ISOTHERMAL DECOMPOSITION
OF BALTIC OIL SHALE

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Thermal decomposition of oil shale is of great importance to the National economy of Estonia. The investigation of the chemical nature of the shale organic matter is of significant interest as well. Though thermal decomposition of oil shale is used on a commercial scale, the theoretical nature of this process is far from being well understood. Only a profound and thorough study of this complicated process can yield significant improvements to the design of new, and modification of existing, retorting equipment. This work should be aimed at an increase in the yield of liquid products and the improvement of their quality.

The main characteristics of thermal decomposition of oil shale (kukersite) organic matter have been identified by A. F. Dobryansky [1]. Ya. I. Khisin has investigated isothermal decomposition of oil shales, including Estonian shales [2]. His attention was directed mainly at the quantitative side of the formation of thermal decomposition products. That work did not include any data concerning the mechanism of kerogen thermal decomposition. We consider the conclusion made by Ya. I. Khisin that "...the oil from Estonian shales preserves a constant composition during the whole process of its formation..." as being incorrect.

Up to now no data have been available regarding changes in fractional and chemical group composition of shale oil during the isothermal decomposition process. Prolonged experiments at low temperatures have also not been carried out. The results from such experiments could enable one to make some conclusions about yield limits of oil and its fractions.

The aim of this work was the acquisition of data regarding the shale thermal decomposition process. A second objective was the elucidation of mechanisms by which oil fractional components and group compounds are formed. We chose isothermal oil shale decomposition as the method for solving this problem. The decomposition process was performed within the temperature range 300-440 °C, where all the main processes of bitumenization and oil formation occur. Special attention was paid to processes occurring at lower temperatures. We consider the temperature range 300-350 °C as being of special interest. Within this range, single decomposition reactions occur, but they occur with rates which enable a more detailed differential study of this complex process. As a result, prolonged experiments of isothermal decomposition were carried out at the prescribed lower temperatures, e.g. for 750 hours at 300 °C.

Special equipment was used to perform the low temperature isothermal process. This equipment was described by the present author in an earlier publication [3]. Shale samples of 400 g weight were retorted. The retort was placed in an electrically heated metallic bath and the temperature regulated with a thermoregulator.

The oil obtained from shale thermal decomposition was fractionated in a device with 4-5 theoretical plates which separated the product into fractions boiling at < 200 °C, between 200-350 °C, and > 350 °C. At temperatures over 200 °C, vacuum distillation was used and boiling temperatures were reduced by lowering the absolute pressure below atmospheric pressure. Oil fractions obtained from this processing were analyzed for the following variables: content of alkali-soluble components, elemental composition, specific gravity, refractive index, and chemical group composition. The chemical group compositions of the oil fractions were determined chromatographically [4].

The solid residue from the thermal decomposition was extracted with boiling benzene in order to separate the thermobitumen.

Oil shale used in these experiments had the following composition (in %):

Moisture	0.86
Ashes	43.51
CO_2 mineral	12.24
Pyrite	1.63
Organic matter	44.67

The elemental composition of the organic matter (in %) was as follows:

C	76.60
H	9.80
S	1.30
O	12.01
N	0.29

Distillation in an aluminum retort gave the following results (in %):

Oil	29.8
Water	3.1
Semicoke	60.6
Gas and losses	6.5

All yields presented below are given on the basis of absolute dry organic matter.

The results of balance tests of shale isothermal destruction and the distribution of oil between the fractions identified above are presented in Table 1.

Figure 1 illustrates the distribution of organic matter among thermal decomposition products. It is necessary to note that the yield of heavy residue at 360 °C did not reach its presumed maximum, probably because of the short duration of the experiment.
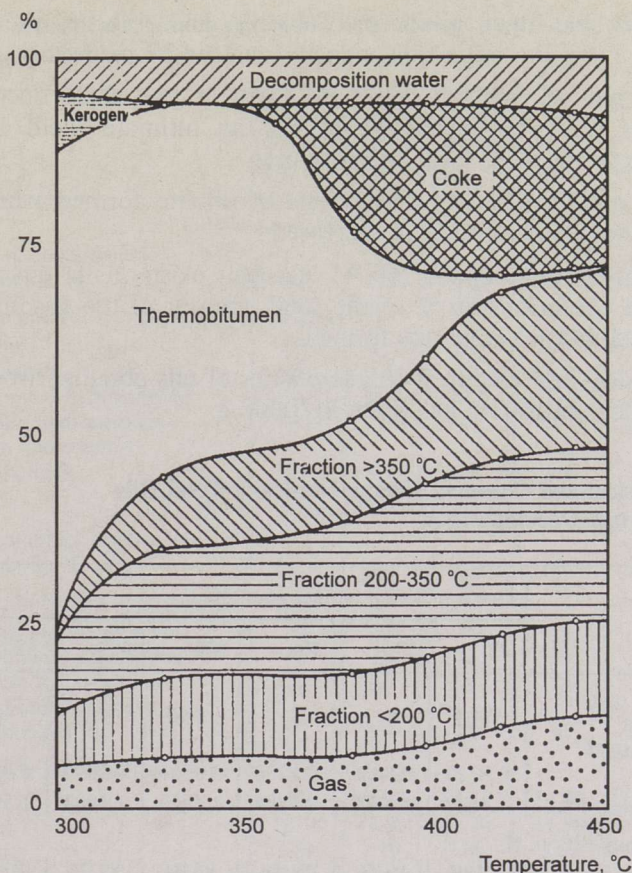
Fig. 1. Distribution of shale organic matter at thermal decomposition

