-65% of mineral part on the average. But the upper limit of organic matter in some “fatty” core layers can overcome 60%.

Independently on the organic matter content of samples, the initial kerogen of kukersite is unique in composition, and products of its thermal decomposition contain large quantities of acid and neutral oxygen compounds as well as unsaturated, saturated, and aromatic hydrocarbons.

The yield of liquid products in industrial apparatus is not high enough and does not exceed 50-55% of the organic matter of the raw material. Relatively low yield of liquid products in the process is caused by partial decomposition of primary products with formation of gas and coke.

The comprehensive investigations of kukersite pyrolysis have shown that the thermal decomposition of kerogen begins at 170–180 °C with evolution of decomposition water, CO_2 and H_2S. Between temperatures 325–410 °C takes place softening (plasticization) stage where up to 90% of the kerogen macro-molecules can be converted into thermobitumen (TB) including some light fractions at optimum combination of time and temperature. TB, the highmolecular non-volatile intermediate product of kerogen thermal cracking is soluble in organic solvents.

The composition and physical characteristics of the polycomponental TB depend on its formation conditions whereas at 325–350 °C begins the pyrolysis of TB into oil fractions, gas and semicoke.

The investigation into the stage of thermobitumen formation is of much interest from the theoretical as well as practical viewpoints because decomposition of kukersite oil shale in industrial apparatus also takes place via this stage.

Transition of kukersite to the plastic state within the temperature range of 350–400 °C at slow heating is one of the characteristics of kukersite causing considerable difficulties at industrial oil production. The operation of apparatus for kukersite thermal decomposition has shown that the processing of bituminizable oil shale is connected with substantial difficulties and sets various requirements for apparatus construction and technological operational parameters.

The troublesome consequences such as sticking of organic matter to the retort walls, formation of hangings, etc. have been eliminated by going through the temperatures of maximum TB formation at a relatively high speed (not less than 3–4 °C/min). At that, special efforts, mainly fast heat supply, have been applied to avoid caking and plugging problems of undesirable pitchy plasticization caused by TB formation. Therefore, the knowledge about the thermobitumen formation stage and the behavior of kukersite at this stage may serve as useful information for optimal operation of technological equipment as well as for the design of apparatus used in thermal processing of kukersite oil shale.

The formation of TB from oil shale, has been studied intensively in the middle of the last century is again of interest. The main purpose of the former investigations has been to understand the origin and composition of oil shale. At that, the individual effects of time or temperature at various constant values of the other parameter on the yield of TB, semicoke and volatiles at low temperature pyrolysis of oil shale and enriched kerogen in open retorts was studied. A convincing co-effect of temperature, time and heating rate on the maximum yield of TB and characteristics of the products is evident in the works cited in the last century without any mathematical interpretation.

The present theses sets the goal on the description of kinetics of thermobitumen formation in laboratory closed and open systems. The results would give a theoretical bases for the hypothesis to increase in liquid products yield and decrease in losses of the potentially useful organic matter by elimination of the secondary processes of kukersite organic matter decomposition into gas and coke. Reduction in gas and coke formation is achieved by terminating the thermal decomposition process under low-temperature region, at the stage of formation of the primary product – thermobitumen.

LIST OF PUBLICATION

The present dissertation is based of the following papers, which are referred to in the text by their Roman numerals I-VI.

I. Soone, J., Zaidentsal, A., Muoni, R. 2008. Yields and properties of thermal bitumen obtained from combustible shale. – Solid Fuel Chemistry, vol 2, No. 2, p 74-79.

II. Tiikma, L., Zaidentsal, A., Tensorer, M. 2007. Formation of thermobitumen from oil shale by low temperature pyrolysis in an autoclave. – Oil Shale, vol 24, no 4, p 535-546.

III. Johannes. I., Zaidentsal, A. 2008. Kinetics of low-temperature retorting of kukersite oil shale. – Oil Shale, vol 25, no 4, p 412-425.

IV. Johannes, I., Tiikma, L., Zaidentsal, A., Luik, L. 2009. Kinetics of kukersite low-temperature pyrolysis in autoclaves. – Journal of Analytical and Applied Pyrolysis, vol 85, p 508-513.

V. Johannes, I., Tiikma, L., Zaidentsal, A. 2010. Comparison of the thermobituminization kinetics of Baltic oil shale in open retorts and autoclaves. Oil Shale, vol 27, no 7, p 17-25.

THE AUTHOR'S CONTRIBUTION TO PUBLICATION

Article I: the experimental part, discussion of the results and writing of the paper were done by the author.

Articles II-V: the papers reflect the investigations in the frames of projects SF 014722s06, SF 0140028s09, ETF 7292 where the author took part as the principal investigator. The author's individual share was working through and revision of the corresponding literature, and practical participation with the co-authors in the huge experimental part of the work, in discussion of the results, in their mathematical modelling and formation of the manuscripts.

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1 LITERATURE REVIEW

1.1 Kukersite oil shale

1.1.1 Kerogen – the organic substance

Kerogen is an amorphous substance of dark to light brown color. It forms small clots of 20-150 μm dimensions inside oil shale material. Kerogen is a high-molecular heteroatomic substance of complicated structure. Only a small part of kerogen is extractable with solvents at room temperature and normal pressure. Negligible solubility of kerogen gives rise to the assumption that its macromolecules are of three-dimensional structure and relatively large size [2-5].

Kerogen of kukersite is a macromolecular substance of natural cross-linked polymer type of practically homogenous composition. According to [6] kerogen of kukersite has highly aliphatic structure and its main structural element is a long straight chain with odd number of carbon atoms (fragments of saturated and unsaturated fat acids of the source organic matter). The presence of polycarbonyl structures in the form of cycles is also established. The main bridges connecting the structural units of kerogen in the macromolecule are ester and ether groups [7].

All that characteristic features of kukersite kerogen determine its specific behavior in the thermal decomposition process - relatively poor thermal stability of its macromolecule, high reactivity of primary products of decomposition and high probability of their aromatization [8].

According to the last studies by NMR [9], macromolecule of kerogen is highly aliphatic, with the ratio of aliphatic to aromatic carbons *ca* 4–5. It was given the model of kukersite kerogen with the empirical formula $C_{421}H_{638}O_{44}S_4NCl$, according to which the elemental composition of kerogen should be, %: C – 76.9; H – 9.7; O – 10.7; S – 1.9; N – 0.2; Cl – 0.5, and the atomic ratio of H/C 1.515. Kukersite's kerogen contains less than 1% natural soluble bitumens. At that, the chemical composition of kerogen is supprisingly stable in all its deposits as far the differences do not overcome analysis errors.

At laboratory standard retorting the organic matter (OM) is distributed between 65.6% oil, 10.7% gases, 18.3% semicoke and 5.4% pyrolytic water [10].

1.1.2 Mineral part of kukersite oil shale

The mineral part of oil shale prevails over the organic part. The composition of the mineral part is diverse. The main rock forming components are argillaceous, aleuric-argillaceous, carbonaceous, argillaceous-carbonaceous, siliceous and siliceous-argillaceous material of detrital-pelitomorphic texture [11]. The main mineral groups are carbonates, silicates and aluminum silicates, quartz, and sulfides. Occasionally are present different sulfates, phosphates, sometimes halides, amorphous silica, and other minerals [12-14]. An example of the kukersite mineral composition published by Dilaktorsky [15] is presented in Table 2.

Table 2. Mineral composition of the inorganic part of kukersite oil shale [15]

Mineral	Chemical Formula	Content, %
Tiff	$CaCO_3$	58.2
Dolomite	$CaMg(CO_3)_2$	12.6
Quartz	SiO_2	11.8
Pyrite	FeS_2	3.4
Mica	$K_2O\cdot Al_2O_3 \cdot 6SiO_2$	4.0
Hydromica	$K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$	10.0

1.2 Decomposition of oil shale

A number of experimental studies on the decomposition process of kukersite oil shale have been carried out. Different schemes of decomposition have been proposed but what all of them have in common is the sequence of intermediate stages of kukersite oil shale conversion into end products [16-23].

Kogerman [24] presented the pyrolysis of kukersite as a range of sequential processes as follows:

Below 150 °C – separation of water and occludive gases,

170–180 °C – beginning of kerogen destruction,

320–340 °C – active destruction of kerogen, beginning of gas evolution in large quantities,

380–390 °C – beginning of destruction of polymerization products forming liquid products (oil),

415–420 °C – endothermic reactions of coke formation.

According to Ya. I. Khisin [25] decomposition of kukersite oil shale starts at 170-180 °C, when changes in oil shale appearance become apparent but no significant quantities of vapor and gas products are emitted. In the process of thermal decomposition of kukersite oil shale first is formed pyrogenetic water at 270-290 °C, then gas at 325-350 °C and oil at the same temperature as gas but with a certain time lag. In that temperature range the organic substance of kukersite oil shale melts with formation of soluble in benzene pyrobitumen (this term is used by Ya. I. Khisin for thermobitumen). Besides, Khisin states that:

1) about 80% of pyrogenic water is evolved before the beginning of bitumen formation, while only 14-15% of total oil is evolved to that time;

2) a significant part of gas evolves at the beginning of pyrobitumen (thermobituimen) formation. After that gas evolution slows down and increases again alongside the decomposition of thermobitumen;

3) evolution of oil, which accompanies pyrobitumen formation, is slow at the beginning of the process but then outpaces the rate of pyrobitumen formation.

K. Luts views the first stage of kukersite oil shale decomposition as an independent process of deoxidation of kerogen with formation of “asphalt”, which is cracked into oil, gas, and coke. Oil is subjected to consequent cracking into light fractions and coke; the light product might also be completely cracked to gas [26, 27].

A. F. Dobryanski defines the process of kukersite oil shale thermal decomposition [28] as a consequent transformation of heavy products to the light ones via strictly defined stages:

- Deoxidation is the first visible stage of transformation, which is characterized by kerogen stabilization accompanied by intermolecular regroupings;
- Formation of pyrobitumen in the course of thermolysis of stabilized kerogen. The process is accompanied by evolution of additional water and leads to the formation of the first modification of liquid soluble bitumen (thermobitumen), which consists of molecules of various size;
- Cracking of thermobitumen with formation of oil. In the course of the further transformations the second modification of bitumen is formed and light oil is evolved. The transformation of thermobitumen is accompanied by evolution of middle oil fractions and formation of the first modification of “coke”. Thermal decomposition of “coke” results in formation of heavy oil and stable solid residue.

1.3 Physical and chemical transformations taking place at the stage of thermobitumen formation

Before reviewing various processes taking place at thermobitumen formation, it is advisable to have a look at physical changes of kukersite oil shale at 350-410 °C.

After oil shale is heated up to 350-360 °C, gradual and accelerating with rising temperature softening of oil shale is observed. Oil shale passes into the so-called plastic state, which is equivalent to bituminization in chemical sense. Oil shale plasticity reaches its maximum and then diminishes as temperature rises. Plasticity disappears completely at about 420 °C. Thermal conductivity of oil shale in the plastic state is lower than that in the solid state. Hence, temperature rise inside the shale oil lump is retarded during the heating process and, as a result, the transition from the plastic to the solid state progresses at a slower rate. Gas evolution from inside the lump is retarded too [29].

Baltic shale oil exhibits plasticity at the lowest temperature and is softened the most in comparison with other solid fuels [30].

Plasticity is the physical reflection of the chemical restructuring of oil shale at the initial stage, when cracked at the first stage kerogen has not lost the most part of the liquid organic matter. That liquid material destroys the solid structure of oil shale and leaves the mineral components in the state of suspension.

It is also worth mentioning the influence of heating rate and particle size on the plastic state of oil shale. The more fine is the particle, the higher degree of plasticity it gets. The temperature region of the existence of plastic state is widening and shifting to the higher temperatures at the heating rate of 10 °C per min [31]. The first stage of the process is inevitably connected with the second one, characterized by formation of thermobitumen and evolution of volatiles.

The series of the decomposition processes of the depolymerization products at the second stage is determined to a great degree by the specific features of the chemical structure of the organic matter of oil shale. At first takes place the breakage of very unstable oxygen-oxygen bonds (the so-called oxygen bridges, whose amount in kerogen may be large enough). Then sulfur separates. After that the breakage of weakened bonds at carbon atoms situated in the beta-position to the conjugated and normal double bond takes place. Further decomposition proceeds in regions with conjugated carbonyl groups, ester groups, and, at last, links of relatively long, branched in the first place, aliphatic saturated chains are being ruptured [6].

1.4 Secondary processes at thermal decomposition of kerogen macromolecule

The specific features of kerogen chemical nature determine the inevitability of singular secondary processes taking place at the stage of thermobitumen formation. In the first place, it is the closure into unsaturated cycles of remnants of destroyed structures with conjugated double bonds, as well as active interaction of fragments with “naked” functional groups, which are characterized by high reactivity [32, 33].

The main result of those secondary condensation reactions is formation of thermostable molecules, which accumulate in thermobitumen. At the same time the composition and properties of volatile substances, which evolve in the period of active bituminization, cannot remain unchanged in the process to the very end.

More than that, the share of the “primary” product (light fragments formed directly during the breakdown of depolymerization products of kerogen) should be rather small, when compared with the total sum of volatile products, even at that stage. Besides the formation of thermobitumen, the secondary processes of destruction and condensation of its molecules with the formation of the “secondary” volatiles as well as of thermostabilized residue of ordered aromatic structure are continuously taking place.

The indirect confirmation of that are data obtained by Kask on the changes in composition of thermobitumen in the course of the process. Gubergritz [6] gives the direct confirmation by additional handling of experimental data of Aarna and Kask [34, 35]. The results presented in the Table 3 show active and relatively regular increase in time of phenol concentration, redistribution of functional groups with the decline of concentration of less stable carbonyl functions, and progressive rise in the degree of unsaturation of oil molecules {$n_c = 101 - 600[H + 0.08125(O + S + N)]/C$ [6]}. That is the result of development of not only the processes of destructive nature but also of the secondary reactions. The data in Table 4 below show that the share of the "secondary" product in the interval of 0.6 to 5 h from the beginning of the process is 53% from the total amount of evolved oil. During the last 1.5 h the percentage reaches 73.6%. Correspondingly, the amount of thermobitumen formed in that process is not 70% of the source kerogen but about 78% because more than 10% of themobitumen has been decomposed to the moment.

Table 3. Composition and yield of volatile products of oil shale decomposition [34]

Items	Time intervals, h						
	0-0.6	0.6-1.5	1.5-3.5	3.5-7	7-12	12-24	24-48
Total yield of volatiles from the start of the experiment (on kerogen basis), wt %	10.03	18.31	26.68	33.51	40.78	52.48	62.95
Oil yield at the time interval, g/100 g	5.04	6.52	7.25	5.80	5.94	10.05	9.03
Oil yield based on the sum of volatiles, wt %	50.1	78.7	86.6	85.0	81.8	86.0	86.1
Degree of oil unsaturation, n_c	12.7	14.1	15.0	16.3	16.5	16.9	18.5
Atom ratio 100H/C	168	166	166	166	166	164	163
Atom ratio 100(O+S)/C	7.50	6.23	5.46	5.34	4.95	4.47	4.00
Content of phenols in oil, wt %	19.7	26.7	28.9	28.1	27.7	28.2	26.3
Content of hydroxyl group, g-equiv./100 g	0.176	0.266	0.271	0.197	0.199	0.177	0.157
Content of carbonyl group, g-equiv./100 g	0.175	0.03	0.066	0.056	0.048	0.039	0.032
Gas yield based on the sum of volatiles, wt %	27.0	28.7	10.2	12.0	16.4	11.5	11.9
Degree of gas saturation	0.437	0.439	0.461	...	0.121	...	...

Table 4. Products' yield in isothermal decomposition of kerogen (g/100 g) at 360 °C [6]

Interval, h	Yield during the interval, %		n_c of oil	Distribution of oil		Amount of decomposed thermobitumen, not less	Actual yield of thermobitumen, not less	Share of decomposed thermobitumen based on the total amount, %	Share of "secondary" product in oil, %
	TB	Oil		Primary	Secondary				
0-0.6	19.5	5.0	12.7	5.0	-	-	19.5	-	-
0.6-1.5	20.0	6.6	14.1	4.0	2.6	2.6	22.6	11.5	39.4
1.5-3.5	29.0	7.2	15.0	2.9	4.3	4.3	33.3	14.8	60.0
3.5-5.0	1.5	1.9	15.8	0.5	1.4	1.4	2.9	48.3	73.6

According to Karavaev [36], it is not possible to determine unmistakably the quantitative yield of thermobitumen by direct measurements even in the first period without considering the results of the secondary reactions. That complicates the attempts to describe analytically the kinetics of kerogen decomposition in that period. The existing literature data confirm the revealed tendency for changes in the yield and composition of volatiles and thermobitumen under the influence of the secondary reactions.

Oil evolved in the period of low-temperature isothermal decomposition of oil shale during the first 0.6 h is most similar to the primary one and is distinguished by the high content of oxygen and sulfur, which is similar to that of thermobitumen. The oil also has the lowest degree of dehydrogenation and unsaturation, low phenol content, and the highest ratio of concentrations of carbonyl and hydroxyl groups in oil [34].

The specific features of low-temperature isothermal decomposition of kukersite are determined by the peculiar physical conditions of the process, which has impact on the composition of volatiles. During the whole heating period at low temperature region only relatively light products are being distilled and evolved from the system. Not-distilled fragments are partly subjected to destruction to the degree, which is determined by the low temperature potential of the system, and partly they interact and become the source of larger thermostabilized molecules.

The energy level of the system is not sufficient for destruction of the thermostabilized molecules and for their distillation. Though the rate of the secondary reactions at low temperature is relatively low (it is assumed by the analogy with alkanes that the rate is substantially lower than the rate of cracking reactions below 500 °C), the quantity of products taking part in the secondary reactions is quite considerable [37].

The following low-temperature transformations of such a product can be only of the intermolecular rearrangement type with redistribution of hydrogen and separation of small unsaturated fragments or by direct dehydrogenation of the non-volatile part and interaction of evolved hydrogen with volatile olefins [38]. As a result a certain additional quantity of light volatile products of saturated character is formed and further unsaturation and thermostabilization of condensed systems low in hydrogen takes place. N. I. Zelenin and K. B. Chernyshova pointed to similar transformations in their research [39].

The degree of unsaturation of the hydrocarbon part of gas declines from 0.44-0.46 to 0.12 with time. Summary content of olefins in gas drops to 4.85%, while that of saturated hydrocarbons increases up to 66.7%. Intensive formation of the latter is not possible without dehydrogenation and unsaturation of the heavier non-volatile products of decomposition of kerogen [34].

1.5 Stage of formation of thermobitumen in the general scheme of kukersite oil shale decomposition

In this work the intermediate stage of thermobitumenization was of interest.

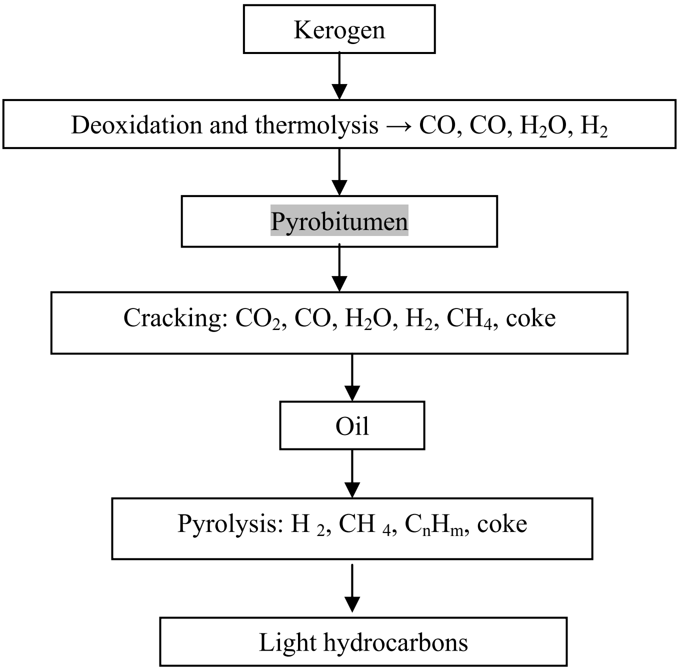
In accordance with rising and declining yield of thermobitumen, the themobituminization stage is possible to formally divide into two periods: the formation and decomposition of thermobitumen [40, 41].

K. Luts [42] has stated that at the formation of thermobitumen two processes proceed simultaneously: the first one is the formation of thermobitumen itself, and the second is the subsequent decomposition of thermobitumen. The rate of the first process is faster than that of the second one because thermobitumen is more stable than kerogen in relation to temperature. As thermobitumen is accumulating, more oil is formed but the amount of thermobitumen is diminishing in accordance with the rate law.

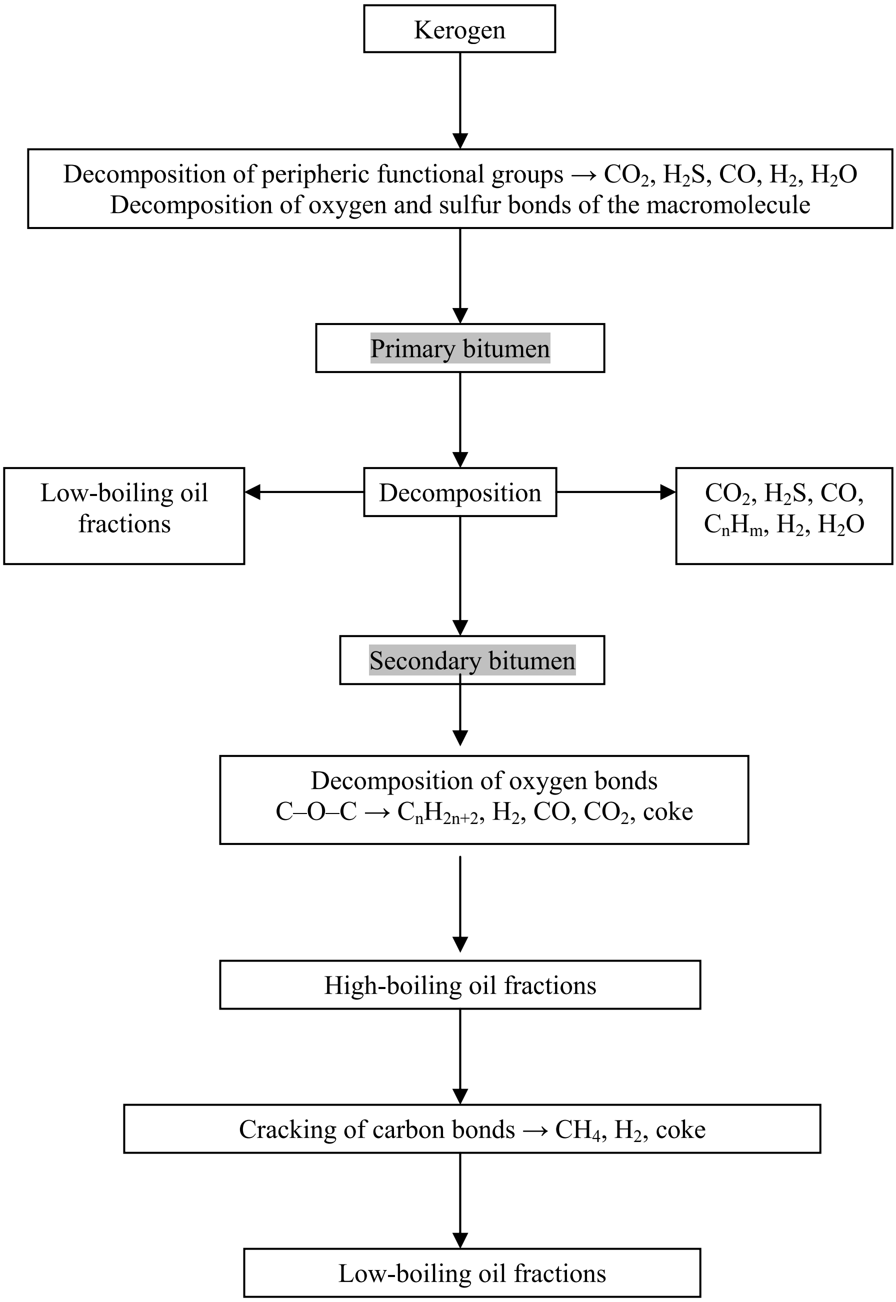
The validity of Luts's statement is confirmed by the experiments by N. V. Popov and V. P. Tsybasov even in the case of constant temperature.

The conditions of thermal decomposition (temperature, heating rate, size of shale oil piece, etc) obviously determine not only the final results but also the mechanism of the process. According to schemes proposed by K. Luts and A. Aarna (schemes I and II), decmposition is viewed as a sequential transition of kerogen into thermobitumen and thermobitumen into oil and coke. Scheme II is based on a vast experimental data on isothermal decomposition of oil shale, mostly at low temperatures [44]. The formation of decomposition products under those conditions is characterized by the following diagrams (Fig. 1).

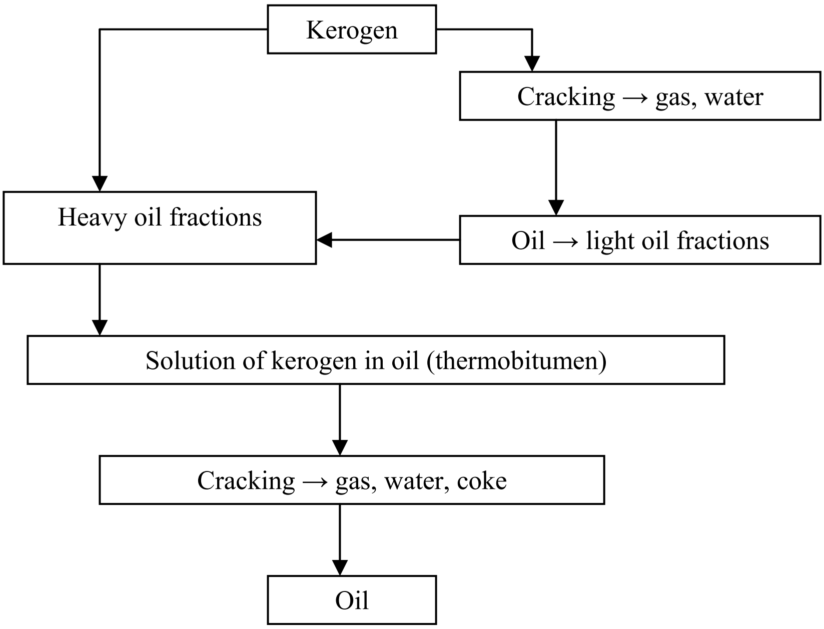
I. According to K. Luts [42] and A. F. Dobryansky [2] kerogen passes the pyrobitumen phase and subsequent formation of gas, coke and oil:



II. According to A. Ya. Aarna [44] formation of two subsequent forms of bitumen takes place:



III. According to A. K. Mityurev thermobitumen is solution of kerogen in oil [45]:



IV. According to A. Ya. Aarna and E. T. Lippmaa parallel decomposition of the kerogen, kerogen’, thermobitumen’, thermobitumen’’, and coke’ take place [46]:

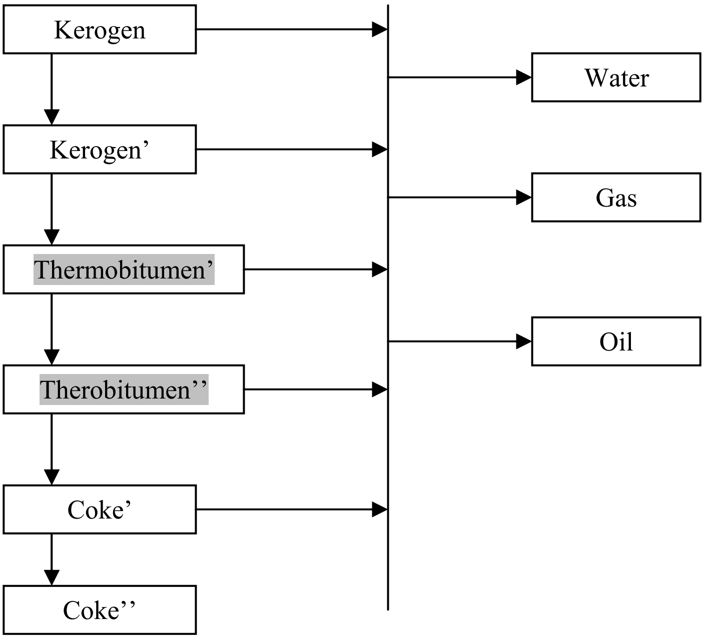


Fig. 1. Schemes of oil shale decomposition.

