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STEPWISE THERMAL DECOMPOSITION OF KUKERSITE

Considering the chemical composition of shale oils they are, as a rule, far from the state of thermodynamic equilibrium [1, 2] and, hence, the processes of their secondary transformation are expected to continue during the whole period of the shale degradation products stay in the hot zone. Earlier we noted a remarkable role of secondary reactions on final stages of semicoking of a Lower Eocene oil shale of Uzbekistan [3]. In the present study Middle Ordovician oil shale "kukersite" (Estonia) was used as the subject as a shale to a great extent different from the above-mentioned.

Characteristics of the initial shale (wt. %): analytical moisture W^a 1.6, ash A^d 33.1, mineral carbon dioxide $(CO_2)_M{}^d$ 5.1, organic matter (OM) $[OM^d = 100 - A^d - (CO_2)_M{}^d]$ 61.8. Elemental composition of kerogen (wt. %): C 76.0, H 9.4, S 1.1, N 0.3, O (by difference) 13.2; atomic H/C ratio 1.48.

Thermal destruction of the shale was performed in an electrically heated Fischer retort using heating rate of 5 °C/min up to the final temperatures of 400, 430, 460, 490 and 520 °C, later an additional experiment has been carried out with the final temperature of heating 505 °C. At each of the terminal temperatures shale was heated isothermally for 20 minutes. Thus, a stepwise thermal decomposition of the shale was realized with the aim of elucidating processes that take place on the final stages of semicoking.

The shale oils obtained were dephenolized using a 10 % aqueous solution of potassium hydroxide and then separated into the chemical group compounds concentrates by thin layer chromatography on silica gel with *n*-hexane as an eluent. The oil fractions obtained as well as gaseous products were analyzed by gas chromatography in columns of different polarity with temperature programming. A Specord 75IR1 spectrometer was used for getting infra-red spectra of the oils and solid residues.

The data on the yield of semicoking products and chemical composition of oils are presented in Tables 1 and 2 as well as in Fig. 1. It follows that the most intensive oil formation takes place in the temperature region 400-440 °C and at 460 °C the bulk of the oil (above 95 %) is already evolved but generation of gaseous products continues. Evidently, starting from the temperatures of about 430-440 °C no considerable oil formation takes place or the processes of its generation and degradation are in equilibrium.

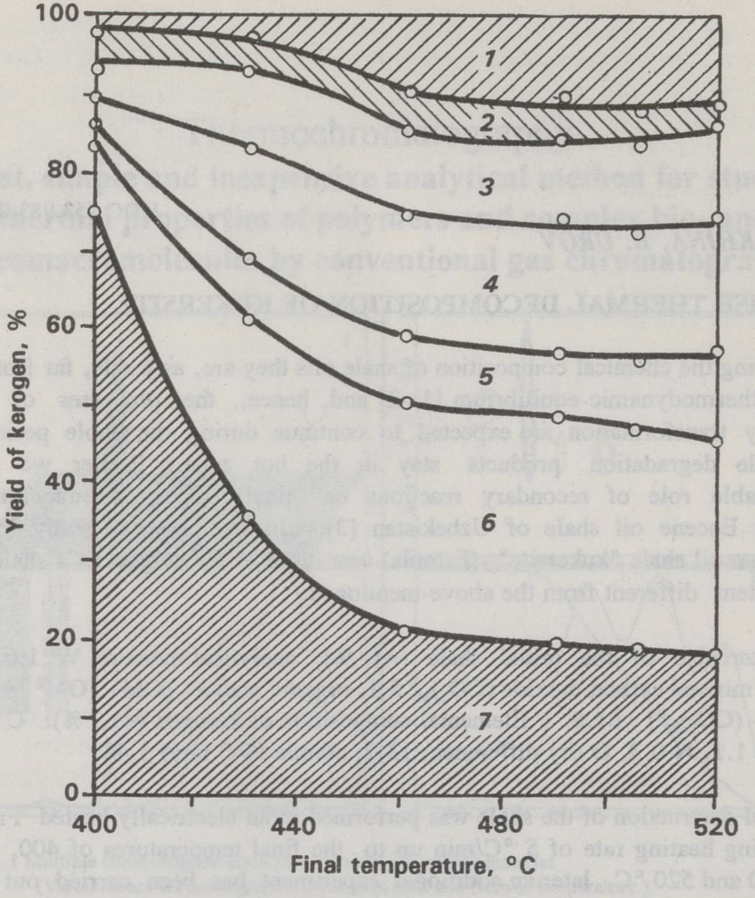

Fig. 1. Formation dynamics of the kukersite thermolysis products on the final stage of semicoking. *1* - gas, *2* - pyrolytic water, *3* to *6* - shale oil (*3* - aliphatic and naphthenic hydrocarbons, *4* - aromatic hydrocarbons, *5* - acidic compounds, *6* - neutral and basic heteroatomic compounds), *7* - non-volatile residue