Table 1. **Balances of Oil Shale Thermal Decomposition**

	Destruction temperature, °C						
	300	330	360	380	400	420	440
Duration, h	744	132	14	8.5	7.5	5.0	6.0
Yield, %, organic matter basis:							
Oil	15.2	37.4	33.2	44.9	51.8	57.8	58.4
Decomposition water	4.5	6.4	6.6	5.8	6.1	6.6	7.5
Gas	5.7	8.0	6.7	6.8	8.4	11.1	12.2
Thermobitumen	65.9	48.2	51.6	24.7	9.7	2.3	2.0
Residue, insoluble in benzene	8.7	0.0	1.9	17.8	24.0	22.2	19.9
Fractional composition of oil, %:							
< 200 °C	27.4	28.2	32.5	24.1	23.4	21.1	21.7
200-350 °C	}72.6	47.3	49.5	44.1	44.6	40.6	40.1
> 350 °C		24.5	18.0	31.8	32.0	38.3	38.2
Yield of fractions, %, organic matter basis:							
< 200 °C	4.2	10.5	10.8	10.8	12.1	12.2	12.7
200-350 °C	}11.0	17.7	16.4	19.8	23.1	23.5	23.4
> 350 ° C		9.2	6.0	14.3	16.6	22.1	22.3

Based on the data given in Table 1 and Fig. 1 the following preliminary, but quite important, conclusions can be made:

1. The light oil fraction begins to form at low shale decomposition temperatures, and it practically reaches its ultimate yield limit 11 % (organic matter basis) at these temperatures.

2. Only middle and heavy fractions of oil are formed when thermal decomposition temperatures are increased.

3. At temperatures up to 360 °C, kerogen exists in its dissolved state. Under these conditions 80 % of the total amount of the gasoline fraction was produced, but no coke was formed.

The physical and chemical characteristics of oils obtained from oil shale isothermal decomposition are given in Table 2.

Table 2. **Physical and Chemical Characteristics of Total Oils from Isothermal Decomposition**

	Decomposition temperature, °C						
	300	330	360	380	400	420	440
Oil yield, %, organic matter basis	15.2	37.4	33.2	44.9	51.8	57.8	58.4
Specific gravity at 20 °C	0.8720	0.8888	0.8780	0.9061	0.9094	0.9215	0.9123
Refractive index $n^{20}{}_D$	1.4822	1.4900	1.4886	1.4933	1.4992	1.5067	1.5141
Elemental composition, %:							
C	82.39	88.68	81.84	82.04	82.24	82.37	82.53
H	12.63	11.62	11.70	11.17	11.13	11.00	10.86
S	0.97	0.82	1.07	0.80	0.76	0.76	0.76
O+N	4.01	4.90	5.39	5.99	5.87	5.87	5.85
Ratio C : H	6.52	7.11	6.99	7.35	7.38	7.50	7.60

The chemical characteristics of oil fractions obtained from oil shale isothermal decomposition are presented in Table 3.

Oil produced at 300 °C contained 15.5 % of alkali-soluble compounds. The determination of oil chemical group composition for this sample proved to be impossible by reason of its insufficient amount.

Experimental data demonstrate that the higher the decomposition temperature the more oxygen one sees in the produced oil. The presence of phenols and aromatic hydrocarbons, which are produced at relatively low reaction temperatures, provides evidence that aromatic structures (or structures close to aromatic rings) exist in kerogen. With an increase in this temperature, the content of paraffinic hydrocarbons decreases and the content of unsaturated hydrocarbons increases. These offsetting effects occur in almost equal quantities. Consequently, the latter compounds are considered secondary products, being formed during the thermal decomposition of the saturated hydrocarbons.