According to data of A. Ya. Aarna and Yu. T. Rikken [47] structural changes in kerogen take place at the early stage of decomposition, when the yield of volatile substances is 2-5%. Breaking of oxygen bonds and formation of new carbon bonds characterize those changes.

Experimental data on isothermal decomposition of oil shale (scheme III proposed by Mityurev [45]) are explained in another way. In accordance with that scheme, kerogen decomposes into oil, gas and water simultaneously, while the light oil is distilled and the heavy oil remains in the liquid phase and dissolves kerogen. That solution of variable concentration is thermobitumen.

According to scheme IV of thermal decomposition all volatile products, including oil, are primary products of decomposition [46].

All the schemes in Fig. 1 have been too complicated for estimation of the current yields of the variety of mean products and for estimation of rate factors for the transformations.

1.6 Yield, composition and properties of thermobitumen

After review of schemes of kukersite oil shale decomposition and of the secondary processes taking place at the stage of thermobitumen formation, the main properties and specific features of thermobitumen are reviewed.

Thermobitumen is a mixture of various substances, which are not able to evolve from the system [46]. The liquid state at the decomposition temperature and solubility in benzene and benzene-ethanol mixture are the most defined and constant properties of thermobitumen. The element and group composition of thermobitumen are constantly changing with time and temperature.

Independent of the decomposition temperature, the first portion of thermobitumen differs in composition from the source kerogen. It contains substantially less heteroatoms, but the relative dehydrogenation process is not very noticeable. Somewhat higher share of volatile substances in the beginning of the first period in comparison with the following portions is explained by relatively uneven distribution of temperature in the oil shale layer and local overheating of some particles situated at the periphery [6].

Kask, Aarna and Lippmaa, Schulman [20, 46, 54], and others have studied the formation of TB in open systems, only Kogerman and Kopwillem [50] and Karavayev [52] have carried out the process in autoclaves. Experiments were made varying heating time and pyrolysis temperature to study their influence on the yield and composition of oil and TB. Kogerman and Kopwillem [50] have concluded that the yield of destruction water under the pressure 100 at is practically the same as that in open retorts and does not depend on pyrolysis atmosphere. So, kerogen should include unstable formations, possible aliphatic compounds, which transform to more stable structures emitting equal quantity of water which does not depend on pyrolysis atmosphere.

Kask and Aarna studied the yield and composition of products depending on pyrolysis conditions in Fischer retort [20, 35, 20, 21], The data obtained are given in Table 5.

Table 5. Yield and elemental composition of products obtained from kukersite [35, 20]

Species	Yield, % TB/OM	Elemental composition, %				H/C	Molec. mass
		C	H	S	O+N		
Initial concentrated shale, (87.25% OM from shale)		82.1	10.63	0.75	6.5	1.55	
TB 275 °C, 456 h	17.9	83.0	10.1	0.50	6.7	1.46	710
TB 300 °C, 387 h	69.8	85.1	8.77	0.32	5.8	1.24	1300
TB 340 °C, 12 h	59.8	83.8	9.78	0.52	5.9	1.40	1240
TB 360 °C, 4 h	63.8	83.6	9.56	0.50	6.3	1.37	790
TB 380 °C, 4 h	35.6	85.3	0.535	0.53	5.3	1.25	651
Organic residue insoluble in benzene (360 °C, 5 h)	1.1	83.3	10.43	0.35	5.9	1.50	

Schulman [54] has reported that the maximum yield of TB is obtained at the temperature range 390–395 °C, and TB is made up to 55–57% of organic matter irrespective of oil shale quality. At these temperatures carbon content of organic solid residue (remained after extraction of TB with a mixture of ethanol-benzene) is of the minimum value.

Aarna, Lippmaa [46, 53], Luts [51], and Kask [35] have shown that TB contains less hydrogen than initial kerogen.

According to Kask and Mihkelson [56], the formula of TB is $C_{54.8}H_{69.4}O_3$ with atomic ratio of H/C 1.27 only. Thus, along with the loss of oxygen with water formation, and that of sulfur with H_2S, also the loss of hydrogen occurs in the TB formation process. TB, formed in an open system under atmospheric pressure is a new formation which contains less both oxygen and hydrogen.

At the first stage, the loss of hydrogen takes place due to emission of water and hydrogen sulfide. The main part of oxygen leaves with carbon dioxide. The oxygen, which is more strongly attached to carbon, remains in solid residue. The higher is the destruction degree, the less is the hydrogen content in TB, and the more stable is the oxygen remained. Decreasing of hydrogen content in TB, compared with that in kerogen, is more obvious if to take into account that at the first stage of thermal stabilization of OM the carbon is lost only as carbon dioxide.

Karavayev and Wener studied TB formation in an autoclave at the temperature range 350–360 °C and residence time 6–8 hours [52]. The yield of TB soluble in benzene was 71.3%, on kerogen basis, the yield of gas over 4%, and its composition was as follows: CO_2 + H_2O (41.5%), C_nH_{2n} (2.0%), CO

(1.8%), H_2 (13.2%), C_nH_{2n+2} (41.5%). So, the gas consisted mainly of saturated hydrocarbons and hydrogen. The oil, which in autoclaves remains together with TB, may be enriched with hydrogen because it is a product of continual destruction and intermolecular reforming of TB. At the same time, a part of primary products of complicated structure should lose the hydrogen and form an insoluble residue. Atomic H/C ratio in the process of TB formation was as follows: initial kerogen 1.46, TB 1.28, oil soluble in alcohol 1.35, TB insoluble in alcohol 1.14.

In [20] and [35] Kask showed that TB is miscellaneous consisting of various molecules which could be divided by solvents into fractions of different molecular mass and properties. It has been proved [20] that when TB is subjected to carbonization, the yield of oil is less than by direct semicoking of oil shale. For example, the yield of oil from kerogen at retorting of the initial shale was 66.0%, but at the two-stage carbonization of oil shale the yield of oil was only 56.9% (including 17.5% in the process of TB formation, 36.2% from retorting of separated TB and 3.2% from semicoking of the residue insoluble in benzene). The total yield of the solid residue increased from 17.9 to 25.6%, respectively. At the same time, the quantity of gas was practically constant (10.3 and 10.7%). The more complete was the low-temperature destruction of kerogen to TB, the more structures in TB appeared to be able to condensate and coke during further carbonization, and the less the material remains which could be destructed to volatiles.

TB obtained in an open system has been characterized by molecular mass, elemental composition [49–56], solvent fractionation [35, 58], infrared spectroscopy [57, 58], and NMR spectroscopy [59]. It was shown [49–56] that molecular mass and elemental composition of TB depend on bituminization conditions. In the composition of TB were found various polycyclic compounds of different molecular mass (average 400–500) connected together by oxygen links [35]. The molecule mass of TB obtained in autoclave was about 350 [9]. At the first stage of bituminization the content of carbon in TB is approximately 82% and that of hydrogen about 10%. At higher temperatures and longer residence time the content of carbon increases and that of hydrogen decreases. Under more rigid conditions of bituminization, as a result of hydrogen redividing, a part of TB becomes so poor in hydrogen that forms insoluble in benzene coke together with mineral part. The content of oxygen in TB is about 7%, and it does not depend on temperature but depends on residence time. At a longer process the oxygen content decreases, reaching 5%. An example of the oxygen distribution is presented in Table 6.

Table 6. The oxygen distribution in TB [56]

Item	%
Carboxyl groups	1.0
Hydroxyl groups	47.7
Carbonyl groups	13.3
Ether groups	21.0
Non-defined function	17.0

The formation of TB as an intermediate pyrolysis state in the temperature range 375–425 °C has been described also to be typical of USA oil shale [60]. Its properties (hydrogen-to-carbon ratios, carbon aromaticity, molecular mass) vary with time and temperature of pyrolysis and depend on the original kerogen structure. Comparative characterization of the Green River shale oil, heavy petroleum oil and oil sand bitumen based on their polarity is given in [61]. Shale oil contains some olefins produced by cracking of hydrocarbon chain. IR spectra show the presence of C=O, –NH_2, –OH groups. The presence of asphaltenes is also asserted.

So, TB is a chemically active intermediate product which yield passes a maximum under the optimum temperature and duration. Composition of TB depends on the pyrolysis conditions and changes at storage. Kinetics of TB formation and secondary cracking has been scarcely studied.

1.7 Kinetics basic principles

Many transformations may occur when a solid sample is heated – melting, sublimation, polymorphic transformation, desolvation or degradation [62]. A simple decomposition reaction follows the scheme

$$\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C}$$

The general form for thermal decomposition of oil shale organic matter would obey the above scheme because it involves the decomposition of oil shale organic matter to produce oil and gas.

The rate of the above reaction is proportional to the current concentration (amount or fraction) of the reactant according to:

$$Rate \propto [A]^n \text{ or } ([\mathrm{A}]_0 - [\mathrm{B}] - [\mathrm{C}])^n \qquad (1)$$

where, A_0 is the initial concentration of A, and n, is the reaction order.

The rate of a reaction is usually studied by following the decrease in reactant concentration or increase in product concentration. Therefore, the reaction rate law becomes:

$$Rate = -d[\mathrm{A}]/dt = d[\mathrm{B}]/dt = d[\mathrm{C}]/dt = k[\mathrm{A}]^{\mathrm{n}} = k([\mathrm{A}]_0 - [\mathrm{B}] - [\mathrm{C}])^n \qquad (2)$$

Where, k is the reaction rate factor. If the evolved gas (C) is efficiently flushed such that [C] ≈ 0, the above equation reduces to:

$$Rate = -d[\mathrm{A}]/dt = d[\mathrm{B}]/dt = k[\mathrm{A}]^{\mathrm{n}} = k([\mathrm{A}]_0 - [\mathrm{B}])^n \quad (3)$$

If the reaction is an elementary unimolecular (n=1) first order reaction, the rate law would be (following only the reactant concentration):

$$Rate = -d[\mathrm{A}]/dt = -k[\mathrm{A}] \quad (4)$$

which upon integration becomes:

$$-\ln [\mathrm{A}]/[\mathrm{A}_0] = kt \quad (5)$$

Pyrolysis kinetics can be studied with thermal analytical methods [62, 63] by measuring a sample mass as it is heated or held at a constant temperature. Due to weight loss during the decomposition, the weight loss data are converted to a normalized form called conversion fraction (α). The conversion fraction ranges from 0 and 1 and is a measure of reaction progress as a function of time or temperature.

There are two approaches utilized to obtain kinetic data – isothermal and nonisothermal methods. For isothermal methods, reactions are followed at several constant temperatures while nonisothermal (dynamic) methods involve heating samples at one or more constant heating rates (usually linear) and following the course of the reaction. Isothermal methods are similar to those used in homogenous kinetics to produce α-time data compared to concentration-time data in homogenous kinetics. On the other hand, nonisothermal analysis produces α-temperature data.

In isothermal thermogravimetric analysis at any time

$$\alpha = (m_0 - m_{\mathrm{t}})/(m_0 - m_\infty) \quad (6)$$

where m_0 is the initial sample weight, m_{t} is the sample weight at time, t, and m∞ is the final sample weight.

In nonisothermal conversion the fraction (α) is expressed as follows:

$$\alpha = (m_0 - m_{\mathrm{T}})/(m_0 - m_\infty) \quad (7)$$

where, m_{T} is the sample weight at temperature T.

Using conversion fraction, the rate expressions defined in Eqs. (4) and (5) can be written as:

$$\mathrm{d}\alpha/dt = k\,(1 - \alpha) \quad (8)$$

$$-\ln(1-\alpha) = kt \quad (9)$$

According to the schemes brought in Fig. 1, the oil shale thermal decomposition is a complicated process where the parallel–consequent decomposition of organic matter into gaseous, liquid and solid products takes place. Every reaction in the complex schemes can be generally expressed as:

$$d\alpha/dt = k\,f(\alpha) \tag{10}$$

$$g(\alpha) = k\,t \tag{11}$$

where, $f(\alpha)$ is the differential reaction model and $g(\alpha)$ is the integral reaction model.

The temperature dependence of the every rate factor (k) is described by the Arrhenius equation [64]:

$$k = A\,e^{-Ea/RT} \tag{12}$$

where, A is the pre-exponential (frequency) factor, E_a is activation energy, T is absolute temperature and R is the absolute gas constant. Substitution of Eq. (12) into Eqs. (10) and (11) gives:

$$d\alpha/dt = A\,e^{-Ea/RT} f(\alpha) \tag{13}$$

and

$$g(\alpha) = A\,e^{-Ea/RT}\,t \tag{14}$$

The traditional thermogravmetric investigation of the thermobituminization kinetics is impossible because TB is nonvolatile and remains in the cubic residue.

Compilation for kerogen thermobituminization of a satisfactory decomposition scheme, creation of the according kinetic models, and estimation of the rate factors and kinetic constants for the limiting reactions in open and closed assays are the targets of this work.

2 EXPERIMENTAL AND METHODS

The main part of the experimental study of the doctoral work was conducted in the former Institute of Oil shale of Tallinn Technical University located in two places: using open Fischer retorts – in Kohtla –Järve, and using autoclaves in Tallinn. The autoclavic study was supported by Estonian Ministry of Education and Research by financiering the projects SF 0142722s06 and SF0140028s09 and supervised by H. Luik, and by Grant 7292 of Estonian Science Foundation

2.1 Autoclave process

Investigation of the autoclavic thermobituminization was necessary as the basis for understanding of the sub-and supercritical dissolution processes of kerogen being the main objects of the projects above. With the aim to obtain sufficient quantity of organic decomposition products for analysis, the initial natural "fatty" kukersite consisting 50.5% of kerogen was applied in all the subprojects carried out using autoclaves.

In the experiments described in this thesis 4.0 g of powdered and dried kukersite samples were heated in 20 ml microautoclaves. The autoclaves were weight, and placed into a muffle oven with five nominal temperatures in the range 340–380 °C. After definite residence times between 45 and 1200 min 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, marked as TBO) was removed from the solid residue in a Soxhlet extractor with benzene. Noteworthy is that unlike retorting experiments (P. 2.2) alcohol was not added into the solvent because there was found no effect in case of TBO when the traditional mix of the solvents, benzene + alcohol was applied. Mass of the solid residue 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 at 800–850 °C from the acid-treated and dried residues. Estimation of the exact mass of the target product, TBO, was to some extent problematic because the lighter fractions of the oil formed could be partly lost at evaporation of the solvent applied, or the solvent bound with TBO could not be entirely removed. 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. According to the second approach, the yield of TBO formed was found subtracting the mass of gas and organic solid residue from the initial mass of kerogen. In this case, the yield of TBO could be overestimated due to inclusion of the decomposition water, or underestimated when the yields of gas or solid residue were overestimated. That is the reason why the both results of TBO, obtained directly by evaporation of the benzene extract and as the difference, are given in the tables, figures and have been applied in calculations of the rate coefficients.

The elemental composition of the TBO was estimated with “Costech” analyzer. The functional group composition was investigated by FTIR-spectroscopy “Interspec 2020”. The group composition was determined by thin-layer chromatography (TLC). The content of maltenes in TBO was found by exhaustive extraction of TB with n-hexane in Soxhlet extractor.

2.2 Retorting

The experiments on shale bituminization were performed in an aluminum Fischer retort. The ordinary 32.3% kukersite was used in the retorting experiments. A shale sample was heated in the Fischer retort according to the ISO 674-74 standard. The method consisted in the following: a fuel sample was heated in an aluminum retort to a specified temperature in the range from 370 to 410 °C; the isothermal exposure time was 20–60 min. The rates of heating to 220 °C, from 220 to 310 °C, from 310 to 370 °C, and from 370 to 410 °C were 20, 9, 7, and 6 °C/min, respectively. The products of decomposition were collected in a receiver cooled with water; tar and water condensed, whereas gaseous substances released were vented to the atmosphere through a wet gas meter. The semicoke residue in the retort was weighed. The receiver flask was weighed together with the condensation products. The weight of water in the receiver was determined by volumetry (distillation with toluene), and the weight of tar was calculated by difference. The total weight of water in the receiver involved the sample moisture and the pyrogenetic water formed by decomposition of the fuel. The gas yield was determined as the difference between the initial sample weight and the total yield of semicoke, tar, and water. The results of analysis were calculated on a dry fuel basis and OM basis. The shale moisture was determined in accordance with the EVS 668:1996 standard. A weighing bottle with a sample of about 1 g was dried for 5 min in a drying oven preheated from 155 to 160 °C. Thereafter, the samples were cooled for 2–3 min and placed in a desiccator; 20 min later, the samples were weighed. As a result, the shale sample weight decreased. Analytical moisture was calculated from the equation

$W = 100 - (M_1/M)\cdot 100$ wt %,

where M_1 is the sample weight after the analysis, and M is the initial sample weight.

The ash content of shale was determined according to EVS 669:1996. A sample of about 1 g placed in a boat was arranged in a muffle furnace at room temperature. The furnace temperature was increased to 250 °C for 30 min, to 500 °C for another 30 min, and then to 815±15 °C for 60 min. After the heating, the boat was removed from the muffle furnace, and the sample was cooled to room temperature in a desiccator and weighed. The results of analysis were calculated by the equation $A=(M_1/M)\cdot 100$ %.

To experimentally study the formation of thermal bitumen from kukersite in a Fischer retort, we determined the organic matter of shale to be 32.3%; the yield of tar was 24%. A Costech 4010 analyzer was used to perform elemental analysis.

Oil shale with the following technical characteristics was used in the experiments: moisture content, 0.6%; shale ash content, 48.6% (on a dry matter basis); shale sulfur content, 1.2%. The product yields of shale semicoking in a Fischer retort were the following: tar, 21%, semicoke, 72.3%; pyrogenic water, 1.6%; gas and losses, 5.1%.

The extraction of thermal bitumen from the solid residue obtained in a Fischer assay with an alcohol–benzene mixture was performed in a Soxhlet apparatus. The extraction was continued until the solvent in the extractor became colorless. Thereafter, the alcohol–benzene mixture was distilled from the dissolved thermal bitumen in a glycerol bath and the thermal bitumen sample was dried to constant weight in a vacuum oven. The yield of thermal bitumen was calculated with reference to the concentration of the organic matter of shale. The concentration of malthenes was determined in accordance with the EVS 652:1994 standard. Pentane was used as an extractant for the extraction of malthenes from thermal bitumen. The percentage of malthenes was calculated from the equation $M_m = 100 - (M_1/M)\cdot 100$ wt %, where M_1 is the sample weight on a filter after extraction and drying to constant weight, and M is the total sample weight. The IR spectra were measured on an Interspec 2020 FTIR spectrometer.

3 RESULTS AND DISCUSSION

3.1 Autoclave process

(Papers II and IV in APPENDIX A)

3.1.1 The dependence of TBO yield on bituminization temperature and residence time

The thermobituminization experiments with kukersite in autoclave were carried out at different temperatures (340-380 °C) and residence times from 20 min to 10 hours. The experimentally estimated yields of the products in percentages from organic matter at various pyrolysis times and temperatures are given in Table 7.

The results are given in Figure 2. It demonstrates that pyrolysis process of kukersite in autoclaves consists of three stages:

1) Heating of shale till plastic condition and formation of TBO and gas from OM. The quantities of TBO and gases increase until the maximum yield of TBO. At shorter residence time organic solid residue consists of undestructed OM and TBO with high-molecular mass insoluble in benzene;

2) An equilibrium between formation and cleavage of TBO. The yield of TBO is maximum (up to 90% from OM of the initial shale) and practically constant. The quantity of gas is growing and organic solid residue is minimal. The lower the temperature, the longer the steady-state stage.

3) Further destruction of obtained TBO to gas, coke and oil. The oil formed makes TBO more easily extractable from the solid residue but a part of OM is lost with coke. The length of these stages depends on temperature and is shorter at higher temperatures.

Table 7. Distribution of kukersite kerogen between pyrolysis products TBO (x_1), solid residue ($y + x_3$), and gas (x_2) in time (%)

Time (min)	x_1		$y + x_3$		x_2
	By weight	From difference[a]	By weight	From difference[b]	By weight
Nominal temperature 340 °C					
180	27.07	27.30	65.12	65.35	7.58
360	77.42	72.77	17.82	13.17	9.415
480	81.45	77.31	12.95	8.80	9.74
1200	87.82	85.41	2.67	4.52	9.38
Nominal temperature 350 °C					
150	57.84	58.57	33.20	34.70	7.91
240	82.34	75.02	15.86	9.37	8.93
360	87.27	85.61	4.70	3.83	9.58
600	80.66	79.19	8.77	8.10	11.88
Nominal temperature 360 °C					
93	47.32	38.82	54.92	46.42	6.27
120	81.61	49.04	42.59	10.10	8.39
180	85.46	78.54	11.65	4.721	9.82
210	89.31	84.73	6.40	1.814	8.88
240	79.43	80.67	8.469	9.877	10.69
300	78.00	77.32	12.50	11.81	10.61
420	77.01	74.22	12.56	9.78	13.21
Nominal temperature 370 °C					
10	1.21	2.29	96.81	97.89	0.90
20	2.15	4.45	93.24	95.54	2.31
30	6.88	11.60	84.45	89.18	3.95
40	12.85	13.80	81.60	82.55	4.60
50	16.38	20.74	82.87	77.23	6.39
60	42.32	39.24	52.74	49.66	8.02
120	89.44	86.30	5.57	2.42	8.14
180	85.32	82.80	6.55	4.03	10.65
360	73.82	67.22	18.18	11.59	14.60
Nominal temperature 380 °C					
45	8.77	10.68	84.18	86.09	5.14
60	32.91	36.78	57.59	61.46	5.63
90	83.02	82.74	9.30	9.02	7.95
120	89.44	83.07	7.78	1.42	9.15
180	85.93	82.16	5.240	1.47	12.60
240	65.24	64.14	18.14	17.04	17.72
300	64.72	55.61	24.32	15.21	20.07
420	59.04	54.96	23.31	19.13	21.83

[a] $100 - (y + x_3 + x_2)_{exp.}$

[b] $100 - (x_1 + x_2)_{exp.}$

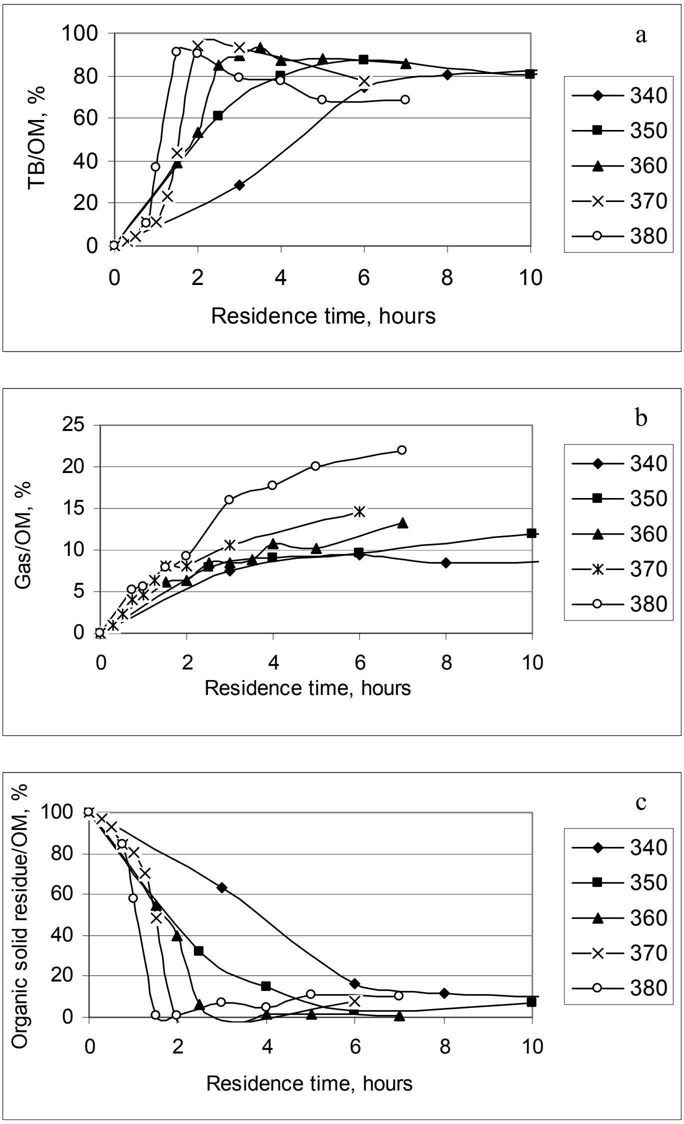


Figure 2. Effect of time on the distribution of initial OM between TBO (a), gas (b) and organic solid residue (c) at different nominal temperatures, °C.

3.1.2 The composition of TBO

The composition of TBO characterized by its part soluble in hexane, sc. maltenes, is presented in Table 8.

Table 8. The content of maltenes in TBO (obtained at 380 °C) depending on residence time

Residence time	TBO/OM, %	Maltenes/TBO, %	Maltenes/OM, %
45 min	8.8	61.7	5.4
2 hour	32.9	36.1	11.9
3 hours	87.7	45.25	40.5
5 hours	64.7	66.6	43.2

It can be seen from Table 8 that at a short pyrolysis time when the quantity of TBO is small, the share of maltenes is great because light destruction products are formed at the beginning of TBO formation. For comparison, the elemental composition of the initial kerogen, TBO, natural bitumens from kukersite and industrial semicoking oil from open-system retorts are given in Table 9.

Table 9. Elemental composition of different organic species from kukersite OM

	Yield, kerogen basis, %	Elemental composition, %					H/C
		C	H	S	N	O by difference	
Initial kerogen [9]	100	77.3	9.8	1.7	0.4	10.8	1.52
Retort oil [10]	65.6	83	9.9	1.1	0.1	5.9	1.43
TBO, 360 °C, 3 h, autoclave (this work)	89.6	83.4	9	0.8	0.8	6	1.29
TB, 360 °C, 4 h, retort [46]	63.8	83.6	9.6	0.5	—	6.3	1.38
Natural bitumoids [10]	0.71	71.8	10.5	—	0.5	17.3	1.75

Table 9 demonstrates that the high yield of OM from kerogen obtained by extraction of TBO under its optimum low-temperatures pyrolysis conditions is contributed by low H/C ratio.

The elemental composition of TBO obtained at 360 °C at different residence times is given in Table 10.

Table 10. Dependence of elemental composition of TB on residence time (360 °C)

Time, h	Yield, %	Elemental composition, %					H/C
		C	H	S	N	O (by difference)	
1.5	36.0	78.5	9.5	0.9	< 0.75	10.2	1.45
2	53.6	81.4	9.2	0.9	< 0.75	7.7	1.36
3	89.6	83.4	9.0	0.8	< 0.75	6.0	1.29
5	83.0	84.8	8.6	0.7	< 0.75	5.1	1.22

It was shown in [35] that in retorting at low rate of thermolysis, the elemental composition of TB did not depended on temperature but on depth of thermolysis, beginning with 82% carbon, 10% hydrogen and 7% oxygen, while at higher rates the content of carbon increased at simultaneous decrease of hydrogen and oxygen content. The elemental composition of TBO obtained in autoclaves at optimum residence time for every temperature, having minimal quantity of coke, could vary only due to differences in quantity of emitting gases. As the last was not considerable (Figure 2b), TBO composition should differ not much. The chemical group composition of commercial retort oil from oil shale processing factory, and TBO and maltenes from TBO obtained in this work are given in Table 11.

Table 11. Chemical group composition of different species of shale oil by TLC, %

Compounds	Retort oil [65]	TBO	Maltenes
		360 °C, 3 h	
Aliphatic hydrocarbons	11.1	3.7	5.8
Monocyclic aromatic hydrocarbons	5.4	2.0	2.5
Polycyclic aromatic hydrocarbons	23.1	4.3	20.2
Neutral oxygen compounds	16.7	9.3	22.3
High polar compounds	43.7	80.7	49.2

The composition of soluble in hexane maltenes obtained in this work using an autoclave is similar to that of the industrial retort oil containing less high-polar compounds than TBO. Low amounts of aliphatic and monocyclic hydrocarbons in TBO express that the product requires further upgrading for being suitable as a liquid, especially as motor fuels. Ratio of total alkenes to alkanes in aliphatic hydrocarbons was 0.86:1. The composition of the hydrocarbons determined by GC is given in Table 12.