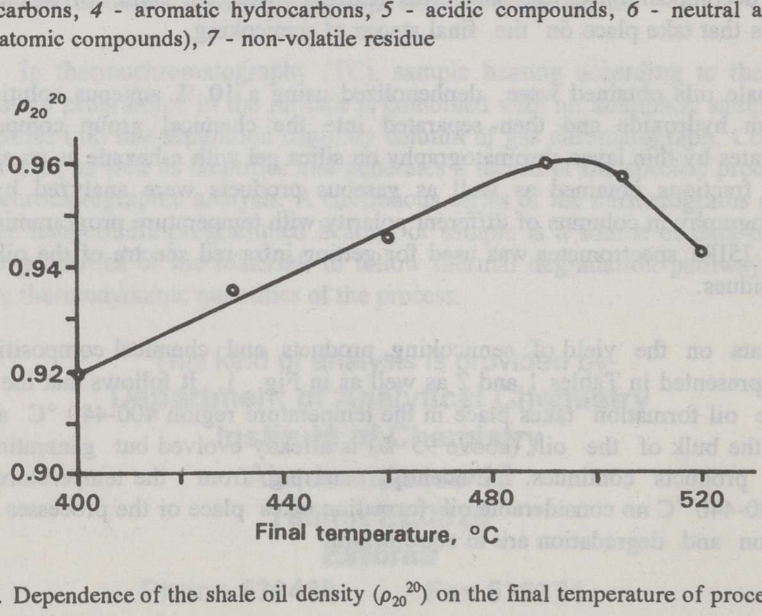

Fig. 2. Dependence of the shale oil density (ρ_{20}^{20}) on the final temperature of processing

Table 1. **Yield of Thermolysis Products (wt. %)**

Product	Final temperature of heating (°C)					
	400	430	460	490	505	520
On the dry shale basis						
Shale oil	11.1	35.8	39.7	40.5	39.4	41.7
Pyrolytic water	2.7	2.5	2.9	2.9	3.0	1.8
Solid residue	80.8	59.0	49.1	47.6	46.2	46.6
Gas and losses (by difference)	5.4	2.7	8.3	9.0	11.4	9.9
On the kerogen basis						
Shale oil	18.0	57.9	64.2	65.5	63.8	67.5
Pyrolytic water	4.4	4.0	4.7	4.7	4.9	2.9
Solid residue*	74.8	35.5	21.6	20.1	18.6	19.0
Gas and losses (by difference)	2.8	2.6	9.5	9.7	12.7	10.6

*On the basis of the data on its yield and composition [W^a, A^d, $(CO_2)_M{}^d$].

The curve for density of the oils obtained (Fig. 2) may be explained as a result of intensifying distillation off heavier fractions of oils with increasing temperature and destruction of the primary oil at temperatures higher than 490 °C where distillation cannot more compensate degradation processes. In this aspect, the oil decomposition processes can also occur at lower temperatures but there the high-boiling fractions distillation effect prevails.

And not only distillation. Though the oil yield, kerogen basis, stays practically constant in the temperature region 460-520 °C, it does not mean that shale oil is not generated in this region. Evidently, oil formation and its degradation processes compensate each other there.

Table 2. **The Chemical Group Composition of Shale Oils (wt. %)**

Group of compounds	Final temperature (°C)					
	400	430	460	490	505	520
Hydrocarbons:						
Aliphatic and naphthenic	19.3	16.5	17.5	16.6	16.7	16.3
Monocyclic aromatic	4.4	3.7	4.4	3.9	4.1	3.0
Bi- and polycyclic aromatic	14.3	21.2	19.3	20.4	21.1	18.1
Heteroatomic compounds:						
Neutral and basic	48.0	46.1	45.7	45.0	45.8	42.6
Acidic	14.0	12.5	13.1	14.1	12.3	20.0