Table 3. **Chemical Characteristics of Oil Fractions from Isothermal Decomposition**

	Decomposition temperature, °C					
	330	360	380	400	420	440
1. Fraction < 200 °C						
Content of alkali-soluble compounds, %	3.37	2.15	2.80	2.94	3.14	3.64
Group composition of dephenolated fraction, %:						
Paraffins	34.6	30.2	26.8	24.7	21.1	21.4
Naphthenes	6.6	6.0	6.2	6.0	7.3	7.4
Unsaturated hydrocarbons	39.2	48.0	47.8	49.0	55.2	52.5
Aromatic hydrocarbons	13.1	11.5	11.7	13.7	11.3	13.4
Oxygen and sulphur compounds	6.5	4.3	7.5	6.6	5.2	5.3
2. Fraction 200-350 °C						
Content of alkali-soluble compounds, %	17.4	15.5	18.4	22.0	23.0	23.2
Group composition of dephenolated fraction, %:						
Paraffins and naphthenes	34	19	18	16	16	14
Unsaturated hydrocarbons	26	26	27	29	33	34
Aromatic hydrocarbons	7	16	14	19	19	19
Oxygen and sulphur compounds	33	39	41	36	32	33
Elemental composition of dephenolated fraction, %						
C	83.86	84.45	84.57	84.83	85.06	84.56
H	12.34	11.88	11.70	11.90	11.88	11.92
S	1.31	1.10	0.86	0.83	0.89	0. 98
O+N	2.49	2.57	2.87	2.44	2.17	2.14

We consider our experimental data sufficient to prove that the main part of the light, low-boiling fractions are formed during the primary decomposition of kerogen, and not during the subsequent thermal cracking of heavy oil.

The formation of shale oil fractions also depends on the duration of the isothermal decomposition tests. The results of experiments carried out at two temperatures, and varying treatment times, are presented in Table 4.

As seen from the data in Table 4, heavy oil fractions are the principal products during prolonged experiments at a fixed temperature. For example, at 330 °C, a prolonged heating time yields 11.3 % more of the low-boiling fraction (below 200 °C), 109 % more of the medium-boiling fraction (200-350 °C), and a dramatic 2200 % more of the high-boiling fraction (over 350 °C). It is evident that low-boiling fractions form directly from kerogen. The second important fact is that the maximum portion of light oil forms only after kerogen is transformed into its soluble state thermobitumen.

Investigation of the benzene-insoluble part formed at temperatures below 360 °C indicates that its elemental composition differs only slightly from kerogen. Consequently, coke does not form below 360 °C and the

insoluble residue consists of undecomposed kerogen. The benzene-soluble fraction of the solid residue was studied by K. Kask. Results of this work are presented in Table 5.

Table 4. **Effect of Experiment Duration on Thermal Decomposition**

	At 330 °C		At 360 °C	
	46 h	132 h	6 h	14 h
Yield of decomposition products, %, organic matter basis:				
Oil	18.2	37.4	16.3	33.2
Pyrogenic water	6.2	6.4	3.8	6.6
Gas	6.4	6.0	4.4	6.7
Thermobitumen	68.0	48.2	65.0	51.6
Insoluble residue	1.2	0.0	16.5	1.9
Yield of oil fractions, %, organic matter basis:				
< 200 °C	9.3	10.5	8.5	10.8
200-350 °C	8.5	17.7	7.5	16.4
> 350 °C	0.4	9.2	0.3	6.0
Specific gravity of oil at 20 °C	0.8748	0.8888	0.8735	0.8780
Refractive index $n^{20}{}_D$	1.4868	1.4900	1.4820	1.4868
Elemental composition of oil, %:				
C	81.18	82.66	83.23	81.84
H	12.69	11.62	12.33	11.70
S	2.23	0.82	1.36	1.07
O+N	3.90	4.90	3.08	5.39
Ratio C : H	6.40	7.11	6.75	6.99

Table 5. **Thermobitumen Characteristics (after K. Kask)**

	Decomposition temperature, °C			
	330	360	380	400
Duration of experiment, h	132	14	6	6
Yield of thermobitumen, %, organic matter basis	48.2	51.6	35.6	21.7
Elemental composition, %:				
C	86.96	85.74	85.32	84.50
H	8.43	8.43	8.35	9.02
S	0.36	0.31	0.53	0.57
O+N	4.25	5.52	5.30	5.91
Molecular mass	805	703	651	486
Empirical formula	C_nH_{2n-39}	C_nH_{2n-41}	C_nH_{2n-35}	C_nH_{2n-24}

An analysis of those data shows that an increase in reaction temperature produces a gradual decrease in the molecular weight of thermobitumen. Simultaneously, the bitumen becomes more hydrogen-deficient. Based on these data, the conclusion can be drawn that during the thermal decomposition of kerogen, it is transformed into the relatively

high molecular weight primary bitumen. Further decomposition of the primary bitumen occurs with the formation of the light oil and the secondary bitumen.