Table 12. Composition of alkenes and alkanes, %

Number of C atoms	Alkenes	Alkanes
11	0.5	—
12	0.8	0.7
13	—	9.2
14	11.8	8.9
15	2.3	13.2
16	36.3	26.4
17	2.5	17.7
18	23.3	12.4
19	3.2	7.6
20	13.1	2.4
21	—	—
22	5.0	1.5
23	—	—
24	1.2	—

It is known [23] that olefins C_{13}-C_{17} form at the beginning of kukersite destruction. That was explained by instability of isostructures, compared with the normal ones. The same tendency was discovered in the composition of maltenes from TB.

The composition of functional groups typical of maltenes and asphaltenes was investigated using infrared spectroscopic (IRS) method. The infrared spectra are presented in Figure 3. Visible adsorptions are qualitatively similar, and differences between these two objects can be seen only in quantitative characters of hydrogen substituents in aromatic nucleus. IRS confirms the presence of benzene nucleus at 1600 and 1500–1515 cm^{-1}. The substituents are bound in different positions of benzene nucleus. The absorption typical of methyl, methylene and methyne groups in alkyl chains appears at 3000–2800, 1400–1300 and at 725 cm^{-1}. Absorptions at 2960, 2872, 1460 and 1380 cm^{-1} caused by CH_3 groups in different positions as well as those at 2930, 2860 and 790–720 cm^{-1} (CH_2 groups) are considerable. The most of methylene and methyne groups are bound to form different ring structures such as cyclic hydrocarbons and aromatic compounds. The peak at 1150 cm^{-1} refers to oxygen-carbon bond in the phenol molecule. The absorption in the region 1400–1470 cm^{-1} belongs to hydrogen in the CH_2 and CH_3 groups of aliphatic structures. Peaks in the region 2850–3000 cm^{-1} belong to alkanes, which are present in both maltenes and asphaltenes. C=O-containing compounds with the absorption maximum at 1700 cm^{-1} are clearly distinguishable.

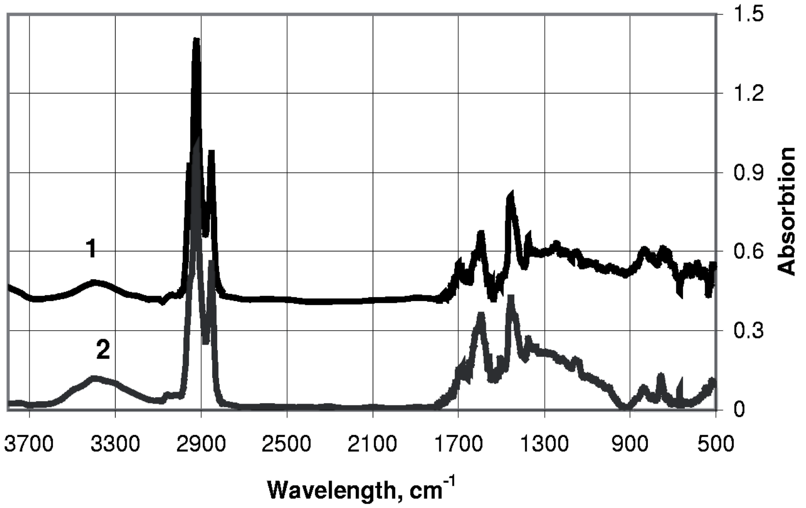


Figure 3. FTIR spectra of maltenes (1) and asphaltenes (2) from TBO obtained at 360 °C, 3 hours.

3.1.3 Thermobituminization scheme and derivation of algorithms for estimation of rate factors

In this work, the complicated thermal decomposition of oil shale in autoclaves was approximately described by kinetics of phase transformations characterized by the corresponding rate factors k_1 - k_4. The procedure for estimation of the rate factors was worked out.

The simplified scheme applied for modelling kinetics of the pyrolysis reactions in autoclaves is presented in Figure 4.

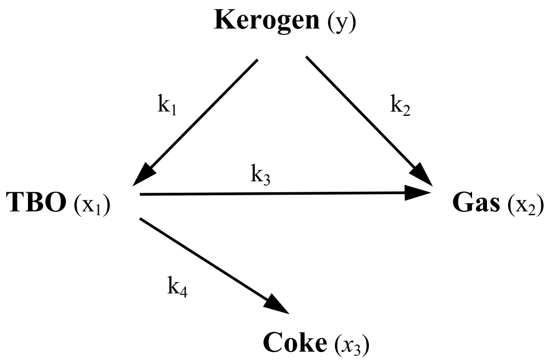


Figure 4. Scheme for phase transformations at low-temperature pyrolysis of kerogen in autoclaves.

Admitting that the thermal decomposition pathways presented in Figure 4 obey the first order kinetic equations, rate of every phase transformation can be described by a modification of Eq. 4 and 5 presented in p. 1.7.

So, concentration of the initial kerogen (y) should decrease in time as follows:

$$-dy/dt = (k_1 + k_2)y = k_y y \qquad (3.1.1)$$

and the total decomposition rate factor (k_y) can be found from the slope of the integrated form of Eq. (3.1.1) as follows:

$$\ln y = \ln y_0 - k_y (t-t_0) \qquad (3.1.2)$$

Before the coke formation has started, the value of y should be equal to the percentage of experimentally estimated organic solid residue, and the value of k_y should be constant. So, under the isothermal conditions, since the nominal temperature is attained and coke is not formed yet, Eq. (3.1.2) should express a straight line.

The linear parts of the plot of logarithm from the percentage of the current organic solid residue (Fig. 2c) versus time for the five nominal temperatures tested are presented in Figure 5. The values of k_y found from the slopes of the straight lines are given in the first row of Table 13.

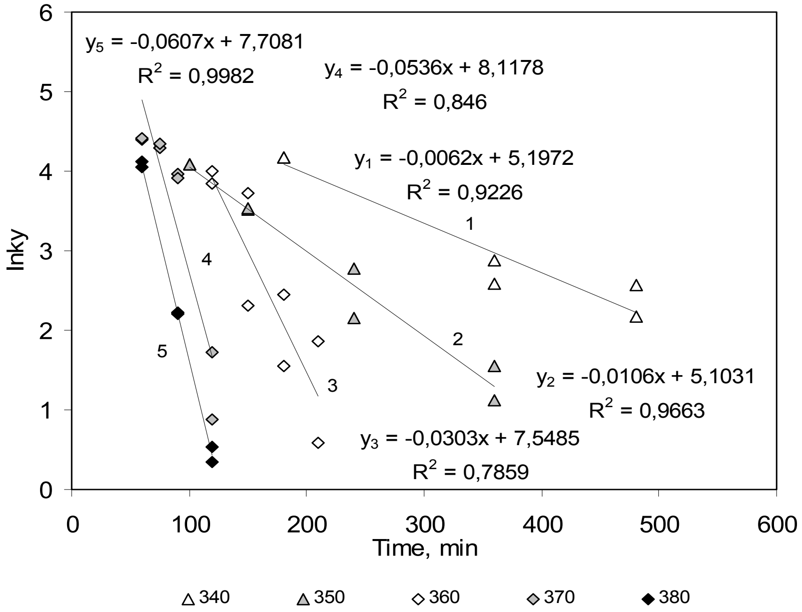


Fig. 5. Plot of ln y versus time for estimation of k_y at nominal temperatures (°C): (1)-340, (2)-350, (3)-360, (4)-370, and (5)-380.

According to the scheme in Fig. 4, the concentrations of TBO (x_1), gas (x_2) and coke (x_3) should increase as follows:

$$dx_1/dt = k_1y - (k_3 + k_4)\, x_1 = k_1y - k_{TBO}\, x_1 \qquad (3.1.3)$$

$$dx_2/dt = k_2y + k_4x_1 \qquad (3.1.4)$$

$$dx_3/dt = k_3x_1 \qquad (3.1.5)$$

The differential equations (3.1.1) and (3.1.3)–(3.1.5) represent a system with four independent unknown rate factors k_1–k_4. Algorithms for estimation of the coefficient were deduced dividing Eqs. (3.1.3)–(3.1.5) with Eq. (3.1.1) and thereafter multiplying with k_y. As results, linear relationships were revealed between the relative increase in the concentration of any product with the corresponding decrease in the concentration of initial kerogen versus the current ratio of the TBO and kerogen concentrations

$$- k_y(dx_1/dy) = k_1 - k_{TBO}(x_1/y) \qquad (3.1.6)$$

$$- k_y(dx_2/dy) = k_2 + k_4(x_1/y) \qquad (3.1.7)$$

$$- k_y(dx_3/dy) = k_3(x_1/y) \qquad (3.1.8)$$

where the values of k_1 and k_2 occur as intercepts, and of k_{TB}, k_3 and k_4 as slopes.

$$k_3 = k_{TBO} - k_4 \qquad (3.1.9)$$

The rate factors of TBO cracking, k_{TBO}, k_3 and k_4 were calculated by Eqs. (3.1.6), (3.1.7) and (3.1.9) only for the nominal temperature 340 °C. At higher temperatures the cracking took place mainly after exhaustion of the initial kerogen when the values of y and d_y in denominators of Eqs. (3.1.6) and (3.1.7) were too small for correct calculations. For better estimation of the coefficients, the region of TBO decrease after its maximum was examined. When there was no practical contribution from decomposition of the initial kerogen, Eq. (3.1.3) was reduced to a simpler form analogous to Eq. (3.1.1) as follows:

$$-dx_1/dt = (k_3 + k_4)x_1 = k_{TBO}x_1 \qquad (3.1.10)$$

where the total decomposition rate factor(k_{TBO}) of TBO was found from slope of the integrated form of Eq. (3.1.10) as follows

$$\ln x_1 = \ln x_{1,0} - k_{TBO}(t - t_0) \qquad (3.1.11)$$

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

Noteworthy is that in this case, the initial time, t_0 and concentration $x_{1,0}$ were not zero but corresponded to the beginning of the linear relationship between ln x_1 and time being valid when there is no practical contribution from k_1y in Eq. (3.1.3).

After the value of k_{TBO} was found, the rate factorsfor parallel formation of gas and coke from TBO were calculated using the proportional relationships

$$k_3 = - k_{TBO}\, dx_3/dx_3 \qquad (3.1.12)$$

and

$$k_4 = - k_{TBO}\, dx_2/dx_1 \qquad (3.1.13)$$

The temperature profiles of the reaction mixtures recorded experimentally (Figure 6) revealed that the nominal temperature was attained after an hour.

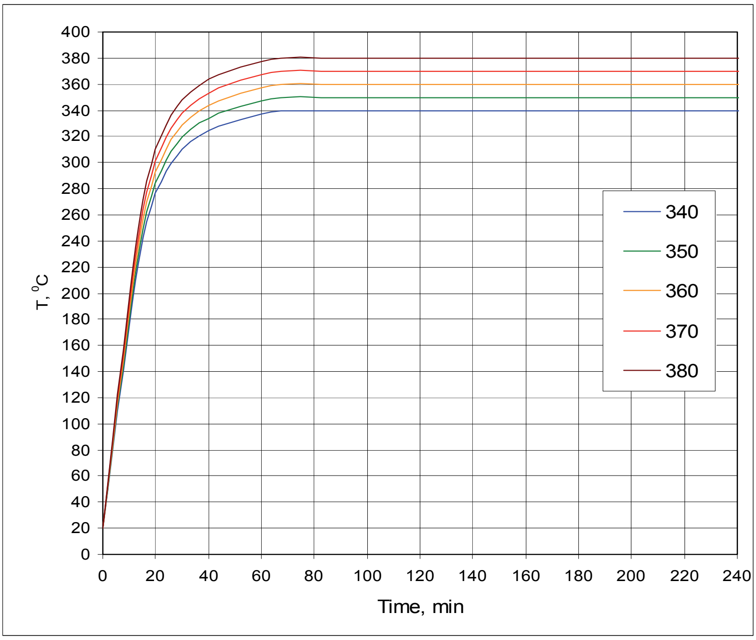


Figure 6. The reaction current temperatures at different nominal temperatures (°C).

For calculation of the rate factors by Eqs. (3.1.1) – (3.1.13) only the experimental data from Fig. 2a,b, and c obtained at the isothermal periods were applied. As far the solid residue consisted of not decomposed kerogen and coke formed, the real values of y and dy calculated by means of k_y and y_0 were used.

The more detailed explanation of the kinetic approach is given in the *Original Publication IV*. The rate factors found according to the algoritms deduced are given in Table 13.

Table 13. Rate factors, 1/min

Rate factor (1/min)	Nominal temperature (°C)				
	340	350	360	370	380
k_y	8.68E-03	1.12E-02	4.01E-02	4.25E-02	5.14E-02
k_1	8.43E-03	9.25E-03	3.81E-02	3.88E-02	3.08E-02
k_2	2.52E-04	1.95E-03	1.99E-03	3.70E-03	2.06E-02
k_{TBO}	5.65E-05	3.27E-04	3.37E-04	9.30E-04	1.56E-03
k_3	5.27E-05	2.10E-04	1.27E-04	7.72E-04	1.08E-03
k_4	2.76E-06	1.17E-04	2.10E-04	1.58E-04	4.76E-04

The values of apparent activation energy (*E*) and frequency factor (*A*) for formation of TBO and gas from kerogen, and gas and coke from TBO at the low-temperature pyrolysis of kerogen were found from the intercept and slope of the depicted in Figure 7 Arrhenius linear relationship

$$\ln k_{\mathrm{i}} = \ln A_i - E_i/RT \qquad (3.1.14)$$

where *R* is gas constant 8.314 J/mol, are presented in Table 14.

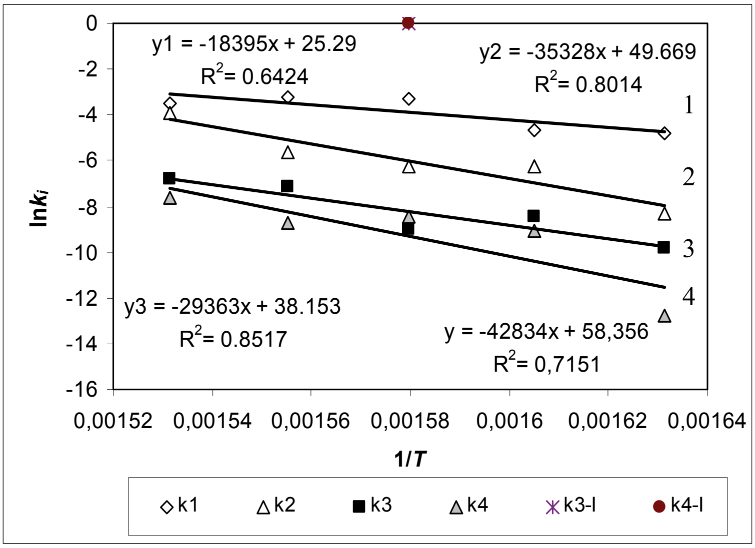


Figure 7. Arrhenius plot of rate factors (1/min): (1) k_1, (2) k_2, (3) k_3, and (4) k_4.

Table 14. Apparent kinetic constants for pyrolysis of kerogen between 340 and 380 °C

	k_1	k_2	k_3	k_4
$a = \ln A$	25.3±9.9	49.7±11.8	33.15±19.21	58.36±11.6
$-b = E/\mathrm{R}$	(1.84±0.63)E+04	(3.53±0.74)E+04	(2.94±1.23)E+04	(4.28±0.74)E+04
R^2	0.642	0.801	0.852	0.715
A (1/min)	9.62E+10	3.73E+21	3.70E+16	2.22E+25
E (kJ/mol)	153	294	244	356

3.1.4 Prediction of the current distribution of the pyrolysis products at non-linear increase of temperature

A step-by-step approach was applied to calculate the concentrations of the pyrolysis products in time under non-linear increase of temperature. For this aim, the following route was used:

- The time dependence of temperature (T) in °C was calculated for definite (20 min) time intervals according to equation

$$T_t = T_{\mathrm{nom}} - (T_{\mathrm{nom}} - T_{\mathrm{room}}) \exp(-\beta t) \qquad (3.1.15)$$

where the heating rate characteristic β, in 1/min, for the autoclave applied was found from the empirical polynomial relationship

$$\beta = 60/0.0001T^2_{\mathrm{nom}} - 0.4073T_{\mathrm{nom}} + 887.57 \qquad (3.1.16)$$

- The values of the rate factors at every mean temperature of the time intervals were calculated introducing the corresponding kinetic constants from Table 14 into the exponential form of Eq. (3.1.14).

- The current share of not decomposed (insoluble in benzene) kerogen was calculated as follows:

$$y_{\mathrm{n}} = y_{\mathrm{n-1}}/\exp[(k_1 + k_2)(t_{\mathrm{n}} - t_{\mathrm{n-1}})] \qquad (3.1.17)$$

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

The current yield of TBO was calculated using the relationship deduced from Eq. (3.1.6)

$$x_{1,n} = x_{1,n-1} + [(y_{n-1} - y_n)k_1/(k_1 + k_2)][k_1 - (k_3 + k_4)x_{1,n-1}/y_{n-1}] \quad (3.1.18)$$

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

The current gas yield was calculated using the relationship deduced from Eq. (3.1.8)

$$x_{2,n} = x_{2,n-1} + [(y_{n-1} - y_n)k_2/[(k_1 + k_2)][k_2 + k_4 x_{1,n-1}/y_{n-1}] \quad (3.1.19)$$

where at $t_{n-1} = 0$ min, $x_{2,n} = 0\%$

The current coke yield was calculated as the difference

$$x_{3,n} = 100 - (y_n + x_{1,n} + x_{2,n}) \quad (3.1.20)$$

When the nominal temperature was attained, the concentrations of the initial kerogen at time t was calculated basing on the not decomposed kerogen concentration y_{nom} at time t_{nom} as follows:

$$y = y_{nom}/\exp[(k_y(t_n - t_{nom})] \quad (3.1.21)$$

The yield of the total solid residue at time t was calculated as the sum of the current values of y and x_3.

Comparison the yields of the products predicted by Eqs. (3.1.14) – (3.1.21) and the experimental results in Figure 8, 9 and 10 show satisfactory agreement.

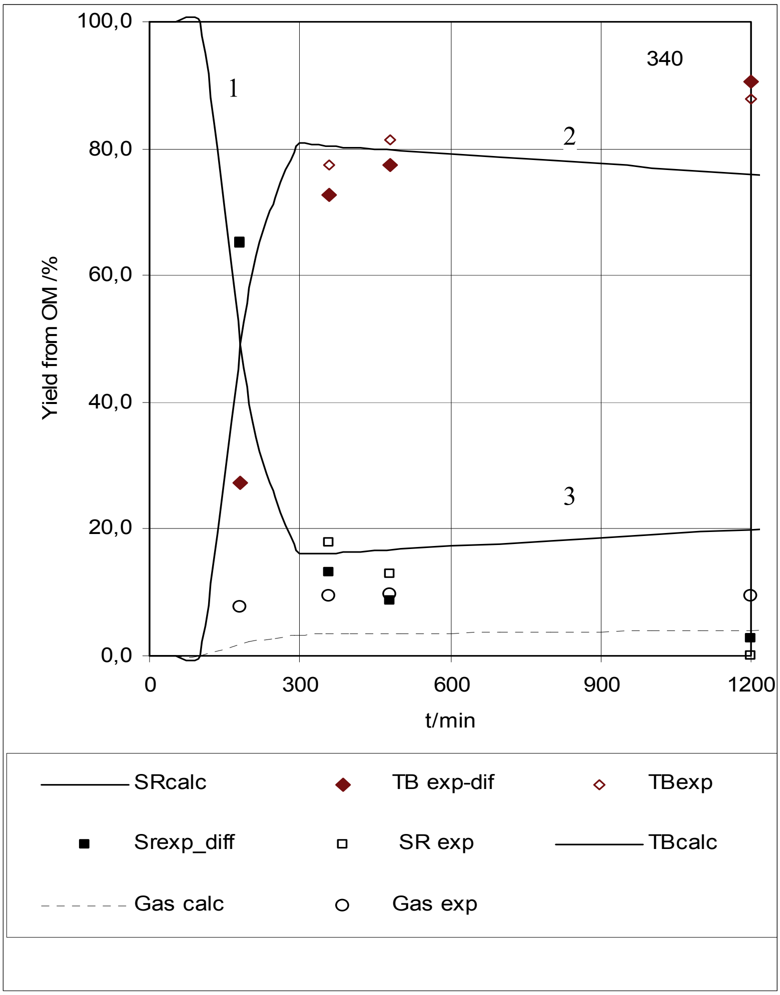


Figure 8. Effect of time on the distribution of kerogen between its pyrolysis products at nominal temperature 340 °C: (1) solid residue, (2) TBO, and (3) gas. Curves: calculated; bright points: experimental by weight; dark points: experimental from difference.

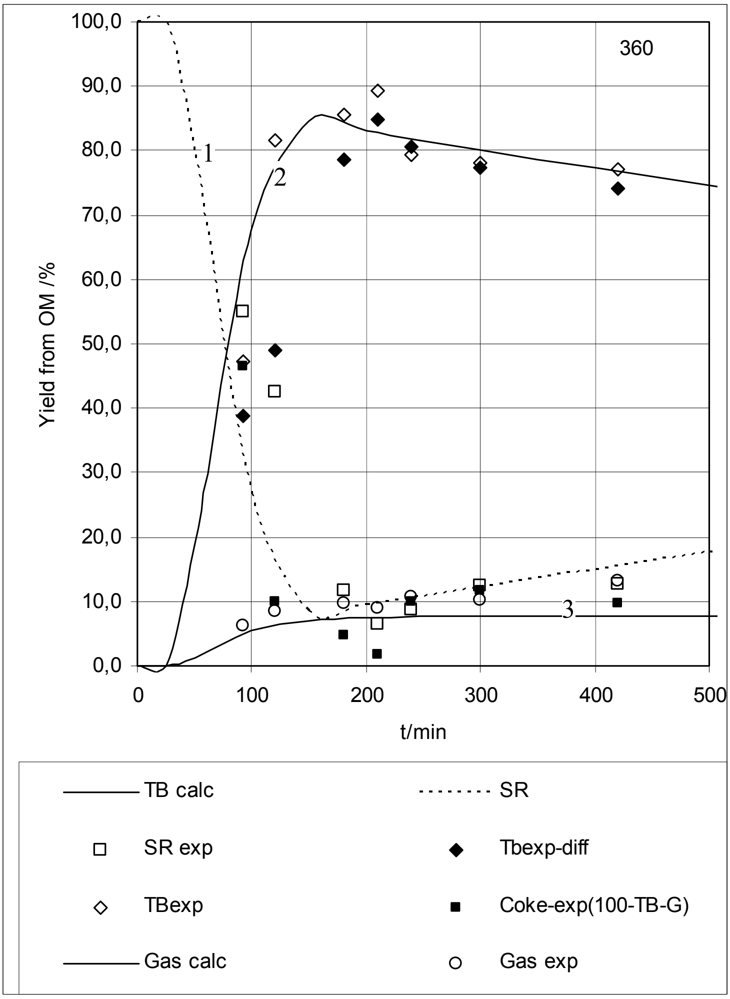


Figure 9. Effect of time on the distribution of kerogen between its pyrolysis products at nominal temperature 360 °C: (1) solid residue, (2) TBO, and (3) gas. Curves: calculated; bright points: experimental by weight; dark points: experimental from difference.

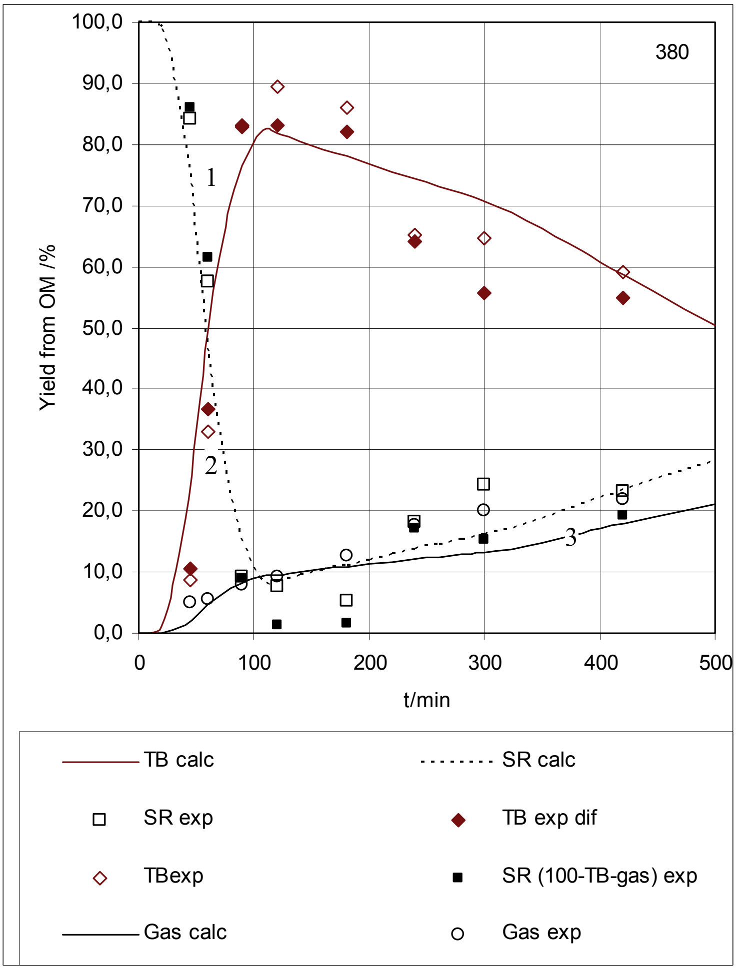


Figure 10. Effect of time on the distribution of kerogen between its pyrolysis products at nominal temperature 380 °C: (1) solid residue, (2) TBO, and (3) gas. Curves: calculated; bright points: experimental by weight; dark points: experimental from difference.

The results presented in Figures 8-10 prove suitability of the model proposed and algorithms deduced for prediction of the co-effect of temperature and duration on the yields of kerogen decomposition products at low-temperature pyrolysis in laboratory autoclaves.

3.2 Retorting

(Papers I and III in APPENDIX A)

As a rule, a retorting process begins under non-isothermal heating up conditions. In this work, the experiments were conducted in an aluminium retort by heating the kerogen up to the nominal temperature according to the experimental conditions described in 2.2. The results of the experiments are given in Table 15.

Table 15. Effect of nominal temperature (°C) and total time (min) on the yield of products (% from kerogen) at non-isothermal retorting of kukersite

Temperature, °C	Time, min	Oil	Gas	TB	Maltenes in TB	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		14.09
	63	29.63	7.06	53.50	n.d.	9.81
410	55	30.12	5.98	53.90		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

The scheme applied for autoclavic process (Figure 4) consisting of parallel-consequent phese transformations was modified for retorting and will be described in p. 3.2.1 below. Nevertheless, the non-linear increase of temperature made the process too complicated for calculation of the rate factors. So, the experimental data for estimation of kinetic constants were taken from the thesis of Schulman [54] who had applied a specific device for isothermal retorting. The time dependencies of the yields of volatiles, TB and solid residue obtained in are shown in Figure 12. 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

Figure 11 after every 50 minutes and from Figure 11b after every 5 minutes. The extrapolated data are presented in Table 16.

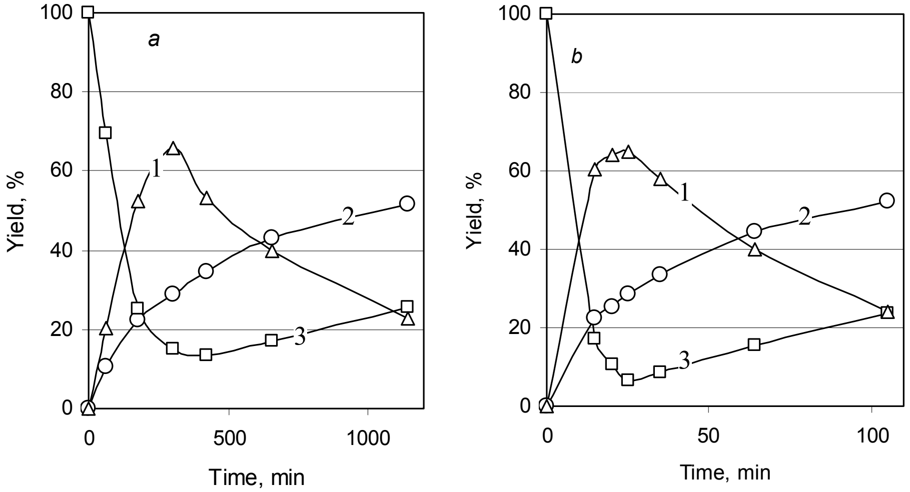


Figure. 11. Effect of retorting time on the yield of thermobitumen (1), volatiles (2) and solid residue (3) at isothermal retorting temperatures 350 °C (a) and 386 °C (b) by Schulman [54]

Table 16. Yield of pyrolysis products, % from OM, extrapolated from Figure 11

350 °C				386 °C			
Time, min	Solid residue	Thermobitumen	Volatiles	Time, min	Solid residue	Thermoitumen	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

3.2.1 Estimation of rate factors and kinetic constants

For description of the thermobituminization kinetics in open retorts the scheme analogous to the autoclavic process (Fig. 4) was applied. Only, in open retorts x_1 marks TB, not TBO, and x_2 – the sum of oil and gas, not only gas.