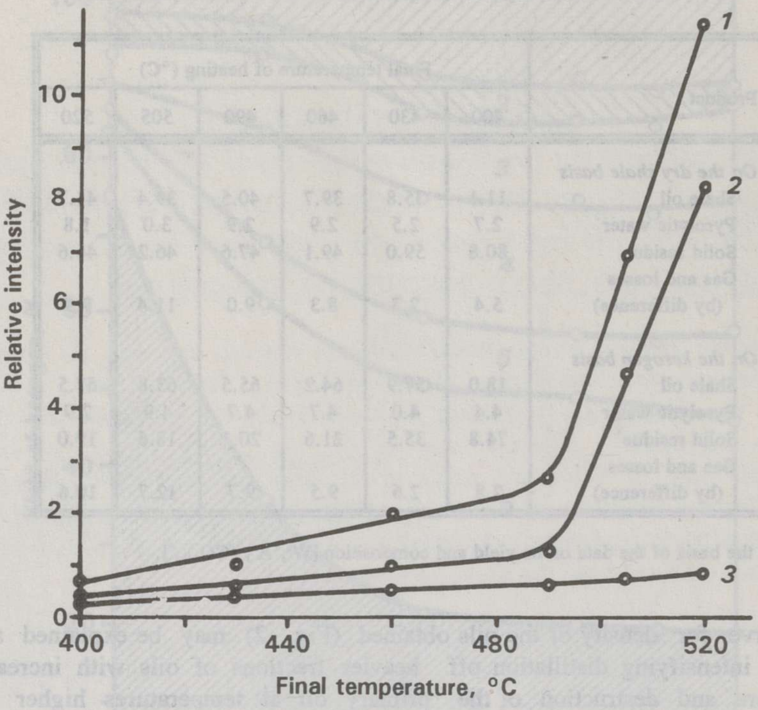

Fig. 3. Relative intensity of some absorption bands in the IR-spectra of solid residues (cm^{-1}): *1* - 1610/2930, *2* - 780/2930, *3* - 780/1610

Table 3. **Composition of the Thermolysis Non-volatile Residues**

Index	Final temperature (°C)*					
	400	430	460	490	505	520
Analytical moisture W^a, %	0.8	1.0	1.3	1.4	1.1	1.4
Ash A^d, %	36.9	54.2	62.7	64.0	64.8	65.4
Carbon dioxide of carbonates $(CO_2)_M{}^d$, %	5.9	8.5	10.1	9.9	10.3	9.4
Total sulfur $S_t{}^d$, %	1.2	1.1	0.8	0.5	0.5	n.d.
Pyritic sulfur $S_s{}^d$, %	0.4	0.3	tr.	abs.	abs.	abs.
Organic matter [100 - A^d - $(CO_2)_M{}^d$], %	57.2	37.3	27.2	26.1	24.9	25.2
Ultimate analysis of organic matter:						
Carbon, %	82.2	72.2	81.2	78.7	84.2	77.3
Hydrogen, %	8.6	5.6	4.9	4.2	2.9	1.7
Sulfur, %	1.4	2.2	3.0	1.9	2.0	n.d.
Atomic H/C ratio	1.26	0.93	0.72	0.64	0.41	0.26

* tr. = traces, n.d. = not determined, abs. = absent

The data on chemical composition of shale oils by gas chromatographic analysis also reveal the secondary cracking reactions gathering speed as temperature in the retort increases, especially in the region about 430 °C. Thus, the concentration ratio of light *n*-alkanes C_9-C_{17} to that of heavier ones C_{18}-C_{23} makes up 4.6 at the final temperature of heating 400 °C, 8.4 at 430 °C, 10.3 at 460 °C and 16.7 at 520 °C. The corresponding values for the concentration ratios of cresols to 5-methyl-resorcinol are 0.6, 1.0, 1.1 and 1.2; for methyl-*n*-octyl-ketone to methyl-*n*-pentadecyl-ketone 2.6, 4.0, 4.0 and 4.6.

The yield of non-volatile residue stays relatively constant starting from 460 °C (Table 1; Fig. 1) though its atomic ratio H/C decreases up to 520 °C (Table 3) and a notable aromatization begins at 490 °C (Fig. 3). The most substantial loss of organic carbon, hydrogen, sulfur and organic matter as a whole in the form of volatile products takes place in the temperature region 400-430 °C (Fig. 4). Organic sulfur seems to be quite stable as compared with carbon and, especially, hydrogen, though it is known that in most cases carbon-sulfur bonds are not thermally stable.

It is interesting to note that pyritic sulfur practically disappears from the solid residue at 460 °C already. We are of opinion that this is caused by elimination of pyritic sulfur by formation of hydrogen sulfide (as a result of reactions with the hydrogen-containing destruction products, including water).