We are of the opinion that no sharp qualitative differences exist between the secondary bitumen and the heavy part of shale oil. Some portion of the heavy fractions of shale oil already forms at lower temperatures but is simply not distilled at the low temperature of the thermal processing. To procure evidence for this assertion, some data on thermobitumen distillation under vacuum are presented in Table 6.

Table 6. **Vacuum Distillation of Thermobitumen at 1 mm Hg (after K. Kask)**

Decomposition temperature, °C	Distillation temperature, °C	Distillation balance, %			Distillate molecular weight	Phenols content, %	Elemental composition of distillate, %			
		Distillate	Residue	Losses			C	H	S	O+N
300	301	8.8	89.1	2.1	320	43	84.33	10.50	0.35	4.82
360	354	22.0	72.8	5.2	322	46	83.22	10.23	0.45	5.70
380	360	39.1	59.9	1.0	325	54	84.62	9.50	0.45	5.43

As seen from these data, an essential part of thermobitumen is distilled under vacuum and more distillate is produced from bitumen formed at higher temperatures. As for the chemical composition, thermobitumen distillate does not differ from heavy fractions of shale oil and represents a continuation of the high-boiling part of the shale oil.

The results of our experiments with isothermal destruction allow us to specify a conceptual mechanism for the thermal destruction of kerogen, which is valid for Baltic shale kerogen.

During the first stage of destruction, peripheral functional groups of kerogen are split off. This is accompanied by the release of gas and pyrogenic water. Since most of the pyrogenic water already separates at low temperatures, the conclusion can be drawn that this water forms from unstable hydroxyl groups. As during the first stage, carbon monoxide and hydrogen sulfide are formed, since C—O and C—S bonds are also split. During this stage the destruction of the basic macromolecule does not yet take place. It only begins when peripheral functional groups are split off as a result of breaking of the less stable oxygen and sulfur bonds. As a result, the primary bitumen is formed. During this process numerous new side chains are formed. These side chains of the primary bitumen decompose yielding gases and low-boiling oil fractions. The remaining nucleus is much poorer in hydrogen and contains more stable oxygen bonds. Then the splitting of oxygen bonds begins. This is accompanied by the formation of larger structural units that pass into the high-boiling oil fraction or remain as an insoluble component in the residue. We consider it correct to call the thermobitumen formed during this decomposition stage, secondary, since it totally differs from the primary product of kerogen decomposition.

The thermal decomposition of the secondary bitumen occurs until its molecular weight has reached 400-500. At such a high degree of

decomposition there are no unstable oxygen bonds present and further decomposition occurs through the splitting of carbon-carbon bonds. When the reaction temperature is high enough for the distillation of the heavy part, it will be distilled. Otherwise this residue undergoes liquid-phase cracking. It is quite clear that cracking of such a stabilized, and probably highly aromatic product, yields no ¹ow-boiling fractions and coke and gas are the main products.

As seen from the experimental data, at 330 °C already 80 % of fraction boiling up to 200 °C is formed. The other 20 % of the gasoline fraction is formed only at temperatures over 400 °C, accompanied with a noticeable increase in the yields of coke and gas. This provides an obvious assurance that the primary products of decomposition are cracked.