Like in autoclaves, the current concentration of the initial kerogen insoluble in organic solvents (y) should decrease with time as follows:

$$-\,\mathrm{d}y/\mathrm{d}t = (k_1 + k_2)y = k_y y, \qquad (3.2.1)$$

and the total decomposition rate factorof kerogen (k_y) can be found from the slope of the integrated form of Eq. (3.2.1) as follows:

$$\ln y = \ln y_0 - k_y t \qquad (3.2.2)$$

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. (3.2.2) would express a straight line whose slope is equal to k_y. The experimental results in Table 16 depicted in Figure 12 in the form of Eq. (3.2.2) 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 Figure 13 are brought in the first column of Table 17.

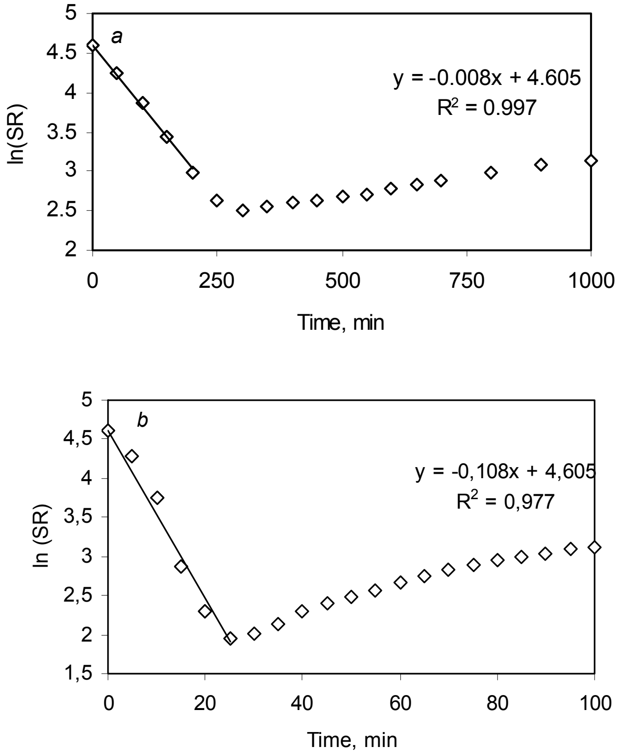


Figure 12. Plot of logarithm from the yield of solid residue versus time at retorting temperatures 350 °C (a) and 386 °C (b) for estimation of k_y.

Table 17. Rate factors 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

Analogously to the autoclavic process described by Figure 4, concentration of TB (x_1), volatiles (x_2) and coke (x_3) change with time as follows:

$$dx_1/dt = k_1 y - (k_3 + k_4)\, x_1 = k_1 y - k_{TB}\, x_1 \qquad (3.2.3)$$

$$dx_2/dt = k_2\, y + k_4\, x_1 \qquad (3.2.4)$$

$$dx_3/dt = k_3\, x_1 \qquad (3.2.5)$$

Dividing Eqs (3.2.3), (3.2.4) and (3.2.5) with Eq. (3.2.1) 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

$$Y_i = -k_y \mathrm{d}x_i / \mathrm{d}y = a + bx_1/y, \tag{3.2.6}$$

where when $i = 1$: $a = k_1$ and $-b = k_{\mathrm{TB}}$, 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. (3.2.6) by means of the rate factor k_y from Table 17 using the exponential form of Eq. (3.2.2)

$$y = 100/\exp(k_y t) \tag{3.2.7}$$

The coefficient k_3 was found from the difference

$$k_3 = k_{\mathrm{TB}} - k_4 \tag{3.2.8}$$

Introducing the data series from Table 16 into Eq. (3.2.6) gives satisfactory linear plots of Y_i versus x_1/y (Figure 12). The rate coefficients, equal to the corresponding regression constants, at the two temperatures applied are presented in Table 17.

The kinetic constants (E_i and A_i) in the Arrhenius relationship

$$k_i = A_i \exp\left(-E_i / \mathrm{R}T\right) \tag{3.2.9}$$

were calculated using the data given in Table 17 as follows:

$$E_i = [\mathrm{R}(T_1 T_2) \ln(k_{i1}/k_{i2})] / (T_2 - T_1) \tag{3.2.10}$$

$$A_i = k_i \exp(E_i/\mathrm{R}T) \tag{3.2.11}$$

The kinetic constants found are presented in Table 18. 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 [66, 40]. The activation energy for transformation of TB into gas, 183 kJ/mol, coincides with the value estimated by Kotkas in the individual gasification of shale oil [67], 45 kcal/mol = 188 kJ/mol.

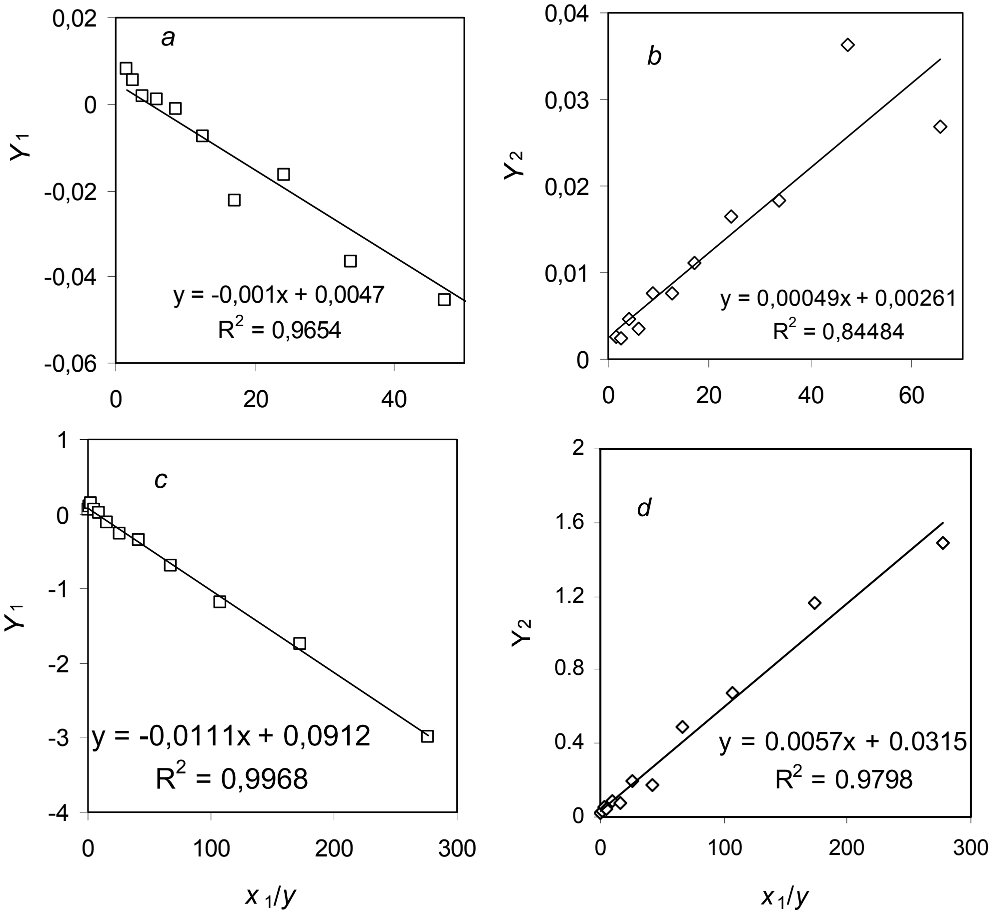


Fig. 13. Depiction of Equation (3.2.6) for estimation of k_1 and k_{TB} (a and c), and k_2 and k_4 (b and c) at temperatures 350 °C (a and b) and 386 °C (c and d).

Table 18. 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

3.2.2 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

$$B_i = \mathrm{d}x_{ij} / \mathrm{d}x_i \tag{3.2.13}$$

Understandably, the share of the second component is 1 – B_i. The experimental data in Table 4-9 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

$$B_i = a_B + b_B \, \mathrm{t} \tag{3.2.14}$$

shown in Figure 14. 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.

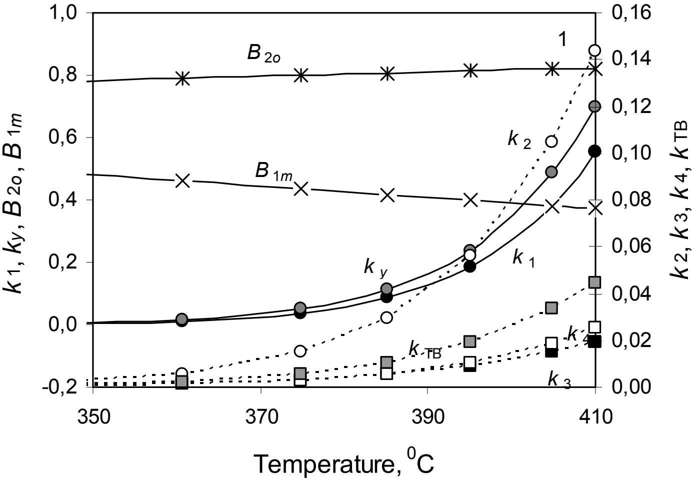


Figure 14. Effect of temperature on the rate coefficients, 1/min, and on the share factors of malthenes in thermobitumen, B_{1m}, and of oil in volatiles, B_{2o}, formed.

3.2.3 Prediction of current concentrations of the pyrolysis products

As described above, thermal decomposition of kukersite in Fischer retort is conducted under 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 factors and share factors were calculated for every temperatute step. For this aim

- 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 factors(k_i) were calculated by Eq. (3.2.9) using the corresponding apparent kinetic constants from Table 18, and (ii) the share factors (B_i) were calculated by Eq. (3.2.14).

The factors found are depicted in Figure 14 where for better understanding the plain curves belong to the left axis and the dotted curves to the right one.

The results obtained evidence that at the low-temperature region formation of TB from kerogen is preferred, and the rate factor 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. (4.2.1) integrated in the ranges of time t_{n-1} and t_n

$$y_n = y_{n-1}/\exp[(k_1 + k_2)(t_n - t_{n-1})] \qquad (3.2.15)$$

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

$$y = y_{nom} /\exp[k_y(t - t_{nom})] \qquad (3.2.16)$$

- the current yield of TB was calculated using the relationship deduced from Eq. (3.2.6)

$$x_{1,n} = x_{1,n-1} + [(y_{n-1} - y_n)k_1/(k_1 + k_2)][k_1 - (k_3 + k_4)x_{1,n-1}/y_{n-1}], \qquad (3.2.17)$$

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

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

$$x_{2,n} = x_{2,n-1} + [(y_{n-1} - y_n)k_2/[(k_1 + k_2)][k_2 + k_4 x_{1,n-1}/y_{n-1}], \qquad (3.2.18)$$

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

- the current coke yield was calculated as the difference

$$x_{3,n} = 100 - (y_n + x_{1,n} + x_{2,n}) \qquad (3.2.19)$$

- 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 Figure 14 as follows:

$$x_{1m,\mathrm{n}} = x_{1m,\mathrm{n}-1} + B_1(x_{1,\mathrm{n}-1} - x_{1,n}) \tag{3.2.20}$$

$$x_{2o,\mathrm{n}} = x_{2o,\mathrm{n}-1} + B_2(x_{2,\mathrm{n}-1} - \mathrm{x}_{2,\mathrm{n}}) \tag{3.2.21}$$

- 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 (3.2.15)–(3.2.21) for the two nominal temperatures tested in this work are presented in Figure 15*a* and *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), 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 15 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 (Fig. 15a), but at 410 °C (Fig. 15b) already after 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 in this work with the data predicted using in Eqs (3.2.15)–(3.2.21) the kinetic constants found by means of experimental data obtained under the isothermal conditions about fifty years earlier by Schulman [54] 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 Figure 15 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 thermobituminization ($t_{\max}$) enabling the maximum 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.

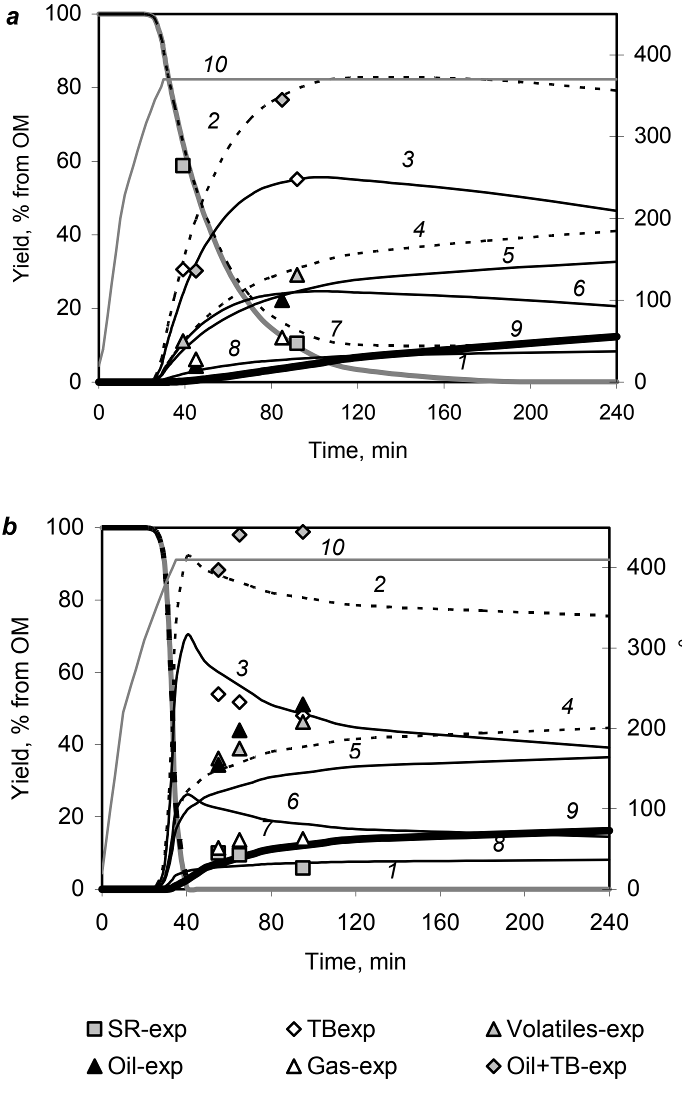


Figure 15. Effect of retorting time at nominal temperature 370 °C (a) and 410 °C (b) on the distribution of kerogen decomposition products: 1 – kerogen, 2–TB + oil, 3 – TB, 4 – volatiles, 5 – oil, 6 – malthenes, 7 – solid residue, 8 – gas, 9 – coke, and 10 – the current temperature. Curves – calculated, points – experimental.

3.3 Comparison of the thermobituminization kinetics of kukersite in open retorts and autoclaves

(Paper V in APPENDIX A)

As is it was described above, 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 in the open retorts and into the liquid extract in autoclaves, the direct comparison of the pyrolysis kinetics in the two devices was complicated. Furthermore, the heating regimes were different in the devices either.

3.3.1 General algorithms for estimation of kinetic characteristics

It was considered the separate kinetics for autoclaves and retorts in the previous chapters. Now let's look at a unified approach. In spite the differences in the composition of the extracts and volatiles, the complicated thermal decomposition of oil shale both in open retorts and autoclaves can be approximately described by the common first order parallel-consequent phase transformations (with the corresponding concentration symbols in parenthesis) given in Fig. 16:

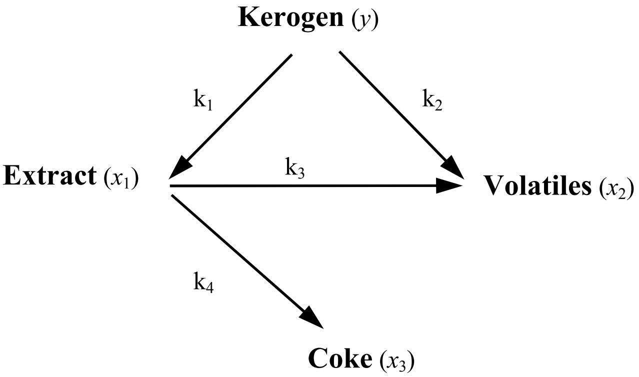


Figure 16. General scheme for phase transformations at low-temperature pyrolysis of kerogen in autoclaves and retorts.

The differential equations for the kinetic scheme proposed for the both devices are expressed like in Parts 3.1 and 3.2 as follows:

$$-dy/dt = (k_1 + k_2)y = k_y y \qquad (3.3.1)$$

$$dx_1/dt = k_1 y - (k_3 + k_4)\, x_1 = k_1 y - k_{TB(TBO)}\, x_1 \qquad (3.3.2)$$

$$dx_2/dt = k_2y + k_4x_1 \tag{3.3.3}$$

$$dx_3/dt = k_3x_1 \tag{3.3.4}$$

For estimation of the rate factors, distribution factors and kinetic constants the analogous linear relationships were applied as given in parts 3.1 and 3.2.

The kinetic constants found for the both devices are presented in Table 19.

Table 19. Apparent kinetic constants

Rate factor, 1/min	Retort		Autoclave	
	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

3.3.2 Compensation effect between the kinetic constants

Noteworthy is that a clear linear relationship (correlation coefficient R = 0.99) is kept between all the kinetic constants found for both open retorts and autoclaves as follows:

$$\ln A = 2.23(\pm 2.29) + 0.174\ (\pm 0.009)E \tag{3.3.5}$$

The relationship is depicted in Figure 17.

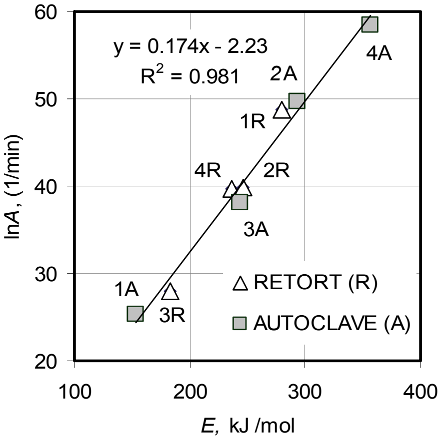


Figure 17. Relation between the low-temperature pyrolysis apparent kinetic constants in two devices.

The differences between the 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 thermobitumen 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 (TBO) is advanced in open retorts in comparison with gas formation under pressure in autoclaves;
- $E_{3R} < E_{3A}$ – coke formation from high molecular thermobitumen (TB) is superior than from the oil containing TBO;
- $E_{2R} \approx E_{4R}$ but $E_{2A} < E_{4A}$ – 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.

3.3.3 General algorithms for prediction of current concentrations of the pyrolysis products

The thermal decomposition of kukersite in the 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 for the both devices using the same form of equations as follows:

$$y_n = y_{n-1}/\exp[(k_1 + k_2)(t_n - t_{n-1})] \qquad (3.3.6)$$

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

$$x_{1,n} = x_{1,n-1} + [(y_{n-1} - y_n)k_1/(k_1 + k_2)][k_1 - (k_3 + k_4)x_{1,\,n-1}/y_{n-1}] \qquad (3.3.7)$$

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

$$x_{2,n} = x_{2,n-1} + [(y_{n-1} - y_n)k_2/[(k_1 + k_2)]][k_2 + k_4 x_{1,\,n-1}/y_{n-1}] \qquad (3.3.8)$$

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

$$x_{3,n} = 100 - (y_n + x_{1,n} + x_{2,n}) \qquad (3.3.9)$$

$$x_{2o,n} = x_{2o,n-1} + B_o(x_{2,n-1} - \mathrm{x}_{2,n}) \qquad (3.3.10)$$

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

One of the defining factors of the pyrolysis kinetics is heating rate. Understandable, that the heating rate applied at retorting of oil shale in 50 cm^3 open retorts does not coincide with that in 20 cm^3 autoclaves placed into an oven preheated to the nominal temperature. To compare the efficiency of the devices, the current yields of the products were predicted for the both devices under the temperature profiles described earlier as characteristic to autoclavic experiments.

The yields of the pyrolysis products in the both devices were calculated as sums of n ten-minute steps which temperatures were approximated to the isothermal mean values of the steps. The rate factors for the every increasing temperature step were calculated introducing the kinetic constants from Table 19 into Arrhenius relationship. The corresponding yields of the phases were found by Eqs. (3.3.7)–(3.3.10). 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. (3.3.6) and (3.3.11). In retorting the values of the target product, (TBO) were found adding the current oil yield to the corresponding extract yield (x_1), and of the gas yield, subtracting oil yield (x_{2o}) from total volatiles (x_2). The current yields of the organic solid residue were found as sums of the corresponding not decomposed kerogen (y) and coke formed (x_3).

Examples illustrating predicted current changes during pyrolysis of oil shale in the both devices at the nominal temperatures 350 and 370 °C are presented in Figure 18.

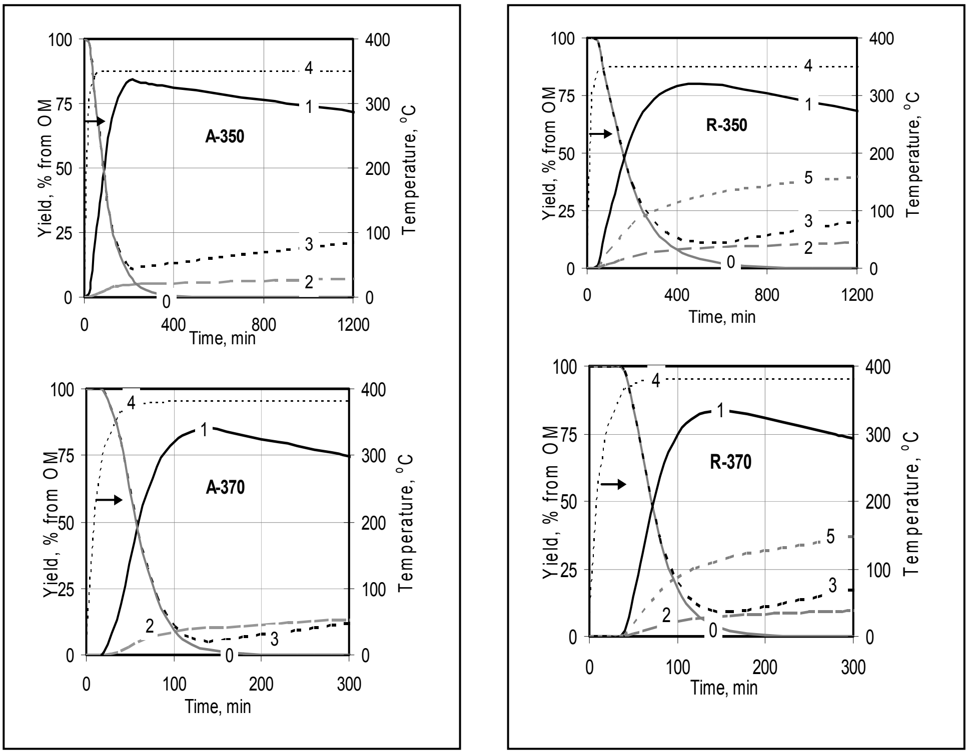


Figure 18. Effect of pyrolysis duration on the yield of the phases, % from initial kerogen at nominal temperatures 350 and 370 °C in open air retorts (R) and autoclaves (A): 0 – kerogen, 1 –TBO, 2 – gas, 3 – organic solid residue, 4 – temperature, °C.

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 kerogen current decomposition degree (curve 0) and yield of the target product, TB (TBO) (curve 1), are affected mainly by the pyrolysis duration and temperature whereas the reactor type has a minor effect.
- In the both devices the decomposition of TB (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.

CONCLUSIONS

The following new results were obtained in the frames of this doctoral thesis.

1. Kinetics of the complicated thermobituminization process of oil shale was described by scheme of phase transformations.
2. A first order parallel-consequent kinetic model was derived for description of the co-effect of time, nominal temperature and heating rate on the yield of different phases (volatiles, extract and solid residue) at low-temperature pyrolysis of kukersite in both laboratory retorts and autoclaves.
3. The rate factors for formation of extracts (thermobitumen in retorts and mix of thermobitumen and oil in autoclaves) and volatiles (oil and gas in retorts, and gas in autoclaves) from kerogen, and secondary volatiles and coke from the extracts, k_1-k_4, were estimated using the experimental results obtained at isothermal retorting. The apparent activation energies (E_1-E_4) and frequency factors (A_1-A_4) for the transformations were calculated. The distribution factors of the components of the phases (maltenes–asphaltenes) in the extracts from autoclaves) and oil–gas in the volatiles from retorting) were estimated.
4. A linear relatiationship between the values of $\ln A_{1\text{-}4}$ and $E_{1\text{-}4}$ common for the both devices was revealed.
5. 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 given were described, and conditions for the maximum yield of the extract were predicted introducing the constants found into the model deduced. The calculated and the corresponding experimental results agreed satisfactorily.
6. When pyrolysis is conducted under the same heating rate (6 ^{o}/min), the decomposition of kerogen starts in the both devices at the same temperature reaching 10% when the temperature attains 350 °C, whereas the yield of TBO overcomes 80% at an optimum duration depending on the nominal temperature.
7. 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.
8. At the lower nominal temperature, 350 °C, the decomposition of kerogen in autoclaves in the environment of oil formed is slightly faster than in the dry retorting where the oil fractions having boiling point below 350 °C volatilize. Therefore the maximum yield of thermobitumen (*ca* 80%) is attained in the autoclave after 200 minutes and at retorting only after 400 minutes.

9. The maximum total yield of the target product, the sum of thermobitumen and oil from kerogen (TBO, 91%) was obtained at nominal temperature 410 °C after 40 minutes retorting in the both devices.

REFERENCES

1. Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, Vol. A18, Oil Shale by H-J. Weiss, pp. 101-126. VCH Verlag, 1991.
2. *Dobryansky, A. F.* Oil Shales of the USSR. Lengostoptehizdat, 1947 [in Russian].
3. *Fomina, A. S.* Kukersite, its Chemical Nature and Origin. Thesis of DPhil. Acad. Sci. Belorussian SSR, 1962 [in Russian].
4. *Kogerman, P.* Hundred years of the chemical investigation of an oil shale: the chemical constitution of the Estonian oil shale "kukersite" – Oil Shale and Cannel Coal. Glasgow, 1938. P. 115-123.
5. *Kogerman, P. K.* Kerogen of shales as a highmolecular matter, and genesis of shales. Chemistry and Genesis of Fossil Fuels. Transactions of the First SSSR Meeting. Moscow, 1953. – Genesis of fossil fuels. USSR Acad. Sci. Publishing House, 1953. P. 368-375. [in Russian].
6. *Gubergritz, M. Ya.* Thermal Processing of Kukersite Oil Shale. Tallinn, 1966. 356 pp. [in Russian].
7. *Rudin, M. G., Serebryannikov, N. D.* (Eds.). Handbook of Oil Shale Processer. – Leningrad, 1988. 256 pp. [in Russian].
8. *Kaljuvee, E. G.* Main directions of the development of oil shale recovery. – Oil Shale. 1984. Vol. 1, No. 1. P. 40-50 [in Russian].
9. *Lille, Ü., Heinmaa, I., Pehk, T.* Molecular model of Estonian kukersite kerogen as evaluated by ^{13}C MAS NMR spectra. – Fuel. 2003. Vol. 82, No. 7. P. 799–804.
10. *Urov, K., Sumberg, A.* Characteristics of oil shales and shale-like rocks of known deposits and outcrops. Monograph. – Oil Shale. 1999. Vol. 16, No. 3. P. 1–64.
11. *Bondar, E., Koel, M.* Application of supercritical fluid extraction to organic geochemical studies of oil shale. – Fuel. 1998. Vol. 77, No. 3. P. 211-213.
12. *Barshchevsky, M. M., Bezmozgin, E. S., Shapiro, R. N.* Oil Shale Processing Handbook. Leningrad: Gostoptehizdat, 1963. 238 p. [in Russian].
13. *Pokonova, Yu. V., Fainberg, V. S.* Oil Shale Chemistry. Moscow: VINITI, 1985. P. 319 [in Russian].
14. *Bogomolova, M. G., Ivashchenko, G. A., Sharikova, E. A.* Improvements in Methods of Solid Fuel Beneficiation. – Moscow: Nedra, 1985. P. 60-64 [in Russian].
15. *Dilaktorsky, N. L., Galibina, E. A.* On the issue of mineral formation processes, which proceed at oil shale ash heating and solidification of

hydrated products of calcination. In: Oil Shale Ash Materials in Building. Tallinn, 1955 [in Russian].