As in the case of Uzbek oil shales [3], the yield of pyrogenetic water on the kerogen basis is the highest at 490 °C (Table 1). The same is observed as to the yield of hydrogen sulfide in the kukersite semicoking gases (Table 4; Fig. 5). This is probably connected with a high thermal stability of sulfur remaining in the solid residue at higher temperatures and absence of pyritic sulfur that is readily converted to hydrogen sulfide there. As to carbon dioxide and saturated

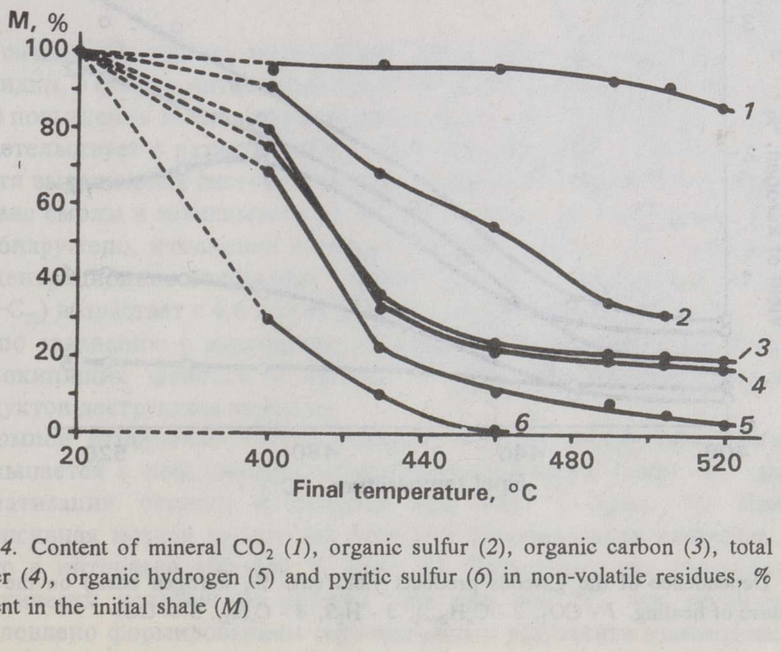

Fig. 4. Content of mineral CO_2 (*1*), organic sulfur (*2*), organic carbon (*3*), total organic matter (*4*), organic hydrogen (*5*) and pyritic sulfur (*6*) in non-volatile residues, % of their content in the initial shale (*M*)

hydrocarbons, the main gaseous destruction products except hydrogen sulfide, their yield kerogen basis increases sharply in the region 430-460 °C, thus indicating acceleration of secondary cracking processes.

On the whole, the influence of secondary reactions is less pronounced when processing kukersite shale than in the case of Uzbek oil shales [3], probably due, at least partially, to the relative enrichment of the former by organic matter and, hence, a greater velocity of the vapours-gases mixture evacuation from the hot zone and, consequently, more limited possibilities for the reactions of this type.

Table 4. **Composition of Thermolysis Gases (vol. %)**

Compound	Final temperature (°C)					
	400	430	460	490	505	520
H_2S	36.2	30.8	22.3	27.7	23.3	19.2
CO_2	29.9	27.9	27.3	23.8	28.9	24.8
CO	15.1	9.4	8.8	6.4	6.5	6.4
H_2	2.6	1.6	2.5	3.3	2.6	6.6
CH_4	5.5	10.3	14.0	13.7	8.0	18.3
C_2H_6	3.9	7.3	9.7	9.3	12.2	9.9
C_2H_4	1.0	1.6	2.2	2.7	3.3	2.7
C_3H_8	1.7	3.7	4.4	4.2	5.3	4.2
C_3H_6	2.2	3.9	4.5	4.5	5.1	4.3
C_4H_{10}	1.1	2.0	2.4	2.4	2.7	2.0
C_4H_8	0.8	1.5	1.9	2.0	2.1	1.6