Based on the results stated above, the following scheme of the thermal decomposition of Baltic oil shale kerogen is proposed:
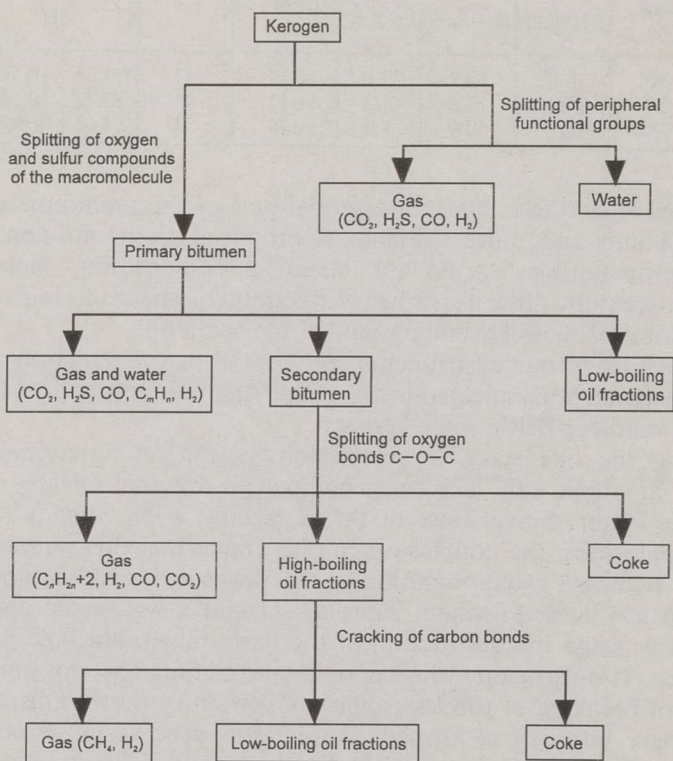

Fig. 2. Proposed scheme for kerogen thermal decomposition

The essential difference between this scheme for kerogen thermal decomposition and prior concepts lies in establishing the low-boiling oil fractions being formed during the primary decomposition. Our scheme coincides well with the results of Estonian shale retorting in commercial units. For example, during the retorting of shale in tunnel ovens, the oil

which is obtained during startup, i.e. at low temperatures, consists mainly of the benzene fraction. We consider this fact very important and useful for designing and operating new retorting units.

Evolution of heavy fractions of oil at higher temperatures promotes coke formation and plugging of the unit. It could be avoided by increasing the partial pressure of oil vapours, especially at the stage where high-boiling fractions are produced. Therefore, an increase in the amount of inert gases should have a favourable effect on heavy oil separation and should prolong the on-line time for the unit.

We consider that the two-stage scheme of kerogen thermal decomposition which we propose is an improvement to the understanding of the process mechanism. The two-step process includes the formation of primary and secondary bitumens. We call the primary product which is formed during the decomposition of the basic kerogen macromolecule the primary bitumen. This material is partially soluble in organic solvents. Our concept for the formation of bitumen completely coincides with observations made by V. Korshak and S. Rafikov [5]. They stated that "low-temperature decomposition consists mainly of splitting chains into long segments" and "at higher temperatures, the splitting of macromolecule peripheral chains, which yields low-molecular weight compounds, becomes more and more apparent...".

There is little use in speaking about a molecular weight for the shale thermobitumen until it forms a unit which is stable at a given temperature, since it passes through several stages during the thermal decomposition. Therefore, dividing the thermal decomposition product into primary and secondary bitumen facilitates the understanding of their formation. According to our scheme, the formation of the secondary bitumen comprises all other stages of thermal decomposition until a stable form is produced with a molecular weight of 400-500. The different stages of decomposition may of course overlap each other during very rapid heating of the shale, but the general mechanism of kerogen thermal decomposition does not change.

Conclusions

1. The mechanism for isothermal decomposition of Baltic oil shale within the temperature range 300-440 °C has been investigated.

2. It was demonstrated that low-boiling fractions of shale oil are formed during primary decomposition of shale organic matter at temperatures below 330 °C. Increases in reaction temperature lead to major increases in the formation of heavy oil fractions accompanied with a small increase in the yield of light oil.

3. The chemical group composition of oil fractions obtained during isothermal decomposition has been investigated. An increase in the amount of unsaturated hydrocarbons occurs at the expense of saturated hydrocarbons. This increase is observed with increases in the processing temperature.

4. It was demonstrated that the thermobitumen structure changes continuously as the degree of thermal decomposition increases. Eventually a stable form of the thermobitumen is produced, with a molecular weight of 400-500.

5. A scheme for kerogen thermal decomposition is proposed. During the first stage, peripheral hetero-groups of the kerogen molecule are attacked and the high molecular weight thermobitumen is formed. Further decomposition of the primary bitumen yields low-boiling fractions of oil and the secondary bitumen. The secondary bitumen subsequently decomposes into heavy oil, coke and gas. The heavy oil is only cracked at temperatures exceeding 400 °C, at which point it yields an additional portion (20 % of the total amount) of low-boiling oil fractions.

Assistent professor K. Kask, Ph. D., senior master E. Petukhov, Ph. D., and laboratory assistant D. Tross have taken part in carrying out this work.

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