16. *Tsybasov, V. P.* Oil Shale. 1933, No. 6, and 1934, No. 3 [in Russian].
17. *Popov, N. V., Tsybasov, V. P., Podkletnov, M. I.* Oil Shale. 1931, No. 1 [in Russian].
18. *Puksov, A.* Oil Shale. 1934, No. 3. P. 31 [in Russian].
19. *Kopwillem, J.* Acta et Comm. Univ. Tartuensis A XVI, 1927, 6.
20. *Kask, K. A.* About bituminizing of kerogen of oil shale-kukersite. Report II. – Transactions of Tallinn Polytechnic Institute. Series A. 1956. No. 73. P. 23-40 [in Russian].
21. *Aarna, A. Y., Kask, K. A.* J. Appl. Chem. 1956. Vol. 28, No. 7, P. 768 [in Russian].
22. *Fomina, A. S.* About some characteristics of kukersite oil shale.– Transactions of Estonian SSR Acad. Sci.. Series of Tech. and Phys.-Math. Sci. 1956, No. 1, P. 42-54 [in Russian].
23. *Tsybasov, V. P.* Transactions of Leningrad Military and Mechanical Institute 1956, No. 5, P. 91 [in Russian].
24. *Kogerman, P., Luts, K., Hüsse, J.* The Chemistry of Estonian Oil Shale. – Moscow-Leningrad: Goshimizdat, 1934. P. 11-102 [in Russian].
25. *Khisin, Ya. I.* Thermal Decomposition of Oil Shales. Gostoptehizdat, – Leningrad-Moscow, 1948 [in Russian].
26. *Luts, K.* Der estländishe Brennschiefer-Kukersit, seine Chemie, Technologie und Analyse, 2 Aufl. Rewal, 1943.
27. *Dobryansky, A. F.* Oil Shale of the USSR. – Leningrad-Moscow: Gostoptekhizdat, 1947. 232 pp. [in Russian].
28. *Dobryansky, A. F.* In: Low-Temperature Catalytical transformations of hydrocarbons. – Leningrad: Leningrad University Publishing House, 1962. P. 12 [in Russian].
29. *Isakov, G. A.* About Melting Properties of Estonian Oil Shale. – Thesis of PhD. Mendeleyev name MKhTI, 1955 [in Russian].
30. *Kozhevnikov, A. V.* Oil Shale IV. Retorting and Oil Processing. – Tartu: State Publishing House “Scientific Literature”, Tartu, 1948. 188 pp. [in Russian].
31. *Vainshtein, Ya. I.* The Influence of Certain Factors on Thermal Decomposition of Gdovian Oil Shale. – Thesis of PhD.
32. *Rakovsky, V. E.* General Chemical Technology of Peat. – Gosenergoizdat, 1949 [in Russian].
33. *Rakovsky, V. E., Kaganovich, F. L., Novichkova, E. A.* Chemistry of Pyrogenetic Processes. – Belorussian SSR Acad. Sci. Publishing House, 1959. 208 pp. [in Russian].
34. *Aarna, A. Ya.* About dynamics of evolution of volatiles in thermal destruction of oil shales. – Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63. P. 65-81 [in Russian].

35. *Kask, K. A.* About bituminizing of kerogen of oil shale-kukersite. Report I. – Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63. P. 51-64 [in Russian].
36. *Karavaev, N. M., Vener, I. M.* In: Chemistry and Genesis of Fossil Fuels. – USSR Acad. Sci. Publishing House, 1953. P. 36 [in Russian].
37. *Aarna, A. Ya., Rikken, Yu. T.* Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63 [in Russian].
38. *Rikken, Y. T.* In: Oil shale. Chemistry and Technology". 1959, No. 3. P. 31 [in Russian].
39. *Zelenin, N. I., Chernyshova, K. B.* Transactions of VNIIPS. 1956, No. 5. P. 237 and 1958, No. 6. P. 144 [in Russian].
40. *Kollerov, D. K.* Rate of thermal destruction of organic matter from oil shales. – Chemistry and Technology of Fuels. 1956, No. 10. P. 55-62 [in Russian].
41. *Kask, K. A.* Composition, Properties and Application of Oil Shale Bitumen. – Thesis of PhD. Estonian SSR Acad. Sci., 1964 [in Russian].
42. *Luts, K.* Chemistry of Estonian Oil Shale. 1934. P. 109-110 [in Russian].
43. *Popov, N. V., Tsybasov, V. P.* Oil Shale. 1931, No. 1 [in Russian].
44. *Aarna, A. Y.* Isothermal destruction of Baltic oil shale. – Transactions of Tallinn Polytechnic Institute. Series A. 1954. No. 57. P. 32–44 [in Russian].
45. *Mityurev, A. K.* Mechanism and kinetics of thermal decomposition of Baltic oil shale. – Transactions of VNIIPS. No. 6. Gostoptehizdat, 1958 [in Russian].
46. *Aarna, A. Y., Lippmaa, E. T.* Thermal destruction of oil shale-kukersite. – Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 3–38 [in Russian].
47. *Aarna, A. Ya., Rikken Yu. T.* On the mechanism of low-temperature decomposition of kukersite oil shale. – Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 53-67[in Russian].
48. *Jefimov, V., Purre, T.* Characteristics of kukersite oil shale, some regularities and features of its retorting. – Oil Shale. 1993. Vol. 10, No. 4. P. 313–319.
49. *Klewer, H. W., Mauch, K.* Über den estlandischen Ölschiefer "Kukersit". – Halle, 1927.
50. *Kogerman, P. N., Kopwillem, J. J.* Hydrogenation of Estonian oil shale and shale oil. – Inst. Petrol. Technol. 1932. Vol. 18, No. 108. P. 833–845.
51. *Luts, K.* Der estländische Brennschiefer Kukersit, seine Chemie, Technologie und Analyse. – Reval, 1934.
52. *Karavayev, N. M., Wener, I. M.* About thermobitum of Gdov oil shale. – Transactions of the Institute of Goryuchih Iskopayemyh. Academy of Sciences of USSR. 1950. Vol. 2. P. 285–295 [in Russian].
53. *Aarna, A. Y.* Dynamic of separation of volatile products at thermal destruction of oil shale. – Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63. P. 65–81 [in Russian].

54. *Schulman, A. I.* Investigation of Bituminizing Process of Shale Organic Concentrate. – Thesis of PhD. Leningrad: VNIINeftekhim, 1968 [in Russian].
55. *Fomina, A. S., Pobul, L. Y., Degteryova, Z. A.* Origin of Kerogen of Baltic Oil Shale and its Chemical Characteristics as Raw Material. – Tallinn: Acad. Sci. Estonian SSR, 1965 [in Russian].
56. *Kask, K. A., Mihkelson, V. J.* The chemical composition of thermobitumen of kukersite oil shale. – Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 68–84 [in Russian].
57. *Aarna, A., Alev, M.* Investigation of low-temperature destruction of kukersite shale by infrared spectroscopy. – Transactions of Tallinn Polytechnic Institute. Series A. 1964. No. 210. P. 3–14 [in Russian].
58. *Broi-Karre, G., Proskuryakov, V.* Investigation of low-temperature destruction of Gdov oil shale concentrate by infrared spectroscopy. – J. Appl. Chem. 1966. Vol. 39, No. 5. P. 1214–1216 [in Russian].
59. *Lille, Ü., Pehk, T., Purre, T., Bitter, L.* Examination of the structure of heavy shale oil by means of NMR-spectroscopy. – Proc. Acad. Sci. ESSR. Chem. 1973. Vol. 22, No 1. P. 17–25 [in Russian with English summary].
60. *Miknis, F. P., Turner, T. F., Berdan, G. L., Conn, P. J.* Formation of soluble products from thermal decomposition of Colorado and Kentucky oil shales. – Energy & Fuels. 1987. Vol. 1, No. 6. P. 477–483.
61. *Sadeghi, K. M., Sadeghi, M-A., Wen Hui Wu, Teh Fu Yen*. Fractionation of various heavy oils and bitumen for characterization based on polarity. – Fuel. 1989. Vol. 68, No. 6. P. 782–787.
62. *Brown, M. E.* Introduction to thermal analysis: Techniques and applications, Chapman and Hall, London, 1988, P. 127-151.
63. *Steinfeld, J. I., Francisco, J. S., Hase, W. L.* Chemical Kinetics and Dynamics, second ed., Prentice Hall, Upper Saddle River, N.J., 1999.
64. *Brown, M. E.* Introduction to thermal analysis: Techniques and applications, 2nd ed, Kluwer, Amsterdam, 2001, Chapter 10.
65. *Laidler, K. J.* The development of the Arrhenius equation. – J. Chem. Educ. 1984. Vol. 61, No. 6. P. 494-498.
66. *Brown, M. E.* Stocktaking in the kinetics cupboard. – J. Therm. Anal. Cal. 2005. Vol. 82, No. 3. P. 665-669.
67. *Luik, H., Vink, N., Lindaru, E.* Upgrading of Estonian shale oil. 1. Effects of hydrogenation on the chemical composition of kukersite retort oil. – Oil Shale. 1996. Vol. 13, No. 1. P. 13–19.
68. *Aarna, A. Y.* About kinetics of thermal destruction of Baltic oil shale. – J. Appl. Chem. 1956. Vol. 29, No. 4. P. 606–610 [in Russian].
69. *Kotkas, R.* Activation energy of thermal decomposition of shale oil. – Processing of Shale Oil and Phenols. Transactions of NIIS. Tallinn: "Valgus", 1976. Vol. 21. P. 30-37 [in Russian].

ABSTRACT

The retorting technologies of kukersite being in use at industrial production of shale oil lose with semicoke arising at the secondary cracking of an intermediate product, thermobitumen (TB), more than one third of organic feedstock for liquid fuels.

In this work, the theoretical basis is described for a new technology where the soluble in organic solvents TB is extracted in the stage of thermobituminization. As a result, more than 80% of organic matter can be liquefied, and the demand for oil shale and amount of hazardous semicoke wastes per oil unit can be both substantially decreased.

A literature review concerning formation and characteristics of TB and pyrolysis kinetics is given.

The laboratory experimental series concerning effects of temperature and duration on the yield of volatiles, benzene (and methanol) extract, and solid residue at low-temperature pyrolysis (340-410 °C) of powdered Kukersite in autoclaves and open retorts are described.

A new kinetic model is proposed simulating the complex pyrolysis process by the first-order parallel phase transformations of kerogen into volatiles (gas and oil at retorting, and gas in autoclaves), extract (TB at retorting, and TBO in autoclaves), and the secondary cracking of the extract into volatiles and coke.

The rate factors (k_1-k_4) and distribution factors (B_i) of the phase components at various temperatures, and the apparent activation energies (E_1-E_4) and frequency factors (A_1-A_4) are estimated for the phase transformations in autoclaves and open retorts introducing the experimental results obtained into the linear algorithms deduced. The common kinetic compensation effect is revealed between the kinetic constants in the both devices.

The time-dependence of the current yields of products is calculated at different nominal temperatures basing on the model created. The predicted results show that at a unified heating regime an insignificant acceleration of the primary and secondary decomposition processes occurs in autoclaves in the environment of the decomposition products in comparison with the retorting tests.

KOKKUVÕTE

Kukersiidist õli tootmiseks tööstuslikult kasutatavates tehnoloogiates jääb vaheproduktina moodustuva termobituumeni (TB) sekundaarsel koksistumisel üle kolmandiku õlitoormest kaduma.

Käesolevas töös kirjeldatakse teoreetilisi aluseid uuele tehnoloogiale, kus orgaanilistes lahustites lahustuv TB ekstraheeritakse termobituminiseerumise etapil. Selle tulemusel vedeldatakse üle 80% orgaanilisest ainest ja väheneb oluliselt nii ühe õliühiku kohta vajatav kukersiidi kogus kui ka ohtliku jäätmena ladestatav või põletatav poolkoksi kogus.

Esitatakse kirjanduse ülevaade TB moodustumisest, omadustest ja pürolüüsi kineetikast.

Kirjeldatakse laboratoorsete katsete seeriaid, millega selgitati temperatuuri ja kestuse mõju lenduvate, benseeni (ja metanooli) ekstrakti ning tahke jäägi saagisele peenendatud kukersiidi madalatemperatuurilisel (340-410 °C) pürolüüsil nii autoklaavis kui ka avatud retordis.

On loodud uus kineetiline mudel, mis simuleerib uuritavat kompleksset pürolüüsiprotsessi esimest järku paralleelsete ja järjestikuliste faasimuutustena, kus lähtekerogeen laguneb lenduvateks (autoklaavis – gaas, retordis – gaas ja õli) ja ekstraktiks [autoklaavis – õli ja TB (nn. TBO), retordis – TB], ning moodustunud ekstrakt laguneb sekundaarse reaktsioonina lenduvateks ja koksiks.

Katsetulemuste viimisel tuletatud lineaarsetesse algoritmidesse on vastavate tõusude ja vabaliikmete järgi määratud faasimuutuste kiirustegurid (k_1-k_4) ja faasikomponentide jaotustegurid (B_i) erinevatel temperatuuridel, ning näivad aktivatsioonienergiad (E_1-E_4) ja sagedustegurid (A_1-A_4). On näidatud, et mõlemale seadmele määratud kineetiliste konstantide puhul kehtib ühtne $\ln A$ ja E vaheline lineaarne sõltuvus, nn. kineetiline kompensatsiooniefekt.

Kasutades loodud mudelit on arvutatud saaduste jooksvad saagised erinevatel nominaaltemperatuuridel. Samal kuumutamiskiirusel prognoositud tulemuste võrdlemisel ilmneb, et suletud ja avatud seadmes on pürolüüsikiirused lähedased. Autoklaavis, kus lagunemine toimub pürolüüsisaaduste keskkonnas, on nii sihtprodukti, TBO moodustumine kui ka TBO ebasoovitav sekundaarne koksistumine vaid mitteoluliselt kiiremad kui retordis.

APPENDIX A

PAPER I

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Yields and Properties of Thermal Bitumen Obtained from Combustible Shale

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Abstract—Currently available data on the thermal bituminization of kukersite are summarized in order to perform the isolation of a maximum amount of liquid organic substances from kukersite through the stage of thermal bitumen formation. To separate organic and mineral shale components, the quantitative yields and properties of thermal bitumen depending on the temperature and isothermal exposure time of a combustible shale sample in a Fischer retort were refined. The experimental temperature range was 370–410°C, and the isothermal exposure time was 20–60 min. Instrumental analysis techniques were used.

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The use of uncommon fuels, including combustible shale, is of increasing current interest as petroleum reserves become depleted and petroleum product prices keep rising. Combustible shale is considered not only an energy reserve but also a promising source for the production of artificial liquid fuel and valuable chemical products.

The Republic of Estonia with its developed shale industry has wide experience in the development and operation of units for the thermal treatment of kukersite. This experience suggests that a number of special features should be taken into account in order to perform the industrial conversion of rich bituminous shale. The thermal treatment of shale is a traditional industrial process for the production of final products such as stove fuel and mazut [1, 2].

It is well known that the decomposition of kukersite occurs in accordance with the following mechanism: As the kerogen is heated above 250°C, the high-molecular-weight kerogen structure begins to decompose into molecules with lower molecular weights. The following empirical formula of the kerogen was proposed: $C_{421}H_{638}O_{44}S_4NCl$ [3–6]. Then, as the temperature is increased to 300°C, about 65–70% kerogen turned into a plastic state; in this case, the duration of kerogen decomposition at 300°C was as long as 370 h. The thermal bitumen formed because of shale heating can be considered a primary product of kerogen decomposition; this product contains the structural groups of kerogen. It was noted that the formation of thermal bitumen accelerated with temperature. A group of compounds capable of dissolving in an alcohol–benzene mixture or benzene in the extraction of a solid residue obtained after the thermal decomposition of shale in a retort or autoclave is referred to as thermal bitumen [7].

The chemical composition and yield of thermal bitumen depend on the conditions of thermal bitumen formation: temperature, process time, and heat transfer, which depends on the design of apparatus. Thermal bitumen is unstable, and it is readily oxidized in air [8].

Thermal bitumen has been prepared and characterized by many researchers in the mid-twentieth century. It was found that light fractions formed at the initial stages of the process positively affected the formation of thermal bitumen. Medium and heavy fractions were formed as the temperature was increased. The formation of thermal bitumen came into play at 360°C; in this case, coke formation was not observed [9].

The thermal decomposition of thermal bitumen occurred to form particles with a molecular weight of 400–500 amu. At the initial stage of the process, the cleavage of unstable oxygen (ether) bonds and weakened carbon–carbon bonds occurred. At temperatures higher than 400°C, heavy tar, which was formed by the decomposition of a portion of thermal bitumen, underwent cracking to result in the formation of an additional amount (20% of the total amount) of low-boiling tar fractions [10]. It was experimentally found that kukersite can be converted into thermal bitumen in a high yield over a wide temperature range: more than 70% of kerogen can be converted into a thermal bitumen state at 330–380°C without a noticeable amount of coke [11]. According to experimental data, the yield of thermal bitumen from shale kukersite was as high as 76%; the molecular weight of thermal bitumen was lower than 1000 amu, and the empirical formula was $C_{65}H_{88}O_4$ [12].

In the bituminization of kukersite in a laboratory retort, organic matter was distributed between volatile products (tar, decomposition water, and gas), thermal bitumen, and semicoke. The amount of the resulting products depended on experimental conditions. Temperature and isothermal exposure time are the main experimental parameters of the thermal bituminization of shale. Based on experimental data, it was proposed to perform the formation of thermal bitumen at a higher temperature for a short heating time [13]. In this case, it was noted that the process duration is important for decreasing the stage of coke formation.

The molecular weight and elemental composition of thermal bitumen depend on process conditions. At the early stage, the carbon and hydrogen contents of the resulting thermal bitumen were about 82 and 10 wt %, respectively. The carbon content increased and the hydrogen content decreased as the temperature or time of thermal bituminization was increased. Under more severe bituminization conditions, a portion of thermal bitumen was depleted in hydrogen because of a hydrogen redistribution so that it was converted into a benzene-insoluble substance, which occurred as a constituent of the solid residue together with mineral matter.

The oxygen content of thermal bitumen was about 7%. The cleavage of oxygen bonds occurred even at a low temperature and primarily depended on process duration [11]. The oxygen content can decrease to 5% or lower as time of thermal bitumen formation increased. Consequently, the thermal decomposition of shale should be performed slowly in order to obtain thermal bitumen with a low concentration of oxygen compounds.

The sulfur content of kukersite was 1.5–1.9%. As the process temperature or isothermal exposure time was increased, the sulfur content of thermal bitumen decreased because of the conversion of the major portion of sulfur into decomposition products.

According to experimental data on the preparation of thermal bitumen in the temperature range 380–410°C with a kukersite flotation concentrate containing, on average, 70% kerogen, the maximum yield of thermal bitumen was found to be 81–83% on a raw material basis at 390°C and an isothermal exposure time of 20 to 40 min [14].

Thermal bitumen containing 31–33% malthenes (medium-molecular-weight fractions of oils and tars soluble in C_5–C_7 paraffin hydrocarbons) and 64–67% asphaltenes (high-molecular-weight compounds soluble in benzene and insoluble in C_5–C_7 paraffin hydrocarbons) was formed at optimum temperature and isothermal exposure duration [14].

To refine conditions reported in publications for the maximum extraction of the organic matter of shale through the stage of thermal bituminization, we heated a kukersite sample in a Fischer retort over optimum temperature and time ranges, which were found previously as conditions required for the maximum yield of thermal bitumen. In this work, experiments were performed in the temperature range 370–410°C, and the isothermal exposure time was varied from 20 to 60 min.

EXPERIMENTAL

The experiments on shale bituminization were performed in an aluminum Fischer retort. Kukersite was used in the experiments. A shale sample was heated in the Fischer retort according to the ISO 674-74 standard. The method consisted in the following: a fuel sample was heated in an aluminum retort to a specified temperature in the range from 370 to 410°C; the isothermal exposure time was 20–60 min. The rates of heating to 220°C, from 220 to 310°C, from 310 to 370°C, and from 370 to 410°C were 20, 9, 7, and 6 K/min, respectively. The products of decomposition were collected in a receiver cooled with water; tar and water condensed, whereas gaseous substances released were vented to the atmosphere through a wet gas meter. The semicoke residue in the retort was weighed. The receiver flask was weighed together with the condensation products. The weight of water in the receiver was determined by volumetry (distillation with toluene), and the weight of tar was calculated by difference. The total weight of water in the receiver involved the sample moisture and the pyrogenetic water formed by the decomposition of fuel. The gas yield was determined as the difference between the initial sample weight and the total yield of semicoke, tar, and water. The results of analysis were calculated on a dry fuel basis.

The shale moisture was determined in accordance with the EVS 668:1996 standard. A weighing bottle with a sample of about 1 g was dried for 5 min in a drying oven preheated from 155 to 160°C. Thereafter, the samples were cooled for 2–3 min and placed in a desiccator; 20 min later, the samples were weighed. As a result, the shale sample weight decreased. Analytical moisture was calculated from the equation $W = 100 - (M_1/M) \cdot 100$ wt %, where M_1 is the sample weight after the analysis, and M is the initial sample weight.

The ash content of shale was determined according to EVS 669:1996. A sample of about 1 g placed in a boat was arranged in a muffle furnace at room temperature. The furnace temperature was increased to 250°C for 30 min, to 500°C for another 30 min, and then to 815 ± 15°C for 60 min. After the heating, the boat was removed from the muffle furnace, and the sample was cooled to room temperature in a desiccator and weighed. The results of analysis were calculated by the equation $A = (M_1/M) \cdot 100\%$, where M_1 is the sample weight after the experiment, and M is the initial weight.

To experimentally study the formation of thermal bitumen from kukersite in a Fischer retort, we determined the organic matter of shale to be 32.3%; the yield

Table 1. Material balance on the Fisher retort

Temperature, °C	Exposure time, min	Material balance, %			
		tar	solid residue	water	gas + losses
370	20	1.4	96.6	0.6	1.4
380	20	2.6	94.4	0.8	2.2
390	20	4.6	92.5	1.0	1.9
400	20	7.8	88.2	1.2	2.8
410	20	11.1	85.2	1.4	2.4
380	30	3.6	93.8	0.7	1.9
390	30	4.4	92.8	0.5	2.2
400	30	10.3	86.3	1.0	2.4
410	30	14.2	81.4	1.2	3.2
370	60	7.2	88.9	0.9	3.0
390	60	10.5	85.3	1.0	3.2
410	60	16.5	79.0	1.6	2.9

Table 2. Yields of thermal bitumen and tar in terms of the organic matter of shale

Temperature, °C	Exposure time, min	Yield, %	
		thermal bitumen	thermal bitumen + tar
370	20	25.9	34.55
380	20	55.29	74.56
390	20	61.61	84.71
400	20	60.40	88.55
410	20	58.90	89.02
370	60	55.11	78.18
390	60	57.0	89.51
410	60	47.8	84.46
380	30	58.0	80.38
390	30	62.1	89.96
400	30	56.9	87.29
410	30	54.9	86.63

of tar was 24%. A Costech 4010 analyzer was used to perform elemental analysis. The elemental composition of shale was calculated using a weighed sample (%): C, 29.8; H, 3.1; S, 1.44; N, 0.1. Shale with the following technical characteristics was used in the experiments: moisture content, 0.6%; shale ash content, 48.6% (on a dry matter basis); shale sulfur content, 1.2%. The product yields of shale semicoking in a Fischer retort were the following: tar, 24%; semicoke, 69.3%; pyrogenic water, 1.6%; gas and losses, 5.1%.

The extraction of thermal bitumen from the solid residue obtained in a Fischer retort with an alcohol–benzene mixture was performed in a Soxhlet apparatus. The extraction was continued until the solvent in the extractor became colorless. Thereafter, the alcohol–benzene mixture was distilled from the dissolved thermal bitumen in a glycerol bath and the thermal bitumen sample was dried to constant weight in a vacuum oven. The yield of thermal bitumen was calculated with reference to the concentration of the organic matter of shale.

The concentration of malthenes was determined in accordance with the EVS 652:1994 standard. Pentane was used as an extractant for the extraction of malthenes from thermal bitumen. The percentage of malthenes was calculated from the equation $M_m = 100 - (M_1/M) \cdot 100$ wt %, where M_1 is the sample weight on a filter after extraction and drying to constant weight, and M is the total sample weight. The IR spectra were measured on an Interspec 2020 FTIR spectrometer.

RESULTS AND DISCUSSION

Table 1 summarizes the yields of semicoking products obtained under varying rated temperature and isothermal exposure time. Table 2 summarizes the yields of thermal bitumen experimentally obtained by Soxhlet extraction with an alcohol–benzene mixture.

Table 3. Effect of process temperature on the elemental composition of thermal bitumen at an exposure time of 20 min

Temperature, °C	Element					H/C ratio
	C	H	N	S	O	
370	76.4	9.7	0.26	0.9	12.74	1.52
380	79.5	9.9	0.30	0.8	9.5	1.49
390	80.3	9.5	0.27	0.8	9.13	1.42
400	81.1	8.9	0.25	0.6	9.15	1.32
410	81.2	8.8	0.26	0.7	11	1.30

The material balance on the Fischer retort clearly indicates that the formation of thermal bitumen occurred simultaneously with tar and gas formation reactions. The resulting solid residue contained both mineral and organic matter from the shale sample as thermal bitumen, a small fraction of coke, and undecomposed organic matter of kukersite. We experimentally supported the previously found dependence of the yield of thermal bitumen on temperature and isothermal exposure time. The lower the temperature of thermal bituminization, the longer the time of an isothermal exposure of the shale sample required for the formation of a larger amount of thermal bitumen, as compared with experiments in which the isothermal exposure time was shorter. If the isothermal exposure time is relatively short, this time is insufficient for transforming the organic matter of kukersite into a plastic state and a substance soluble in alcohol–benzene. It can also be clearly seen that the process of tar formation came into

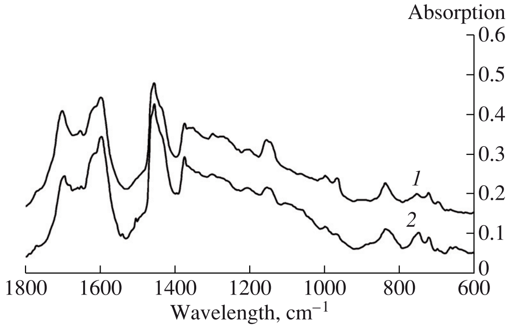

Fig. 1. IR spectra (600–1800 cm^{-1}) of thermal bitumens obtained at 370°C and isothermal exposure times of (*1*) 20 and (*2*) 60 min.

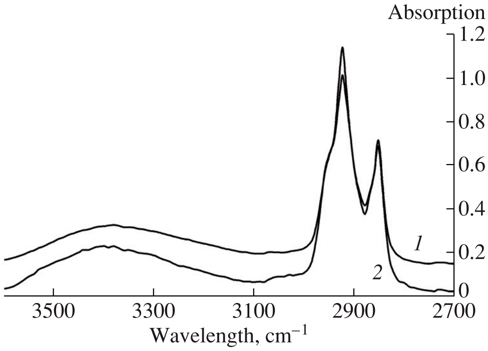

Fig. 2. IR spectra (2700–3600 cm^{-1}) of thermal bitumens obtained at 370°C and isothermal exposure times of (*1*) 20 and (*2*) 60 min.

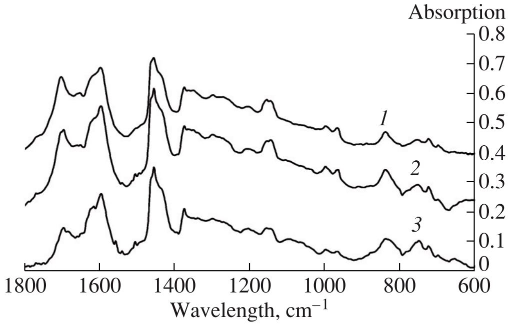

Fig. 3. IR spectra (600–1800 cm^{-1}) of thermal bitumens obtained at (*1*) 370, (*2*) 390, and (*3*) 410°C and an isothermal exposure time of 20 min.