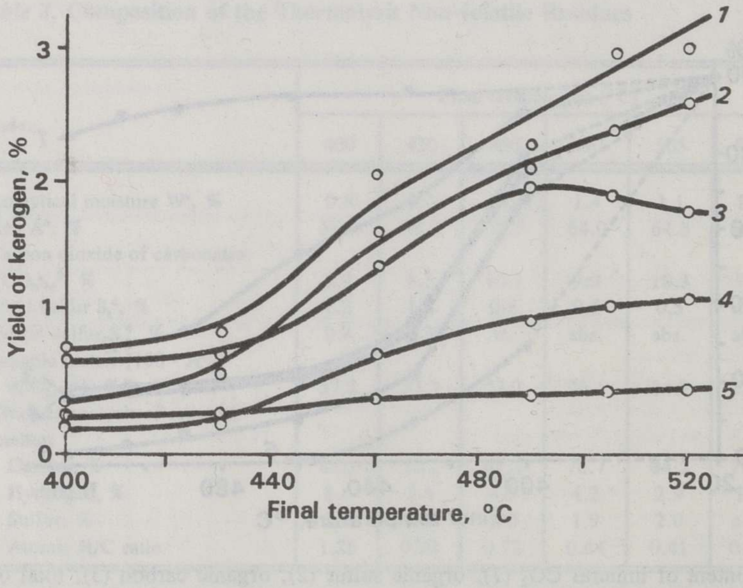

Fig. 5. Dependence of the gaseous products yield (wt. %, kerogen basis) on the final temperature of heating. *1* - CO_2, *2* - C_nH_{2n+2}, *3* - H_2S, *4* - C_nH_{2n}, *5* - CO

Conclusions

1. It has been established that perceivable secondary cracking of the primary shale oil takes place on the final stages of the kukersite shale semicoking it accelerating at temperatures above 430 °C.
2. It is inexpedient to process kukersite at temperatures above 460-470 °C as the oil yield does not increase at higher temperatures noteworthily, its quality as well as that of gaseous products does not improve though energy requiements for heating the shale grows substantially.
3. The role of the shale oil secondary transformation reactions is dependent on the properties of the initial shale: due to a higher velocity of the vapour-gases mixture evacuation from the hot zone it is comparatively limited in the case of the organic rich kukersite.

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СТУПЕНЧАТОЕ ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ КУКЕРСИТА

Резюме

С целью получения дополнительных сведений о масштабе и характере вторичных реакций, протекающих на завершающем этапе полукоксования сланца-кукерсита, проведена серия опытов по термическому разложению сланца в лабораторной алюминиевой реторте при режиме подъема температуры по ГОСТ 3168-66 до конечной температуры 400, 430, 460, 490, 505 и 520 °C с последующим анализом продуктов деструкции.

Из экспериментальных данных следует, что наиболее интенсивное смолообразование имеет место в температурном интервале 400—440 °C, и при достижении температуры 460 °C подавляющая часть (более 95 %) смолы уже выделилась (табл. 1; рис. 1). Начиная с 430—440 °C генерация смолы затухает или процессы ее формирования и деградации находятся в равновесии. Плотность получаемой смолы вначале возрастает (рис. 2), очевидно, в связи с интенсификацией отгонки более тяжелых фракций по мере повышения температурного потенциала, затем снижается; последнее свидетельствует о развитии вторичных деструктивных реакций.

Хотя выраженных систематических изменений в групповом химическом составе смолы в зависимости от конечной температуры нагрева (табл. 2) не обнаружено, изменения в индивидуальном составе существенны. Так, концентрационное отношение "легких" (C_9—C_{17}) *н*-алканов к "тяжелым" (C_{18}—C_{23}) возрастает с 4,6 при конечной температуре 400 °C до 16,7 при 520 °C, по сравнению с вышекипящими заметно повышается концентрация низкокипящих фенолов и кетонов — результат крекинга первичных продуктов деструкции керогена.

Атомное отношение H/C в твердом остатке деструкции монотонно уменьшается с повышением конечной температуры (табл. 3), заметная ароматизация остатка начинается при 490 °C (рис. 3). Наиболее интенсивная потеря нелетучим остатком органического вещества имеет место в интервале 400—430 °C (рис. 4). Интересно, что пиритная сера практически исчезает из остатка уже при 460 °C, что по-видимому, обусловлено формированием сероводорода в результате взаимодействия

этой разновидности серы с водородсодержащими продуктами термолиза, в т. ч. с пирогенетической водой.

Выход газообразных веществ, характерных продуктов крекинга, в расчете на кероген коррелирует с конечной температурой нагрева; особенно заметно в интервале 430–460 °С возрастает выход двуокиси углерода и предельных углеводородов (табл. 4; рис. 5).

На основе полученных данных можно заключить, что переработку кукерсита для производства смолы нецелесообразно проводить при конечной температуре выше 460–470 °С, поскольку при дальнейшем нагреве выход смолы существенно не возрастает, качество ее не улучшается, а энергетические затраты на переработку сланца возрастают.

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