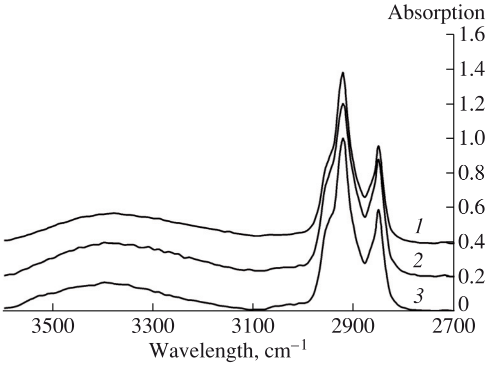

Fig. 4. IR spectra (2700–3600 cm^{-1}) of thermal bitumens obtained at (*1*) 370, (*2*) 390, and (*3*) 410°C and an isothermal exposure time of 20 min.

play with the onset of thermal bituminization; in this case, the gas release occurred slowly. The experiments with 20- and 60-min exposures at 370°C demonstrated the effect of isothermal exposure time on the quantitative formation of thermal bitumen. Based on the experimental data, it is believed that an optimum temperature of thermal bituminization is 390°C at an exposure of 20–30 min, where the yield of thermal bitumen is higher than 60%. A practically maximal recovery (89.96%) of soluble products from the organic matter of kukersite as the sum of thermal bitumen and tar without considerable coke formation can be performed at 390°C and an exposure of 30–60 min.

To characterize thermal bitumen, we studied the samples using elemental analysis and IR spectroscopy. The elemental analysis data indicate that the carbon content of the thermal bitumen increased and the hydrogen content decreased as the temperature of thermal bituminization was increased; this resulted in a decrease in the H/C atomic ratio. Table 3 summarizes the elemental analyses of thermal bitumens.

The elemental analysis of thermal bitumen was compared with the elemental analyses of generator tar and heavy-fraction tar obtained by the distillation of generator tar in order to determine the repeatability of the elemental compositions of the starting material and its products. A comparison of data given in Table 4 exhibited similar elemental compositions, when the yield of thermal bitumen at 390–410°C was almost twice as high as the yield of oils. It is evident that, in the subsequent decomposition of thermal bitumen, the formation of oils was accompanied by an almost equivalent conversion of carbon and hydrogen into coke and gas, respectively.

To obtain data on the group composition of thermal bitumen and changes that occurred under varying experimental conditions, we studied the samples with the use of an IR spectrometer. The resulting spectra

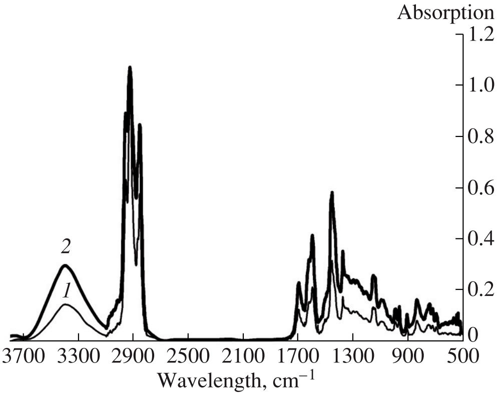

Fig. 5. IR spectra of (*1*) tar obtained in the formation of thermal bitumen and (*2*) tar obtained in the semicoking of kukersite in a Fischer retort.

indicated a set of structures of many compounds formed in thermal bitumen as a result of the thermal decomposition of kukersite. The experimental conditions were the following: the isothermal exposure times were 20 and 60 min, and the process temperature was 370°C. The yield of thermal bitumen under the given conditions was 25.9 and 55.11%, respectively. Figures 1 and 2 show the spectra in different regions. Figure 1 (curve *1*) clearly exhibits a peak at about 970 cm^{-1}, which shows the planar vibration of aromatic hydrogen. This also characterizes possible substitution for hydrogen atoms in a benzene ring. In the region 1000–1100 cm^{-1}, changes in aromatic hydrogen in the benzene ring were observed because of the chemical instability of substituents with increasing exposure duration. In the regions of the vibrations of a carbon skeleton and the carbon–oxygen bond (1100–1300 cm^{-1}), no considerable differences in the spectra were observed. 1300–1500 cm^{-1} is the region of diffraction vibrations of hydrogen in aliphatic structures. The spectra also exhibited no considerable differences in this region. The aromatic ring region at 1600 cm^{-1} was represented by identical absorption bands. A decrease in the intensity of a peak due to carbonyl compounds (esters, ketones, and aldehydes) in the region 1700–1800 cm^{-1} with time was observed. The region of the symmetric stretching vibration of hydrogen in the CH_2 group at 2850 cm^{-1} was represented without considerable differences. Differences in the antisymmetric stretching vibration of hydrogen in the CH_2 group at 2925 cm^{-1} were not observed in the experimental spectra. In these two spectra, the valence bond of oxygen and hydrogen manifested itself as phenolic hydroxyl vibrations. The spectra exhibited no considerable differences.

Table 4. Elemental composition of generator tar and a heavy mazut fraction

Product	Element				H/C ratio
	C	H	S	N + O	
Generator tar	83	9.7	1	6.3	1.40
Heavy tar fraction after distillation	82.2	9.5	0.5	0.2	1.39
Kerogen	76.9	9.7	1.9	10.9	1.51

Table 5. Yield of malthenes under various conditions of thermal bitumen formation

Temperature, °C	Exposure time, min	Yield, %
370	20	13.42
390	20	25.05
400	20	29.38
410	20	19.64

To determine the effect of temperature on the group composition of the resulting thermal bitumen, we measured the spectra of products obtained at 370, 390, and 410°C; the exothermal exposure time was 20 min. Figures 3 and 4 show the spectra. The region at about 970 cm^{-1} demonstrates the effect of increasing temperature on the molecular degradation, which changes the character of hydrogen substitution in the benzene ring in thermal bitumen. No considerable differences between the spectra under comparison were observed in the other regions.

Based on a comparison between the IR spectra of tar obtained in the formation of thermal bitumen (390°C and a 40-min exposure) and tar obtained after a standard process of kukersite semicoking in a Fischer retort, we can conclude that no considerable differences were observed in the spectra; this fact suggests similar mechanisms of tar formation. Figure 5 shows the spectra.

It is well known that the quantitative determination of the concentration of malthenes in thermal bitumen is a characteristic of thermal bitumen. The experimental data given in Table 5 clearly indicate that the yield of malthenes increased to a certain value as the temperature and isothermal exposure time were increased. A maximum amount of malthenes in thermal bitumen was observed at 390–400°C; then, degradation and condensation reactions came into play in thermal bitumen. Because of these reactions, malthenes underwent decomposition with the formation of volatile products and carboides.

CONCLUSIONS

(1) We performed laboratory experiments on the formation of thermal bitumen from kukersite in a Fischer retort heated to 370–410°C at a rate of 6–20°C/min with isothermal exposures of 20, 30, and 60 min. The composition of thermal bitumen depended on process conditions. The effects of temperature and exposure time on the quantitative yield of products were determined.

(2) The stage of primary thermal bitumen formation with a minimum amount of carboides formed was detected. As the temperature was increased at the same exposure time, the yield of thermal bitumen increased to a maximum value of 62.1% at 390°C. At 370–400°C, an increase in the isothermal exposure time resulted in an increase in the yield of thermal bitumen.

(3) The presence of identical functional groups in tar obtained by a standard method for the determination of the quantitative yield of tar in a Fischer retort and in tar from the process of primary thermal bitumen formation suggested the similarity of tar formation mechanisms.

(4) The concentration of malthenes in thermal bitumen changed depending on experimental conditions. At the initial stage of the process, the yield of malthenes was lower than that at a maximum formation of thermal bitumen. Thereafter, the yield of malthenes decreased as the process temperature was increased above 410°C. This was explained by the onset of the active occurrence of condensation reactions and the degradation of primary thermal bitumen to products that are more stable.

REFERENCES

1. *ASTM 31-D3904: Oil from Oil Shale*, 1980.
2. Efimov, V.M., Piik, E.E., and Rappu, L.I., *Khimiya i Tekhnologiya Goryuchikh Slantsev: Trudy NII Slantsev,* 1973, no. 19, p. 29.
3. *Spravochnik slantsepererabotchika* (Shale Processor's Handbook), Grudin, M.G. and Serebryannikov, N.D., Eds., Leningrad: Khimiya, 1988.
4. Dobryanskii, A.F., *Goryuchie slantsy SSSR* (USSR Combustible Shales), Leningrad: Lengostoptekhizdat, 1947.
5. Lille, Ü., Heinmaa, I., and Pehk, T., *Fuel*, 2003, vol. 82, no. 7, p. 799.
6. Lille, Ü., *Oil Shale,* 2003, vol. 3, no. 3, p. 253.
7. Aarna, A., *Põlevkivi*, Tallinn: Valgus, 1989.
8. Khisin, Ya.I., *Termicheskoe razlozhenie goryuchikh slantsev* (Thermal Degradation of Combustible Shales), Leningrad, 1948.
9. Aarna, A.Ya. and Lippmaa, E.T., *Tr. TPI,* 1958, no. 97, p. 15.
10. Aarna, A.Ya., *Tr. TPI*, 1954, no. 57, p. 32.
11. Kask, K.A., *Tr. TPI*, 1955, no. 63, p. 51.
12. Puksov, A., *Cand. Sci. (Eng.) Dissertation*, Tartu: Tartu Univ., 1929.
13. Kask, K.A., *Extended Abstract of Doctoral (Chem.) Dissertation*, Tallinn: ESSR Acad. Sci., 1964.
14. Shul'man, A.I., *Extended Abstract of Cand. Sci. (Eng.) Dissertation*, Leningrad: Lensovet Technol. Inst., 1968.

PAPER II

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pp. 535–546

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FORMATION OF THERMOBITUMEN FROM OIL SHALE BY LOW-TEMPERATURE PYROLYSIS IN AN AUTOCLAVE

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This work presents a review of investigations concerning formation of thermobitumen (TB) and a systematic experimental study of thermobituminization of Baltic oil shale, Kukersite, in autoclaves. The bituminizing process was performed at different nominal temperatures (340-380 °C) and residence times (20 min–10 hours). Distribution of organic matter of the shale between thermobitumen, gas and insoluble in benzene solid residue was studied. Composition of thermobitumen depending on pyrolysis conditions was characterized. The pyrolysis process of kukersite in autoclaves consists of three stages: 1. Formation of TB and gas from kerogen until obtaining the maximum yield of TB. 2. Equilibrium of formation and thermal cleavage of TB molecules. The yield of TB is maximum and practically constant in this stage. The quantity of gas grows continously and that of organic solid residue is minimal. The lower is the temperature, the longer is the thermobituminization stage. 3. Destruction of obtained TB forming gas, coke and oil. The formed oil favors extraction of TB from solid residue, but a part of kerogen gets lost with coke. The duration of these stages depends on the nominal temperature being shorter at higher temperatures.

Introduction

The yield of shale oil obtained by pyrolysis of Baltic oil shale kukersite in industrial retorts is only 14–17%, depending on the retort configuration and by-products of low calorific value, such as gas and semicoke. The semicoke is still sent to the landfills where it represents a hazardous industrial waste.

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At laboratory retorting the organic matter (OM) is distributed between 65.6% oil, 10.7% gases, 18.3% semicoke and 5.4% pyrolytic water [1]. A more complete application of OM of oil shale is topical considering both economical and ecological aspects.

One of the characteristics of kukersite causing considerable difficulties at industrial oil production is its bituminisation – transition to the plastic state within the temperature range of 350–400 °C at slow heating. The troublesome consequences such as sticking of organic matter to the retort walls, formation of hangings, etc. have been eliminated by going through the temperatures of maximum TB formation at a relatively high speed (not less than 3–4 °C/min) [2].

The most widespread oil shales of the world typically form paraffin-rich oil at their retorting. The content of oxygen-containing compounds, including phenols, in these oils is negligible or nil. Volatile products of kukersite decomposition are thermally unstable at the moment of their formation (e.g. oxygen-containing compounds, including high-boiling phenols), and they undergo a considerably more extensive secondary pyrolytic transformation as compared with other shales. As a result, the carbonaceous residue in semicoke is of secondary origin formed at pyrolysis of these unstable compounds.

Kukersite's OM (kerogen) contains less than 1% natural soluble bitumens [1]. The data on thermal transformation of OM have proved its low thermal stability, particularly in the temperature range between 275–300 °C at which up to 30–40% of the decomposition water from its whole potential under semicoking conditions is evolved [3]. At the same time, the splitting of other simple compounds like CO_2, CO, H_2S, lower alkanes and alkenes is observed.

Klewer and Mauch [3] were the first scientists to study the temperature effect on the decomposition of kukersite. According to them, the main amount of destruction water is formed below 320 °C where the OM is destructed to volatile and soluble products and no coke is formed.

Aarna, Kask, Lippmaa, Shulman, Dobrjanski and others [2–20] have studied the formation of TB in open systems, only Kogerman and Karavayev [9] have carried out the process in autoclaves. Experiments were made varying heating time and pyrolysis temperature to study their influence on the yield and composition of oil and TB.

Kogerman [4] presented the pyrolysis of kukersite as a range of sequential processes as follows:

Below 150 °C – separation of water and occludive gases,
170–180 °C – beginning of kerogen destruction,
320–340 °C – active destruction of kerogen, beginning of gas evolution in large quantities,
380–390 °C – beginning of destruction of polymerization products forming liquid products (oil),
415–420 °C – endothermic reactions of coke formation.

Kogerman and Kopwillem [5] concluded that the yield of destruction water under the pressure 100 at is practically the same as that in open retorts and does not depend on pyrolysis atmosphere. So, kerogen should include unstable formations, possible aliphatic compounds, which transform to more stable structures emitting equal quantity of water which does not depend on pyrolysis atmosphere.

Kask and Aarna studied the yield and composition of products depending on pyrolysis conditions in Fischer retort [11–13, 16], obtained data are given in Table 1.

Table 1. **Yield and elemental composition of products obtained from kukersite by Kask [11, 12]**

Species	Yield, % TB/OM	Elemental composition, %				H/C	Molec. mass
		C	H	S	O+N		
Initial concentrated shale, (87.25% OM from shale)		82.1	10.63	0.75	6.5	1.55.	
TB 275 °C, 456 h	17.9	83.0	10.1	0.50	6.7	1.46	710
TB 300 °C, 387 h	69.8	85.1	8.77	0.32	5.8	1.24	1300
TB 340 °C, 12 h	59.8	83.8	9.78	0.52	5.9	1.40	1240
TB 360 °C, 4 h	63.8	83.6	9.56	0.50	6.3	1.37	790
TB 380 °C, 4 h	35.6	85.3	8.85	0.53	5.3	1.25	651
Organic residue insoluble in benzene (360 °C, 5 h)	1.1	83.3	10.43	0.35	5.9	1.50	

Schulman reported [14] that the maximum yield of TB was obtained at the temperature range 390–395 °C, and TB was made up to 55–57% of organic matter irrespective of oil shale quality. At these temperatures carbon content of organic solid residue (remained after extraction of TB with a mixture of ethanol-benzene) was of the minimum value.

Lille [7] gave the model of kukersite kerogen with the empirical formula $C_{421}H_{638}O_{44}S_4NCl$, according to which the elemental composition of kerogen should be, %: C – 76.9; H – 9.7; O – 10.7; S – 1.9; N – 0.2; Cl – 0.5, and the atomic ratio of H/C 1.515. According to the last studies by NMR, macromolecule of kerogen is highly aliphatic, with the ratio of aliphatic to aromatic carbons *ca* 4–5.

Aarna, Kask and Luts came to the conclusion that TB contains less hydrogen than initial kerogen [6, 7, 10, 13]. On the basis of elemental composition, Luts [6] gave the empirical formula of kerogen as $C_7H_{10}O$ and TB as $C_{65}H_{88}O_4$ with the atomic ratio of H/C 1.43 and 1.35, respectively. According to Kask [16], the formula of TB is $C_{54.8}H_{69.4}O_3$ with atomic ratio of H/C 1.27 only. Thus, along with the loss of oxygen with water formation, and that of sulfur with H_2S, also the loss of hydrogen occurs in the TB formation process. TB, formed in an open system under atmospheric pressure is a new formation which contains less both oxygen and hydrogen. At the first stage, the loss of hydrogen takes place due to emission of water and hydrogen sulfide. The main part of oxygen leaves with carbon dioxide. The oxygen, which is more strongly attached to carbon, remains in solid residue. The higher is the destruction degree, the less is the hydrogen content of TB, and the more stable is the oxygen remained. Decreasing of hydrogen content of TB, compared with that of kerogen, is more obvious if to take into account that at the first stage of thermal stabilization of OM the carbon is lost only as carbon dioxide.

Karavayev and Wener studied TB formation in an autoclave at the temperature range 350–360 °C and residence time 6–8 hours [9]. The yield of TB soluble in benzene was 71.3%, on kerogen basis, the yield of gas over 4%, and its composition was as follows: $CO_2 + H_2O$ (41.5%), C_nH_{2n} (2.0%), CO (1.8%), H_2 (13.2%), C_nH_{2n+2} (41.5%). So, the gas consisted mainly of saturated hydrocarbons and hydrogen. The oil, which in autoclaves remains together with TB, may be enriched with hydrogen because it is a product of continual destruction and intermolecular reforming of TB. At the same time, a part of primary products of complicated structure should lose the hydrogen and form an insoluble residue. Atomic H/C ratio in the process of TB formation was as follows: initial kerogen 1.46, TB 1.28, oil soluble in alcohol 1.35, TB insoluble in alcohol 1.14.

Kask [11, 12] showed that TB is miscellaneous consisting of various molecules which can be divided by solvents into fractions of different molecular mass and properties. It has been proved [12] that when TB is subjected to carbonization, the yield of oil is less than by direct semicoking of oil shale. For example, the yield of oil from kerogen at retorting of the initial shale was 66.0%, but at the two-stage carbonization of oil shale the yield of oil was only 56.9% (including 17.5% in the process of TB formation, 36.2% from retorting of separated TB and 3.2% from semicoking of the residue insoluble in benzene). The total yield of the solid residue increased from 17.9 to 25.6%, respectively. At the same time, the quantity of gas was practically constant (10.3 and 10.7%). The more complete was the low-temperature destruction of kerogen to TB, the more structures in TB appeared to be able to condensate and coke during further carbonization, and the less the material remains which could be destructed to volatiles.

TB obtained in an open system has been characterized by molecular mass, elemental composition [3–16], solvent fractionation [11, 18], infrared spectroscopy [17, 18], and NMR spectroscopy [19]. It was shown [3–16] that molecular mass and elemental composition of TB depend on bituminisation conditions. In the composition of TB were found various polycyclic compounds of different molecular mass (average 400–500) connected together by oxygen links [11]. The molecule mass of TB obtained in autoclave was about 350 [9]. At the first stage of bituminization the content of carbon in TB is approximately 82% and that of hydrogen about 10%. At higher temperatures and longer residence time the content of carbon increases and that of hydrogen decreases. Under more rigid conditions of bituminisation as a result of hydrogen redividing a part of TB becomes so poor in hydrogen that forms insoluble in benzene coke together with mineral part. The content of oxygen in TB is about 7%, and it does not depend on temperature but depends on residence time. At a longer process the oxygen content decreases, reaching 5%.

TB is a chemically active intermediate product, whose composition changes at storage.

The formation of TB as an intermediate pyrolysis state in the temperature range 375–425 °C has been described also to be typical of USA oil shale [20]. Its properties (hydrogen-to-carbon ratios, carbon aromaticity, molecular mass) vary with time and temperature of pyrolysis and depend on the original kerogen structure. Comparative characterization of the Green River shale oil, heavy petroleum oil and oil sand bitumen based on their polarity is given in [21]. Shale oil contains some α-olefins produced by cracking of hydrocarbon chain. IR spectra showed the presence of C=O, $–NH_2$, –OH groups. The presence of asphaltenes was also asserted.

Chemical composition of TB from kukersite was studied by Karavajev [9], Aarna, Lippmaa [10] and Kask [16]. For determination of functional groups, elemental analysis and chemical methods had been used. The occurrence of carboxyl, hydroxyl, carbonyl, methoxyl and ether groups had been studied. It was elucidated that TB consists mainly of oxygen-containing compounds including functional groups such as hydroxyl, carbonyl and ether. The share of the carbonyl group was small, including only 2% of total oxygen. It was established that beyond half of the elemental carbon is included into aromatic nucleus. To compare the composition of TB obtained in open or closed systems, the one from Fischer retort contains less oxygen and its molecular mass is greater. TB from autoclave contains also oil.

The above review concerning formation of TB evidences that the studies made preferably in open systems have been carried out about 50 years ago.

The aim of this work was to establish the conditions for kukersite pyrolysis in autoclaves that enable the most complete transformation of its kerogen to TB soluble in benzene. The experimental study of the bituminization process of kukersite was conducted in autoclaves at different temperatures and residence times. The dependence of material balances of the products and TB composition on pyrolysis conditions is described.

Experimental

Materials and methods

Air-dry, finely powdered (0.04–0.1 mm) kukersite, containing 0.8% moisture and 50.5% dry organic matter, was used. 20-ml micro-autoclaves were charged with 4.0 g oil shale, weighed, and placed into a muffle oven with a constant nominal temperature (340–380 °C). The residence time (from placing the autoclaves into oven) was varied from 20 min till 10 hours. The mass of gas formed was determined by the weight loss after discharging.

The thermobitumen and the formed oil were extracted exhaustively with boiling benzene in a Soxhlet extractor. The mass of insoluble in benzene residue was dried at 105–110 °C. The percentage of organic matter in kukersite and residues was estimated by burning out the mass at 825 °C from the acid-treated and dried residues. The solvent benzene was removed from TB in a vacuum rotation evaporator at 60–70 °C and after that keeping the flask in a drying oven at 80 °C during an hour. As noted in [11], removal of benzene traces from TB has been problematic work. The quantity of TB can be a little underestimated due to evaporation of low-boiling destruction products, or overestimated in the case a part of benzene, connected with TB by H-bonds, is not removed. According to the second approach, the mass of TB was found substracting the mass of gas and solid residue from the initial mass of oil shale. In this case the result can be overestimated due to admixture of the decomposition water.

The elemental composition of the TB was estimated with "Costech" analyzer. The functional group composition was investigated by FTIR-spectroscopy "Interspec 2020". The group composition was determined by thin-layer chromatography (TLC). The content of maltenes in TB was found by exhaustive extraction of TB with *n*-hexane in Soxhlet extractor.

Results and discussion

The dependence of TB yield on bituminization temperature and residence time

The thermobituminization experiments with kukersite in autoclave were carried out at different temperatures (340-380 °C) and residence times from 20 min to 10 hours. The results are given in Fig. 1.

Figure 1 demonstrates that pyrolysis process of kukersite in autoclaves consists of 3 stages:

1) Heating of shale till plastic condition and formation of TB and gas from OM. The quantities of TB and gases increase until the maximum yield of TB. At shorter residence times organic solid residue consists of undestructed OM and TB with high-molecular mass insoluble in benzene;

2) An equilibrium between formation and cleavage of TB. The yield of TB is maximum (up to 90% from OM of the initial shale) and practically constant. The quantity of gas is growing and organic solid residue is minimal. The lower the temperature, the longer the steady-state stage.

3) Further destruction of obtained TB to gas, coke and oil. The oil formed makes TB more easily extractable from the solid residue but a part of OM is lost with coke.

The length of these stages depends on temperature and is shorter at higher temperatures.

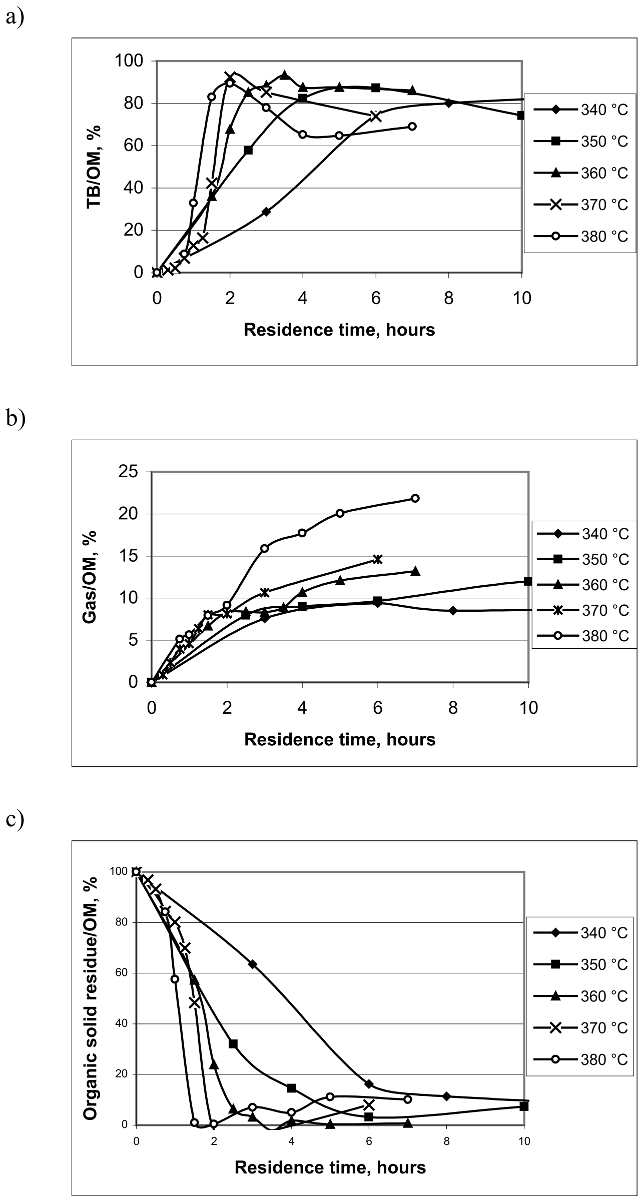

Fig. 1. Effect of time on the distribution of initial OM between TB (a), gas (b) and organic solid residue (c) at different nominal temperatures, ^{o}C.

The composition of TB

The composition of TB was characterized by its part soluble in hexane, maltenes (Table 2).

Table 2. **The content of maltenes in TB (obtained at 380 °C) depending on residence time**

Residence time	TB/OM, %	Maltenes/TB, %	Maltenes/OM, %
45 min	8.8	61.7	5.4
1 hour	32.9	36.1	11.9
2 hours	87.7	45.25	40.5
5 hours	64.7	66.6	43.1

It can be seen from Table 2 that at a short pyrolysis time when the quantity of TB is small, the share of maltenes is great – it is in accordance with the results of Aarna [8] according to which light destruction products are formed at the beginning of TB formation.

For comparison, the elemental composition of the initial kerogen, TB obtained in this work, natural bitumens from kukersite and industrial semicoking oil from open-system retorts are given in Table 3.

Table 3. **Elemental composition of different organic species from kukersite OM**

	Yield, kerogen basis, %	Elemental composition, %					H/C
		C	H	S	N	O (by difference)	
Initial kerogen [7]	100	77.3	9.8	1.7	0.4	10.8	1.52
Retort oil [1]	65.6	83.0	9.9	1.1	0.1	5.9	1.43
TB 360 °C, 3 h, autoclave	89.6	83.4	9.0	0.8	0.8	6.0	1.29
TB 360 °C, 4 h, retort [10]	63.8	83.6	9.6	0.5		6.3	1.38
Natural bitumoids [1]	0.71	71.8	10.5	–	0.5	17.2	1.75

Table 3 demonstrates that the high yield of OM from kerogen obtained by extraction of TB under its optimum low-temperatures pyrolysis conditions is contributed by low H/C ratio.

The elemental composition of TB obtained at 360 °C at different residence times is given in Table 4.

Table 4. **Dependence of elemental composition of TB on residence time (360 °C)**

Time, h	Yield, %	Elemental composition, %					H/C
		C	H	S	N	O (by difference)	
1.5	36.0	78.5	9.5	0.9	<0.75	10.2	1.45
2	53.6	81.4	9.2	0.9	<0.75	7.7	1.36
3	89.6	83.4	9.0	0.8	<0.75	6.0	1.29
5	83.0	84.8	8.6	0.7	<0.75	5.1	1.22

At retorting, the elemental composition of TB did not depend on temperature but on depth of thermolysis [11], beginning with 82% carbon, 10% hydrogen and 7% oxygen at low rate of thermolysis, while at higher rates the content of carbon increased at simultaneous decrease of hydrogen and oxygen content. The elemental composition of TB obtained in autoclave at optimum residence time for every temperature, having minimal quantity of coke, could vary only due to differences in quantity of emitting gases. As the last was not considerable (Fig. 1b), TB composition should differ not much.

The chemical group composition of commercial retort oil from oil shale processing factory, TB, and maltenes from TB are given in Table 5.

Table 5. **Chemical group composition of different species of shale oil by TLC, wt.%**

Compounds	Retort oil [22]	TB 360 °C, 3 h	Maltenes
Aliphatic hydrocarbons	11.1	3.7	5.8
Monocyclic aromatic hydrocarbons	5.4	2.0	2.5
Polycyclic aromatic hydrocarbons	23.1	4.3	20.2
Neutral oxygen compounds	16.7	9.3	22.3
High polar compounds	43.7	80.7	49.2

The composition of soluble in hexane maltenes obtained in this work using an autoclave is similar to that of an industrial retort oil containing less high-polar compounds than TB. Low amounts of aliphatic and monocyclic hydrocarbons in TB express that the product requires further upgrading for being suitable as a liquid, especially as motor fuels.

Ratio of total alkenes to alkanes in aliphatic hydrocarbons was 0.86:1.

The composition of the hydrocarbons determined by GC is given in Table 6.

Table 6. **Composition of alkenes and alkanes, wt.%**

Number of C atoms	Alkenes	Alkanes
11	0.5	–
12	0.8	0.7
13	–	9.2
14	11.8	8.9
15	2.3	13.2
16	36.3	26.4
17	2.5	17.7
18	23.3	12.4
19	3.2	7.6
20	13.1	2.4
21	–	–
22	5.0	1.5
23	–	–
24	1.2	–

It is known [23] that olefins C_{13}-C_{17} form at the beginning of kukersite destruction, that was explained by instability of isostructures, compared with the normal ones. The same tendency was discovered in the composition of maltenes from TB.

The composition of functional groups typical of maltenes and asphaltenes was investigated using infrared spectroscopic (IRS) method. The infrared spectra are presented in Fig. 2. Visible adsorptions are qualitatively similar, and differences between these two objects can be seen only in quantitative characters of hydrogen substituents in aromatic nucleus. IRS confirm the presence of benzene nucleus at 1600 and 1500–1515 cm^{-1}. The substituents are bound in different positions of benzene nucleus. The absorption typical of methyl, methylene and methyne groups in alkyl chains appears at 3000–2800, 1400–1300 and at 725 cm^{-1}. Absorptions at 2960, 2872, 1460 and 1380 cm^{-1} caused by CH_3 groups in different positions as well as those at 2930, 2860 and 790–720 cm^{-1} (CH_2 groups) are considerable. The most of methylene and methyne groups are bound to form different ring structures such as cyclic hydrocarbons and aromatic compounds. The peak at 1150 cm^{-1} refers to oxygen-carbon bond in the phenol molecule. The absorption in the region 1400–1470 cm^{-1} belongs to hydrogen in the CH_2 and CH_3 groups of aliphatic structures. Peaks in the region 2850–3000 cm^{-1} belong to alkanes, which are present in both maltenes and asphaltenes. C=O-containing compounds with the absorption maximum at 1700 cm^{-1} are clearly distinguishable.

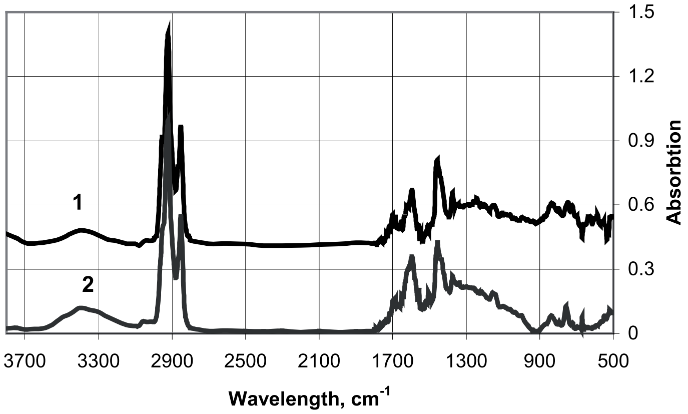

Fig. 2. FTIR spectra of maltenes (1) and asphaltenes (2) from TB obtained at 360 °C, 3 hours.

Conclusions

Experimental sudy of TB formation by low-temperature pyrolysis of kukersite in autoclaves was carried out, and the initial data for calculation of kinetics of kerogen thermobituminization were obtained. Material balances of the pyrolysis products under different pyrolysis conditions were obtained. The residence time for the highest yield of TB and that of the lowest content of insoluble in benzene coke was found for every pyrolysis temperature. The lower the temperature, the longer the steady-state stage during which up to 90% of TB from OM of the initial kukersite was achieved. The composition of TB was characterized by elemental analysis, content of maltenes (soluble in hexane) and asphaltenes and their chemical composition by TLC and IRS. It was found that 90% of TB and 72% of its maltenes consist of oxygen-containing compounds.

It was found that separation of TB from solid residue is a rather slow (laborious) process requiring extraction with a boiling solvent. Process of TB separation and its hydrogenation to meet the requirements of liquid fuels needs further elaboration.

REFERENCES

1. *Urov, K., Sumberg, A.* Characteristics of oil shales and shale-like rocks of known deposits and outcrops // Oil Shale. 1999. Vol. 16, No. 3. P. 1–64.
2. *Jefimov, V., Purre, T.* Characteristics of kukersite oil shale, some regularities and features of its retorting // Oil Shale. 1993. Vol. 10, No. 4. P. 313–319.
3. *Klewer, H. W., Mauch, K.* Über den estlandischen Ölschiefer "Kukersit". – Halle, 1927.
4. *Kogerman, P., Luts, K., Hüsse, J.* The chemistry of Estonian oil shale. – M.-L: Goshimizdat, 1934 [in Russian].
5. *Kogerman, P. N., Kopwillem, J. J.* Hydrogenation of Estonian oil shale and shale oil // Inst. Petrol. Technol. 1932. Vol. 18, No. 108. P. 833–845.
6. *Luts, K.* Der estländische Brennschiefer Kukersit, seine Chemie, Technologie and Analyse. – Reval, 1934.
7. *Lille, Ü., Heinmaa, I., Pehk, T.* Molecular model of Estonian kukersite kerogen as evaluated by ^{13}C MAS NMR spectroscopy // Fuel. 2003. Vol. 82, No. 7. P. 799–804.
8. *Aarna, A. Y.* Isothermal destruction of Baltic oil shale // Transactions of Tallinn Polytechnic Institute. Series A. 1954. No. 57. P. 32–34 [in Russian].
9. *Karavayev, N. M., Wener, I. M.* About thermobitum of Gdov oil shale // Transactions of the Institute of Goryuchih Iskopayemyh. Academy of Sciences of SSSR. 1950. Vol. 2. P. 285–295 [in Russian].
10. *Aarna, A. Y., Lippmaa, E. T.* Thermal destruction of oil shale-kukersite // Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 3–27 [in Russian].
11. *Kask, K. A.* About bituminizing of kerogen of oil shale-kukersite. Report I // Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63. P. 51–64 [in Russian].

12. *Kask, K. A.* About bituminizing of kerogen of oil shale-kukersite. Report II // Transactions of Tallinn Polytechnic Institute. Series A. 1956. No. 73. P. 23–40 [in Russian].
13. *Aarna, A. Y.* Dynamic of separation of volatile products at thermal destruction of oil shale // Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63. P. 65–81 [in Russian].
14. *Schulman, A. I.* Investigation of bituminizing process of shale organic concentrate. Thesis of PhD. Leningrad: VNIINeftehim, 1968 [in Russian].
15. *Fomina, A. S., Pobul, L. Y., Degteryova, Z. A.* Origin of kerogen of Baltic oil shale and its chemical characteristics as raw material. – Tallinn: Acad. Sci. Estonian SSR, 1965 [in Russian].
16. *Kask, K. A., Mihkelson, V. J.* The chemical composition of thermobitumen of kukersite oil shale // Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 68–84 [in Russian].
17. *Aarna, A., Alev, M.* Investigation of low-temperature destruction of kukersite shale by infrared spectroscopy // Transactions of Tallinn Polytechnic Institute. Series A. 1964. No. 210. P. 3–14 [in Russian].
18. *Broi-Karre, G., Proskuryakov, V.* Investigation of low-temperature destruction of Gdov oil shale concentrate by infrared spectroscopy // J. Appl. Chem. 1966. Vol. 39, No. 5. P. 1214–1216 [in Russian].
19. *Lille, Ü., Pehk, T., Purre, T., Bitter, L.* Examination of the structure of heavy shale oil by means of NMR spectroscopy // Proc. Acad. Sci. ESSR. Chem. 1973. Vol. 22, No 1. P. 17–25 [in Russian with English summary].
20. *Miknis, F. P., Turner, T. F., Berdan, G. L., Conn, P. J.* Formation of soluble products from thermal decomposition of Colorado and Kentucky oil shales // Energy & Fuels. 1987. Vol. 1, No. 6. P. 477–483.
21. *Sadeghi, K. M., Sadeghi, M-A., Wen Hui Wu, Teh Fu Yen*. Fractionation of various heavy oils and bitumen for characterization based on polarity // Fuel. 1989. Vol. 68, No. 6. P. 782–787.
22. *Luik, H., Vink, N., Lindaru, E.* Upgrading of Estonian shale oil. 1. Effect of hydrogenation on the chemical composition of kukersite retort oil // Oil Shale. 1996. Vol. 13, No. 1. P. 13–19.
23. *Kuningas, K., Urov, K., Rang, S., Eisen, O.* On the sequence of formation of aliphatic hydrocarbons during the thermal decomposition of the kukersite-shale // Proc. Acad. Sci. ESSR. Chem. 1977. Vol. 26, No. 2. P. 152–154 [in Russian].

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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: $\ln A = 0.176(\pm 0.009)E - 2.59(\pm 2.29)$. 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.

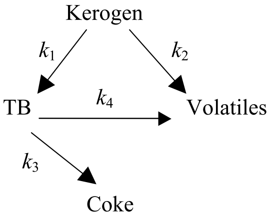

Fig. 1. Scheme of pyrolysis kinetics.

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

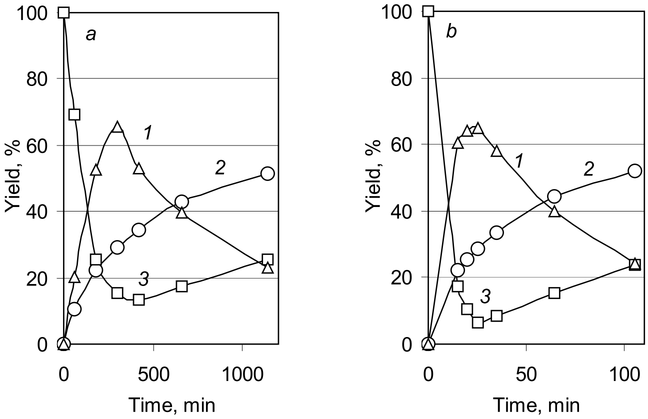

Fig. 2. Effect of retorting time on the yield of thermobitumen (*1*), volatiles (*2*) and solid residue (*3*) at isothermal retorting temperatures 350 °C *(a)* and 386 °C *(b)* by Schulman [15].

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:

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

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.

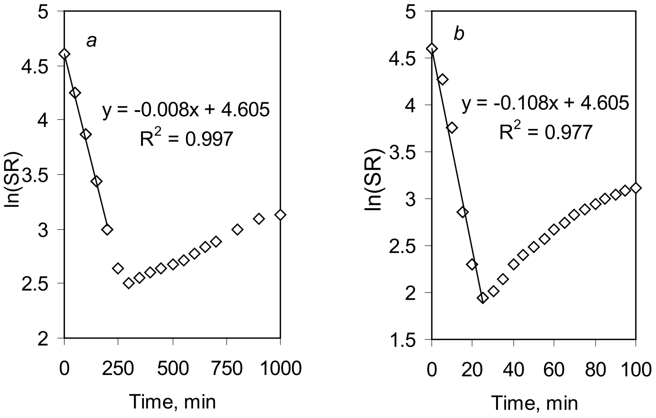

Fig. 3. Plot of logarithm from the yield of solid residue versus time at retorting temperatures 350 *(a)* and 386 °C *(b).*

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:

$$dx_1/dt = k_1y - (k_3 + k_4)\,x_1 = k_1y - k_{TB}\,x_1 \tag{3}$$

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

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

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

$$k_i = A_i\exp(-E_i/\mathrm{R}T) \tag{9}$$

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

$$E_i = [\mathrm{R}(T_1T_2)\ln(k_{i1}/k_{i2})]/(T_2 - T_1) \tag{10}$$

$$A_i = k_i\exp(E_i/\mathrm{R}T). \tag{11}$$

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].

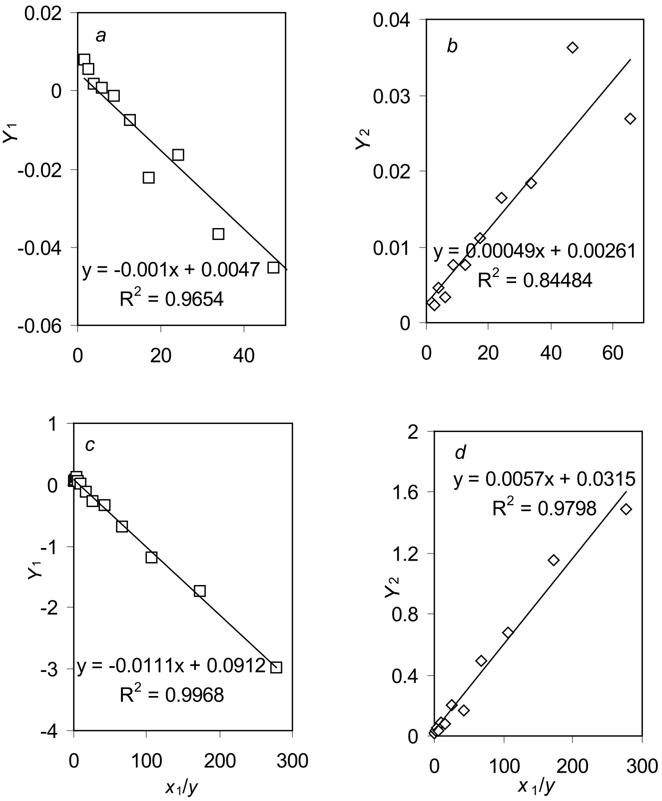

Fig. 4. Depiction of Equation (6) for estimation of k_1 and k_{TB} (*a* and *c*), and k_2 and k_4 (*b* and *c*) at temperatures 350 (*a* and *b*) and 386 °C (*c* and *d*).

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 widespread 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).

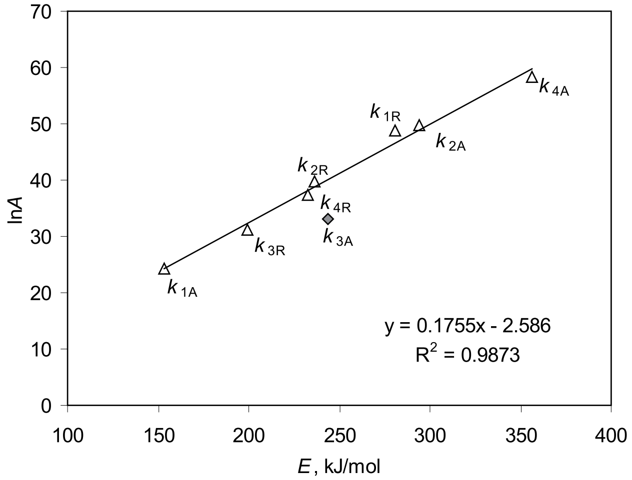

Fig. 5. Plot of ln*A* versus *E* for the rate coefficients k_i at low-temperature pyrolysis of kukersite in the laboratory autoclave (index *A*) and retort (index *R*).

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.

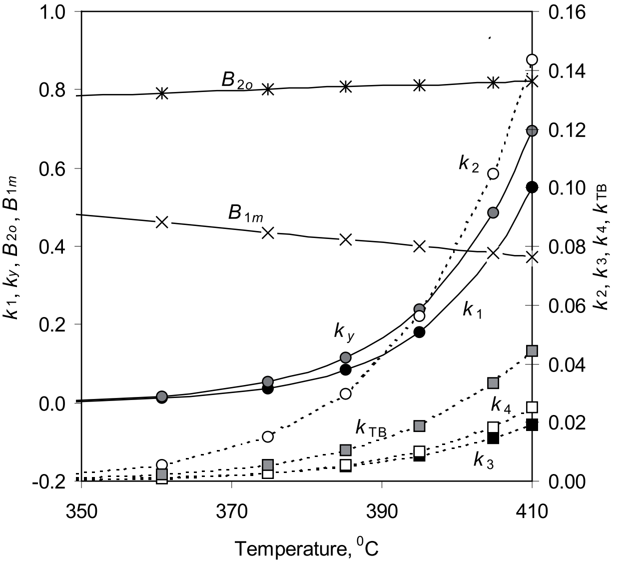

Fig. 6. Effect of temperature on the rate coefficients, 1/min, and on the share factors of malthenes in thermobitumen, B_{1m}, and of oil in volatiles, B_{2o}, formed.

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

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

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

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

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

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

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

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

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

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

- the current coke yield was calculated as the difference

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

- 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:

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

$$x_{2o,n} = x_{2o,n-1} + B_2(x_{2,n-1} - \mathrm{x}_{2,n}) \qquad (21)$$

- 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),

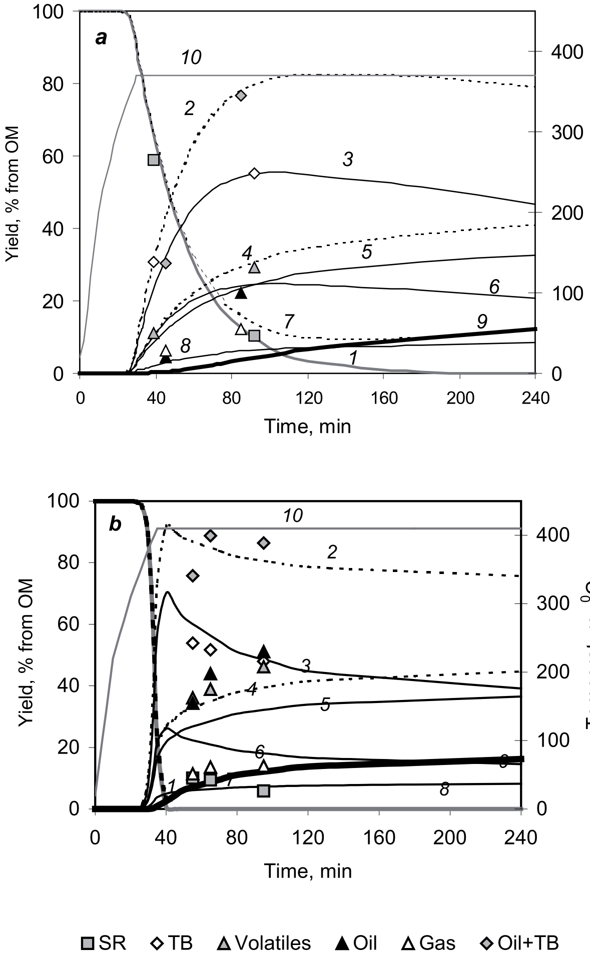

Fig. 7. Effect of retorting time at nominal temperature 370 °C (*a*) and 410 °C (*b*) on the distribution of kerogen decomposition products: *1* – kerogen, *2* – TB + oil, *3* – TB, *4* – volatiles, *5* – oil, *6* – malthenes, *7* – solid residue, *8* – gas, *9* – coke, and 10 – the current temperature.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

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REFERENCES

1. *Klewer, H. W.*, *Mauch, K.* Über den Estländishen Ölschiefer “Kukersit”. – Halle, 1927.
2. *Hisin, Y. I.* Thermal Decomposition of Oil Shales. – Leningrad. Moscow. Gostopizdat, 1948. 172 pp. [in Russian].
3. *Krumin, P.* Review of the Estonian oil shale industry, with brief account of oil shale developments in the United States. Engineering Experiment Station. Circular No 50 // Ohio State University Studies. Eng. series. 1949. Vol. XVIII, No. 6. 126 p.
4. *Aarna, A. Y.* Isothermal destruction of Baltic oil shale // Transactions of Tallinn Polytechnic Institute. 1954. Series A. No. 57. P. 32–34 [in Russian].
5. *Aarna, A. Y.* About isothermal destruction of Baltic oil shale // J. Appl. Chem. 1955. Vol. 28, No. 10. P. 1138–1142 [in Russian].
6. *Aarna, A. Y.* About kinetics of thermal destruction of Baltic oil shale // J. Appl. Chem. 1956. Vol. 29, No. 4. P. 606–610 [in Russian].
7. *Kollerov, D. K.* Rate of thermal destruction of organic matter from oil shales // Chemistry and Technology of Fuels. 1956. Nr. 10. P. 55-62 [in Russian].
8. *Karavayev, N. M., Werner, I. M.* About thermobitumen of Gdov oil shale // Transactions of the Institute of Goryuchih Iskopayemyh. Academy of Sciences of USSR. 1950. Vol. 2. P. 285–295 [in Russian].
9. *Aarna, A. Y., Lippmaa, E. T.* Thermal destruction of oil shale-kukersite // Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 3–27 [in Russian].
10. Thermal Destruction of Shale-Kukersite. M. Y. Gubergrits (ed.). – Tallinn: “Valgus”, 1966. P. 27–32 [in Russian].
11. *Kogerman, P., Luts, K., Hüsse, I.* On the Chemistry of Estonian Oil Shale. – Moscow, Leningrad: Goshimtexizdat, 1934 [in Russian].
12. *Kask, K. A.* About bituminizing of kerogen of oil shale-kukersite. Report I // Transactions of Tallinn Polytechnic Institute. 1955. Series A. No. 63. P. 51–64 [in Russian].

13. *Kask, K. A*. About bituminizing of kerogen of oil shale-kukersite. Report II // Transactions of Tallinn Polytechnic Institute. 1956. Series A. No. 73. P. 23–40 [in Russian].
14. *Fomina, A. S., Pobul, L. Y., Degteryova, Z. A*. Origin of Kerogen of Baltic Oil Shale and its Chemical Characteristics as Raw Material. – Tallinn: Acad. Sci. Estonian SSR, 1965 [in Russian].
15. *Schulman, A. I.* Investigation of Bituminizing Process of Shale Organic Concentrate. – Thesis of cand. sci. Leningrad: VNII Neftekhim, 1968 [in Russian].
16. *Zaidentsal, A. L., Soone, J. H., Muoni, R. T.* Yields and properties of thermal bitumen obtained from combustible shale // Solid Fuel Chemistry. 2008. Vol. 42, No. 2. P. 74–79.
17. *Tiikma, L., Zaidentsal, A., Tensorer, M.* Formation of thermobitumen from oil shale by low temperature pyrolysis in autoclaves // Oil Shale. 2007. Vol. 23, No. 3. P. 535–546.
18. *Johannes, I., Tiikma, L.* Kinetics of oil shale pyrolysis in an autoclave under non-linear increase of temperature // Oil Shale. 2004. Vol. 21, No. 4. P. 273–288.
19. *Johannes, I., Tiikma, L., Zaidentsal, A., Luik, L.* Kinetics of kukersite low-temperature pyrolysis in autoclaves // Abstracts of the 18th International Symposium on Analytical and Applied Pyrolysis. PYROLYSIS 2008. Lanzarote, Canary Islands, May 18–23, 2008.
20. *Galway, A. K.* Is the science of thermal analysis kinetics based on solid foundation? A literature appraisal // Thermochim. Acta. 2004. Vol. 413, No. 1–2. P. 139–183.

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PAPER IV

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Kinetics of kukersite low-temperature pyrolysis in autoclaves

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ABSTRACT

A systematic experimental study of the effect of reaction time on the low-temperature pyrolysis of Baltic oil shale (kukersite) in autoclaves at nominal temperatures 340–380 °C was carried out. The results show an increase in the yields of gas and coke in time, whereas the yield of the target product, soluble in benzene fraction, has a maximum value (*ca.* 90%) and the yield of solid residue has a minimum value at a reaction time depending on the nominal temperature and heating rate. The process kinetics is described approximately by the first order parallel-consequent decomposition of initial kerogen and thermobitumen formed. A mathematical model is deduced for estimation of the rate coefficients and apparent kinetic constants for formation of gas, soluble in benzene phase, and coke at the low-temperature pyrolysis and for prediction of the current yields of the products. The experimental and calculated yields of gas, soluble in benzene phase (thermobitumen and oil) and solid residue (coke and not decomposed kerogen) obtained under non-linear increase of temperature agree satisfactorily.

1. Introduction

The organic matter (kerogen) of Baltic oil shale (kukersite) is a macromolecular resin with an empirical formula $C_{421}H_{638}O_{44}S_4NCl$ [1]. The extraction yield of organic matter from the kerogen by H-bonding solvents attains 0.1, and using non-H-bonding solvents only 0.01% [2]. So, kerogen of kukersite cannot be separated from its mineral part by a simple solvent extraction.

The comprehensive investigations of kukersite pyrolysis published during the last century [3–14] have shown that the thermal decomposition of kerogen begins at 170–180 °C with evolution of decomposition water, CO_2 and H_2S. Between temperatures 250–350 °C takes place softening (plasticization) stage where up to 90% of the kerogen macro-molecules can be converted into thermobitumen (TB) including some light fractions at optimum combination of time and temperature. TB, an high-molecular non-volatile intermediate product of kerogen thermal cracking is soluble in organic solvents. The composition and physical characteristics of the polycomponental TB depend on its formation conditions whereas at 325–350 °C begins the secondary pyrolysis of TB into oil fractions, gas and semicoke.

Up to now, the retorting technologies of oil shale being in use for industrial production of shale oil lost inevitably more than one third of the kukersite organic matter with semicoke [15]. At that, special efforts, mainly fast heat supply, have been applied to avoid caking and plugging problems of undesirable pitchy plasticization caused by TB formation.

The continually increasing demand for liquid fuels and steadily decreasing petroleum reserves have intrigued investigations aimed at more complete transformation of oil shale kerogen into liquid fuels. The earlier laboratory works [16,17] have shown that when TB formed by low-temperature pyrolysis is separated and decomposed in the second pyrolysis stage into oil, the total wastage of organic matter with semicoke overcomes that at kukersite one stage semicoking.

The new generation of effective hydrogenation catalysts created for hydroconversion of heavy oil and asphaltenes [18,19] encourages concepts of successful upgrading of TB into liquid fuels. So, formation of TB from oil shale, studied intensively in the middle of the last century is again of interest. The main purpose of the former investigations [10–14,16,17] has been to understand the origin and composition of oil shale. At that, the individual effects of time or temperature at various constant values of the other parameter on the yield of TB, semicoke and volatiles at low-temperature pyrolysis of oil shale and enriched kerogen in open retorts was studied. The recent experimental results concerning thermobituminization of kukersite in autoclaves without and with addition of different solvents are described in the papers [20] and [21] in this Special Issue. A convincing co-effect of temperature, time and heating rate on the maximum yield of TB and characteristics of the products is evident in the works cited above without any mathematical interpretation.

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In an our previous paper [22] a mathematical model was proposed to describe the co-effects of time and temperature on the oil shale pyrolysis kinetics under conditions of non-linear increase of temperature in autoclaves at nominal temperatures 420–500 °C. An approach was proposed where the pyrolysis process was handled consisting of two separate stages. In the first stage decomposition of oil shale was described by the consequent-parallel reactions "kerogen → oil → gas" and kerogen → gas (k_3). In the second stage the pyrolysis was assumed as cracking of the oil formed by parallel reactions "oil → gas" and "oil → semicoke". At that, the decomposition product "oil" signed the total benzene-soluble product extracted from the autoclave. As a result, the liquid product extracted from autoclaves comprised both TB and oil and is signed here and later as TBO. The weak point of the model was introducing values of the minimum concentration of kerogen matter in solid residue ($x_{0\,\min}$) to define beginning of the second stage, and an equilibrium concentration of the soluble in benzene phase ($x_{1\infty}$) being attained in the second stage. The values of $x_{0\,\min}$ and $x_{1\infty}$ depending on temperature were calculated by stochastic polynomial equations deduced from the experimental results of semicoking. So, the coefficients of the polynoms are not valid at the lower temperature pyrolysis stage characteristic for formation of TB.

The aim of this work was creation of the theoretical basis for prediction of the conditions for the maximum yield of TBO. For this aim:

- a systematic experimental study of the low-temperature thermobituminization of kukersite in autoclaves was conducted,
- a kinetic model was deduced for prediction of the yields of pyrolysis products were the uncertain values of $x_{0\,\min}$ and $x_{1\infty}$ were eliminated,
- the rate coefficients and apparent kinetic constants for the kukersite low-temperature pyrolysis model were estimated.

2. Experimental

In all the experiments 4.0 g of powdered and dried kukersite samples consisting of 50.5% kerogen were heated in 20 ml micro-autoclaves. The autoclaves were weight, and placed into a muffle oven with five nominal temperatures in the range 340–380 °C. After definite residence times between 45 and 1200 min 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's extractor with benzene. Mass

Table 1

Distribution of kukersite kerogen between pyrolysis products TBO (x_1), solid residue ($y + x_3$), and gas (x_2) in time (%)

Time (min)	x_1		$y + x_3$		x_2
	By weight	From difference[a]	By weight	From difference[b]	By weight
Nominal temperature 340 °C					
180	27.07	27.30	65.12	65.35	7.58
360	77.42	72.77	17.82	13.17	9.415
480	81.45	77.31	12.95	8.80	9.74
1200	87.82	85.41	2.67	4.52	9.38
Nominal temperature 350 °C					
150	57.84	58.57	33.20	34.70	7.91
240	82.34	75.02	15.86	9.37	8.93
360	87.27	85.61	4.70	3.83	9.58
600	80.66	79.19	8.77	8.10	11.88
Nominal temperature 360 °C					
93	47.32	38.82	54.92	46.42	6.27
120	81.61	49.04	42.59	10.10	8.39
180	85.46	78.54	11.65	4.721	9.82
210	89.31	84.73	6.40	1.814	8.88
240	79.43	80.67	8.469	9.877	10.69
300	78.00	77.32	12.50	11.81	10.61
420	77.01	74.22	12.56	9.78	13.21
Nominal temperature 370 °C					
10	1.21	2.29	96.81	97.89	0.90
20	2.15	4.45	93.24	95.54	2.31
30	6.88	11.60	84.45	89.18	3.95
40	12.85	13.80	81.60	82.55	4.60
50	16.38	20.74	82.87	77.23	6.39
60	42.32	39.24	52.74	49.66	8.02
120	89.44	86.30	5.57	2.42	8.14
180	85.32	82.80	6.55	4.03	10.65
360	73.82	67.22	18.18	11.59	14.60
Nominal temperature 380 °C					
45	8.77	10.68	84.18	86.09	5.14
60	32.91	36.78	57.59	61.46	5.63
90	83.02	82.74	9.30	9.02	7.95
120	89.44	83.07	7.78	1.42	9.15
180	85.93	82.16	5.240	1.47	12.60
240	65.24	64.14	18.14	17.04	17.72
300	64.72	55.61	24.32	15.21	20.07
420	59.04	54.96	23.31	19.13	21.83

[a] $100 - (y + x_3 + x_2)_{\exp}$.

[b] $100 - (x_1 + x_2)_{\exp}$.

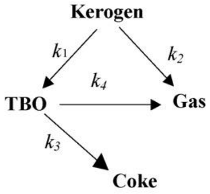

Fig. 1. Simplified scheme for low-temperature pyrolysis of kerogen.

of the solid residue 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 at 800–850 °C from the acid-treated and dried residues. Estimation of the exact mass of the target product, TBO, was to some extent problematic because the lighter fractions of the oil formed could be partly lost at evaporation of the solvent applied, or the solvent bound with TBO could not be entirely removed. The same problem was noticed by some other researchers too [2,23]. In this work, 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. According to the second approach, the yield of TBO formed was found subtracting the mass of gas and organic solid residue from the initial mass of kerogen. In this case, the yield of TBO could be overestimated due to inclusion of the decomposition water, or underestimated when the yields of gas or solid residue were overestimated. That is the reason why the both results of TBO, obtained directly by evaporation of the benzene extract and as the difference, are given in the tables, figures and have been applied in calculations of the rate coefficients.

3. Results and discussion

The experimentally estimated yields of the products in percentages from organic matter at various pyrolysis times and temperatures are given in Table 1.

The simplified scheme applied for modelling kinetics of the pyrolysis reactions is presented in Fig. 1.

3.1. Estimation of rate coefficients and apparent kinetic constants

Admitting that the thermal decomposition pathways presented in Fig. 1 can be described approximately by the first order kinetic equations, concentration of the initial kerogen (y) should decrease in time as follows:

$$-\frac{\mathrm{d}y}{\mathrm{d}t} = (k_1 + k_2)y = k_y y \qquad (1)$$

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

$$\ln y = \ln y_0 - k_y(t - t_0) \qquad (2)$$

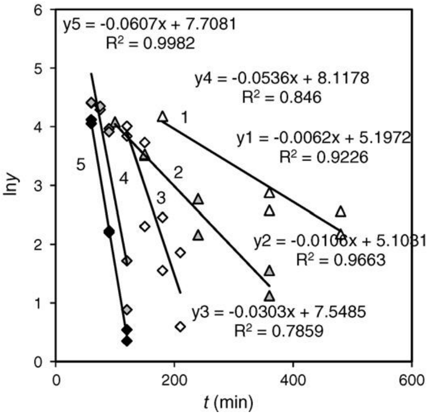

Fig. 2. Plot of ln y versus time for estimation of k_y at nominal temperatures (°C): (1) 340, (2) 350, (3) 360, (4) 370, and (5) 380.

Before the coke formation is started, the value of y should be equal to the percentage of experimentally estimated organic solid residue, and the value of k_y should be constant. So, under the isothermal conditions, since the nominal temperature is attained and coke is not formed yet, Eq. (2) should express a straight line. The linear parts of the plot of logarithm from the percentage of the current organic solid residue versus time for the five nominal temperatures tested are presented in Fig. 2. The values of k_y found from the slopes of the straight lines are given in the first row of Table 2.

According to the scheme in Fig. 1, the concentrations of TBO (x_1), gas (x_2) and coke (x_3) should increase as follows:

$$\frac{\mathrm{d}x_1}{\mathrm{d}t} = k_1 y - (k_3 + k_4)x_1 = k_1 y - k_{\mathrm{TBO}} x_1 \qquad (3)$$

$$\frac{\mathrm{d}x_2}{\mathrm{d}t} = k_2 y + k_4 x_1 \qquad (4)$$

$$\frac{\mathrm{d}x_3}{\mathrm{d}t} = k_3 x_1 \qquad (5)$$

The differential equations (1) and (3)–(5) represent a system with four independent unknown rate coefficients k_1–k_4. Algorithms for estimation of the coefficient were deduced dividing Eqs. (3)–(5) with Eq. (1) and thereafter multiplying with k_y. As results, linear relationships were revealed between the relative increase in the concentration of any product with the corresponding decrease in the concentration of initial kerogen versus the current ratio of the TBO and kerogen concentrations

$$-\frac{k_y \mathrm{d}x_1}{\mathrm{d}y} = k_1 + \frac{k_{\mathrm{TB}} x_1}{y} \qquad (6)$$

Table 2
Rate coefficients (1/min)

Rate coefficient (1/min)	Nominal temperature (°C)				
	340	350	360	370	380
k_y	8.68E−03	1.12E−02	4.01E−02	4.25E−02	5.14E−02
k_1	8.43E−03	9.25E−03	3.81E−02	3.88E−02	3.08E−02
k_2	2.52E−04	1.95E−03	1.99E−03	3.70E−03	2.06E−02
k_{TBO}	5.65E−05	3.27E−04	3.37E−04	9.30E−04	1.56E−03
k_3	5.27E−05	2.10E−04	1.27E−04	7.72E−04	1.08E−03
k_4	2.76E−06	1.17E−04	2.10E−04	1.58E−04	4.76E−04

$$-\frac{k_y \mathrm{d}x_2}{\mathrm{d}y} = k_2 + \frac{k_4 x_1}{y} \tag{7}$$

$$-\frac{k_y\, \mathrm{d}x_3}{\mathrm{d}y} = \frac{k_3 x_1}{y} \tag{8}$$

where the values of k_1 and k_2 occur as intercepts, and of k_{TBO}, k_3 and k_4 as slopes.

The value of k_3 was preferably found from the difference

$$k_3 = k_{\mathrm{TBO}} - k_4 \tag{9}$$

The rate coefficients of TBO cracking, k_{TBO}, k_3 and k_4 were calculated by Eqs. (6), (7) and (9) only for the nominal temperature 340 °C. At higher temperatures the cracking took place mainly after exhaustion of the initial kerogen when the values of y and dy in denominators of Eqs. (6) and (7) were too small for correct calculations. For better estimation of the coefficients, the region of TBO decrease after its maximum was examined. When there was no practical contribution from decomposition of the initial kerogen, Eq. (3) was reduced to a simpler form analogous to Eq. (1) as follows:

$$-\frac{\mathrm{d}x_1}{\mathrm{d}t} = (k_3 + k_4)x_1 = k_{\mathrm{TBO}} x_1 \tag{10}$$

where the total decomposition rate coefficient (k_{TBO}) of TBO was found from slope of the integrated form of Eq. (10) as follows

$$\ln x_1 = \ln x_{1,0} - k_{\mathrm{TBO}}(t - t_0) \tag{11}$$

Noteworthy is that in this case, the initial time, t_0 and concentration $x_{1,0}$ were not zero but corresponded to the beginning of the linear relationship between ln x_1 and time being valid when there is no practical contribution from $k_1 y$ in Eq. (3).

After the value of k_{TBO} was found, the rate coefficients for parallel formation of gas and coke from TBO were calculated using the proportional relationships

$$k_3 = -\frac{k_{\mathrm{TBO}}\, \mathrm{d}x_3}{\mathrm{d}x_1} \tag{12}$$

and

$$k_4 = -\frac{k_{\mathrm{TBO}}\, \mathrm{d}x_2}{\mathrm{d}x_1} \tag{13}$$

The temperature profiles of the reaction mixtures recorded (Fig. 3) revealed that the nominal temperature was attained after an hour. For calculation of the rate coefficients by Eqs. (1)–(13) only the experimental data obtained at the isothermal periods were applied. As far the solid residue consisted of not decomposed kerogen and coke formed, the real values of y and dy calculated by means of k_y and y_0 were used. The rate coefficients found are given in Table 2.

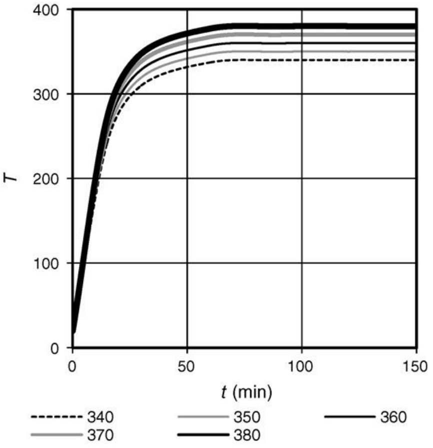

Fig. 3. The reaction current temperatures at different nominal temperatures (°C).

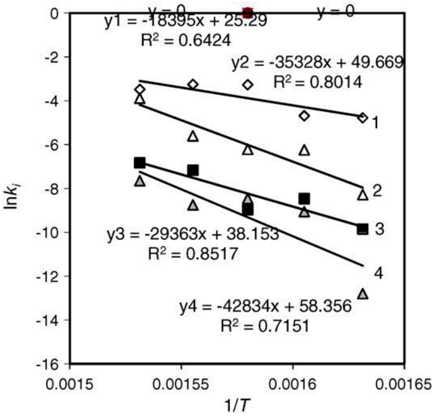

Fig. 4. Arrhenius plot of rate coefficients (1/min): (1) k_1, (2) k_2, (3) k_3, and (4) k_4.

The values of apparent activation energy (E) and frequency factor (A) for formation of TBO and gas from kerogen, and gas and coke from TBO at the low-temperature pyrolysis of kerogen found from the depicted in Fig. 4 Arrhenius linear relationship

$$\ln k_i = \ln A - \frac{E}{RT} \tag{14}$$

where R is gas constant 8.314 J/mol, are presented in Table 3.

3.2. Prediction of the current distribution of the pyrolysis products at non-linear increase of temperature

A step-by-step approach was applied to calculate the concentrations of the pyrolysis products in time under non-linear increase of temperature. For this aim, the following route was used:

- The time dependence of temperature (T) in °C was calculated for definite (20 min) time intervals according to the modified in [22] equation taken from [24]

  $$T_t = T_{\mathrm{nom}} - (T_{\mathrm{nom}} - T_{\mathrm{room}}) \exp(-\beta t) \tag{15}$$

  where the heating rate characteristic β, in 1/min, for the autoclave applied was found from the empirical polynomial relationship

  $$\beta = \frac{60}{0.0001 T_{\mathrm{nom}}^2 - 0.4073 T_{\mathrm{nom}} + 887.57} \tag{16}$$

- The values of the rate coefficients at every mean temperature of the time intervals were calculated introducing the corresponding kinetic constants from Table 3 into the exponential form of Eq. (14).
- The current share of not decomposed (insoluble in benzene) kerogen was calculated as follows:

  $$y_n = \frac{y_{n-1}}{\exp[(k_1 + k_2)(t_n - t_{n-1})]} \tag{17}$$

  where at t_{n-1} = 0 min, y_n = 100%.

Table 3
Apparent kinetic constants for pyrolysis of kerogen between 340 and 380 °C

	k_1	k_2	k_3	k_4
$a = \ln A$	25.3 ± 9.9	49.7 ± 11.8	33.15 ± 19.21	58.36 ± 11.6
$-b = -E/R$	(1.84 ± 0.63)E + 04	(3.53 ± 0.74)E + 04	(2.94 ± 1.23)E + 04	(4.28 ± 0.74)E + 04
R^2	0.642	0.801	0.852	0.715
A (1/min)	9.62E + 10	3.73E + 21	3.70E + 16	2.22E + 25
E (kJ/mol)	153	294	244	356

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

$$x_{1,n} = x_{1,n-1} + \left[\frac{(y_{n-1} - y_n)k_1}{k_1 + k_2}\right]\left[k_1 + \frac{(k_3 + k_4)x_{1,n-1}}{y_{n-1}}\right] \tag{18}$$

where at $t_{n-1} = 0$ min, $x_{1,n} = 0\%$.
- The current gas yield was calculated using the relationship deduced from Eq. (8)

$$x_{2,n} = x_{2,n-1} + \left[\frac{(y_{n-1} - y_n)k_2}{k_1 + k_2}\right]\left[k_2 + \frac{k_4 x_{1,n-1}}{y_{n-1}}\right] \tag{19}$$

where at $t_{n-1} = 0$ min, $x_{2,n} = 0\%$.
- The current coke yield was calculated as the difference

$$x_{3,n} = 100 - (y_n + x_{1,n} + x_{2,n}) \tag{20}$$

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

$$y = \frac{y_{\text{nom}}}{\exp[k_y(t - t_{\text{nom}})]} \tag{21}$$

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

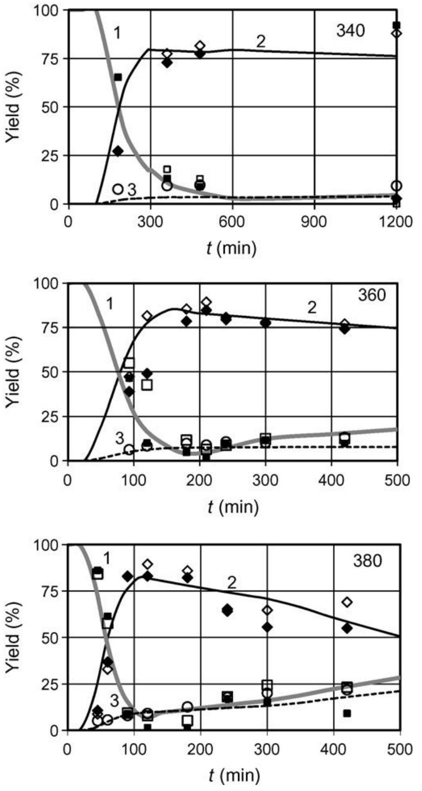

Fig. 5. Effect of time on the distribution of kerogen between its pyrolysis products at different nominal temperatures (°C): (1) solid residue, (2) TBO, and (3) gas. Curves: calculated; bright points: experimental by weight; dark points: experimental from difference.

Comparison the yields of the products predicted by Eqs. (14)–(21) and the experimental results in Fig. 5 show satisfactory agreement.

4. Conclusions

- A possibility was proved for separation about 90% of kukersite organic matter from its mineral matter by means of low-temperature pyrolysis at 340–380 °C in autoclaves and subsequent extraction of the target product, thermobitumen and oil (TBO), with benzene.
- The highest yield of TBO was obtained under the conditions where the initial kerogen was decomposed almost entirely into compounds soluble in organic solvents but the coke formation resulted from the secondary cracking of TBO was scarcely started.
- A step-by-step mathematical model was proposed for prediction of the optimum time for formation of TBO from kukersite in autoclaves considering the co-effects of pyrolysis duration, nominal temperature and non-linear heating rate on the yield of TBO, gas and coke.
- Rate coefficients and apparent kinetic constants for the parallel-subsequent decompositions of kerogen into TBO and gas, and TBO into gas and coke were estimated.

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References

[1] Ü. Lille, I. Heinmaa, T. Pehk, Fuel 82 (2003) 799.
[2] V. Oja, J. Anal. Appl. Pyrolysis 74 (2005) 55.
[3] H.W. Klewer, K. Mauch, Über den estländischen Ölschiefer "Kukersit" Halle, 1927.
[4] Y.I. Hisin, Thermal Decomposition of Oil Shales, Leningrad, Moscow, GOSTOPIZDAT, 1948 (in Russian).
[5] P. Krumin, Review of the Estonian oil shale industry, with brief account of oil shale developments in the United States, Engineering Experiment Station, Circular No 50 in Ohio State University Studies, Eng. Series 18, 1949, 126 pp.
[6] A.Y. Aarna, Trans. Tallinn Polytechnic Inst. Ser. A (57) (1954) 32 (in Russian).
[7] A.Y. Aarna, J. Appl. Chem. 28 (1955) 1138 (in Russian).
[8] A.Y. Aarna, J. Appl. Chem. 29 (1956) 606 (in Russian).
[9] D.K. Kollerov, Chem. Technol. Fuels (10) (1956) 55 (in Russian).
[10] N.M. Karavayev, I.M. Werner, Acad. Sci. SSSR 2 (1950) 285 (in Russian).
[11] A.Y. Aarna, E.T. Lippmaa, Trans. Tallinn Polytechnic Inst. Ser. A (97) (1958) 3 (in Russian).
[12] M.Y. Gubergrits (Ed.), Thermal Destruction of Shale-Kukersite, Valgus, Tallinn, 1966 (in Russian).
[13] P. Kogerman, K. Luts, I. Hüsse, On the chemistry of Estonian oil shale, GOSHIMTEXIZDAT, Moscow, Leningrad, 1934 (in Russian).
[14] K.A. Kask, Trans. Tallinn Polytechnic Inst. Ser. A (63) (1955) 51 (in Russian).
[15] L. Mölder, Oil Shale 21 (2004) 97.

[16] K.A. Kask, Trans. Tallinn Polytechnic Inst. Ser. A (73) (1956) 23 (in Russian).

[17] A.S. Fomina, L.Y. Pobul, Z.A. Degteryova, Origin of kerogen of Baltic oil shale and its chemical characteristics as raw material, Acad. Sci. Estonian SSR, Tallinn, 1965 (in Russian).

[18] J.G. Speight, Catal. Today 98 (2004) 55.

[19] M.S. Rana, V. Såmano, J. Anccheyta, J.A.I. Diar, Fuel 86 (2007) 1216.

[20] L. Tiikma, A. Zaidentsal, M. Tensorer, Oil Shale 24 (2007) 535.

[21] L. Tiikma, I. Johannes, H. Luik, A. Zaidentsal, J. Anal. Appl. Pyrol., Special Issue PYROLYSIS 2008, submitted for publication.

[22] I. Johannes, L. Tiikma, Oil Shale 21 (2004) 273.

[23] M. Garcia-Perez, A. Chaala, H. Pakdel, D. Kretschmer, C. Roy, Biomass Bioenergy 31 (2007) 222.

[24] J.P. Holman, Heat Transfer, 4th ed., NY, 1976.

PAPER V

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

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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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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.

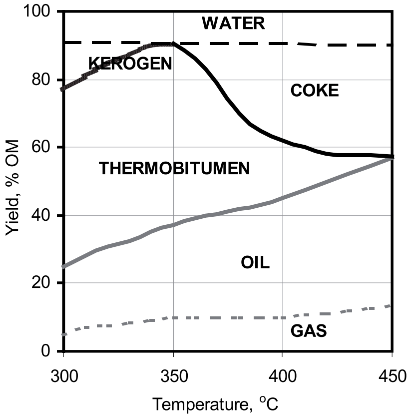

Fig. 1. Distribution of organic matter at pyrolysis of oil shale in open retorts at durations ensuring the maximum yield of TBO [1, 2].

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

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

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

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

$$\ln A = 2.23(\pm 2.29) + 0.174\ (\pm 0.009)E \tag{19}$$

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).

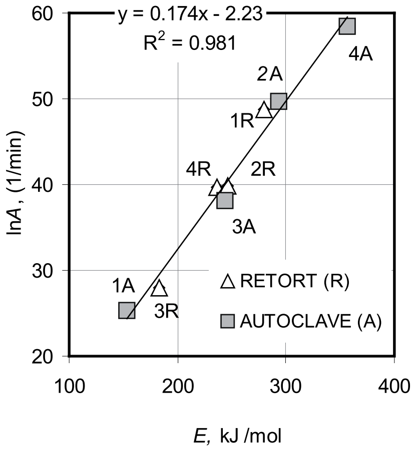

Fig. 2. Relationship between the low-temperature pyrolysis apparent kinetic constants in two devices.

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.

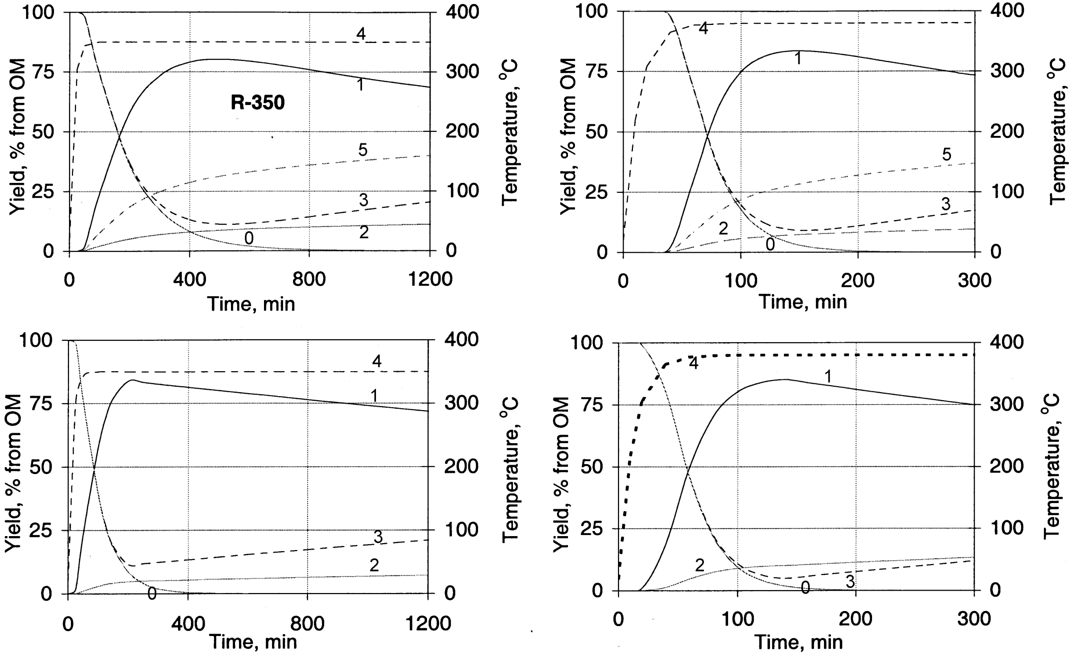

Fig. 3. Effect of pyrolysis duration on the yield of the phases, % from initial kerogen at nominal temperatures 350 and 370 °C in open air retorts (R) and autoclaves (A): 0 – kerogen, 1 – TBO, 2 – gas, 3 – organic solid residue, 4 – temperature, °C.

- 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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REFERENCES

1. *Kask, K. A.* About bituminizing of kerogen of oil shale-kukersite. Report I // Transactions of Tallinn Polytechnic Institute. Series A. 1955. No. 63. P. 51–64 [in Russian].
2. *Aarna, A. Y., Lippmaa, E. T.* Thermal destruction of oil shale-sukersite // Transactions of Tallinn Polytechnic Institute. Series A. 1958. No. 97. P. 3–27 [in Russian].
3. *Zaidentsal, A. I., Soone, J. H., Muoni, R. T.* Yields and properties of thermal bitumen obtained from combustible shale // Solid Fuel Chem. 2008. Vol. 42, No. 2. P. 74–80.
4. *Tiikma, L., Zaidentsal, A., Tensorer, M.* Formation of thermobitumen from oil shale by low-temperatre pyrolysis in an autoclave // Oil Shale. 2007. Vol. 24, No. 3. P. 535–546.
5. *Johannes, I., Zaidentsal, A.* Kinetics of low-temperature retorting of kukersite // Oil Shale. 2008. Vol. 25, No 4. P. 412–425.
6. *Johannes, I., Tiikma, L., Zaidentsal, A., Luik, L.* Kinetics of kukersite low-temperature pyrolysis in autoclaves // J. Anal. Appl. Pyrol. 2009. Vol. 85, No. 1–2. P. 508–513.

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APPENDIX B

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2001 – 2003 Tallinna Tehnikaülikool, Keemia – ja materialiteaduse magistriõppe kava, magistri loodusteaduste kraad.

Töökogemus

Juuni 2002–Oktoober 2002 "Velsicol Eesti" AS, Kohtla-Järve, Estonia

Insener

- Testisin mitmesuguseid naatriumbensoaadi puhastamise filtreid
- Uurisin bensoehappe tootmise protsessi
- Valisin tehnoloogilise seadmistiku

2003–2004 "Viru Keemia Grupp" AS. Kohtla-Järve , Estonia

Tootmisinsener

- Koostasin ohutustehnika eeskirju vahetustele
- Koostasin seadme töönädala, toodangu – ja kvartaliaruandeid
- Kontrollisin toodengu kvaliteeti

Juuli 2004 – Detsember 2004 Medtronic Inc., Distribution Center, Mounds View, MN, USA

Kvaliteedijuhi assistent

- meditsiinitoode tellimuste koostamine

Alates juulist 2005 Tallinna Tehnikaülikool, Põlevkivi instituut

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- analüüsi teostamine analüütilise seadme abil

Alates novembrist 2008 Eesti Energia Õlitööstus AS, Eesti Energia

Projektijuht

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- investitsiooni proektide käivitamine ja teostamine

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Education

1996-2001 Tallinn University of Technology, Chemistry – and Environment Protection Technology. Bachelor degree of science.

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Experience

June 2001–October 2002 "Velsicol Eesti" AS Manufacturer and trader of benzoic acid and food adds Kohtla-Järve, Estonia (www.velsicol.ee)

Engineer

- tested different filters for new sodium benzoate solution filtration system
- studied chemical process of benzoic acid production
- technical data collection

July 2003–June 2004 "Viru Keemia Grupp" AS Manufacturer and trader of petrochemical products Kohtla-Järve , Estonia (www.vkg.ee)

Process engineer

- weekly and decade technical reports of oil refinery process
- technical data collecting and analyzing for daily meetings

July 2004–May 2005 Medtronic Inc., Distribution Center, Mounds View, MN, USA
(www.medtronic.com)

Quality manager assistant

- tracing medical products

July 2005 – November 2007 Tallinn University of Technology, Oil Shale and Fuel Research Department

Chemical engineer

- investigation of estonian oil shale thermal decomposition
- research work

November 2008 – Eesti Energia Oil and Gas Company, Development Department

Project manager

- development projects management
- project technical correspondence and data support

October 2010 – Eesti Energia Oil and Gas Company, Development Department

Manager of the Development Department

- arrangement of department work
- investment and development projects management
- contract review, time and cost control

Special skill & abilities

- computer literate: Word, Excel, Power Point, Photoshop, Chemcad
- experienced at investment and development projects management,
- familiarized with ISO 9001, chemical engineering aspects

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- estonian – intermediate
- english – intermediate

Interests Hockey, Fishing.

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