DEPENDENCE OF THE YIELD AND PROPERTIES OF SEMICOKING OILS ON THE MINERAL CONTENT AND COMPOSITION OF OIL SHALES

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ABSTRACT

Despite numerous investigations on the influence of mineral matter of fossil fuels on the thermal destruction of their organic matter, the data available are scarce and often contradictory. This paper aims at investigating the influence of mineral substances of shales on the yield and composition of shale oils obtained by thermal decomposition in a Fischer retort and by high-rate heating. In experiments natural oil shale samples from different deposits and artificial mixtures were used.

The data obtained indicate that it is the adsorption mechanism that influences the yield and composition of semicoking oils, being typical for all mineral components of shales: more polar components are retained on the surface of the solid decomposition residue and are subjected to secondary destruction reactions to give an additional amount of gaseous products and semicoke. The oil yield on kerogen and its density decrease, the oil is enriched with less polar, in particular, aliphatic, hydrocarbons, while the semicoking gas is enriched with carbon dioxide.

Unlike carbonates, argillaceous minerals reveal, besides the adsorption effect, also a favourable catalytic effect on oil formation. Therefore it is expedient to

enrich some shales, especially those with an appreciable amount of alumosilicates, to some extent only to obtain a maximum oil yield on kerogen.

The degree of influence of the same mineral material on the thermal destruction of organic matter of different shales is different and depends on the composition and structure of their kerogen.

Oil shales are characterized by a high content of mineral substances that may influence and actually influence considerably the yield and chemical composition of the thermal decomposition products of shales, in particular, shale oil. However, the problem is far from being solved.

It is observed practically with all oil shales that with decreasing organic content in the raw material the semicoking oil yield on kerogen decreases. Earlier, at the 4th International Symposium on Analytical and Applied Pyrolysis (Budapest, 1979) the author reported data evidencing it is the adsorption mechanism that influences the yield and composition of semicoking oils, being common for all types of mineral components of shales. The phenomenon consists in that more polar components of shale oils, in particular, heteroatomic (O-, S-, N-) are retained on the surface of the solid decomposition residue and are subjected to secondary cracking reactions with the formation of an additional amount of gaseous products and semicoke, due to which the oil yield on kerogen decreases. Thus, with increasing mineral content in the Kashpir shale (USSR) from 30 to 90% the semicoking oil yield (kerogen basis) decreases from 37 to 13%. At a very low organic content in the rock when the oil-forming ability of kerogen may be compared with the adsorptive capacity of the mineral part, no oil is issued.

For natural oil shales, however, whose mineral content and composition vary in deposition vertically and horizontally, the effect of mineral matter on the oil yield is often very weakly expressed. This is the case, for example, with the dependence of semicoking oil yield (kerogen basis) on the content of kerogen for Lower Eocene oil shales of Central Asia occurring on a wide territory in Uzbekistan and Tadzhikistan(Fig.1).

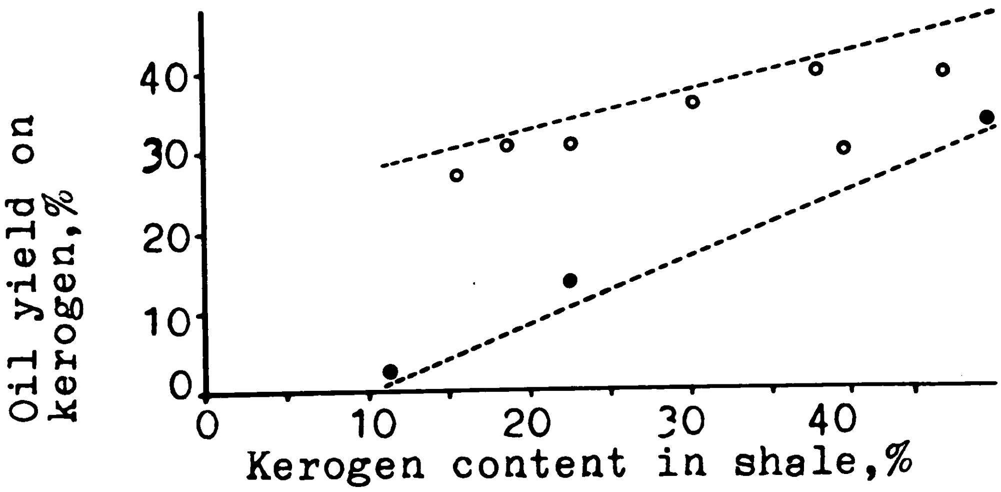

Fig.1. Dependence of the semicoking oil yield (kerogen basis) on the organic content in the shales of Central Asia (deposits: o - Uzbek, • - Tadzhik)

Proceeding from oil shale samples from one section of this basin (the Kapali deposit) pretreated with 10% hydrochloric acid to remove carbonates, the dependence becomes more pronounced (Fig.2). This gives evidence of a considerable effect not only of the content but also composition of mineral part. That can be observed with the Turovo oil shales of Byelorussia which are characterized by great variations in the proportions of carbonaceous and alumosilicate material in the mineral part of the shale. In this case, no clear relationship between the oil yield on kerogen and overall content of mineral components is observed (Fig.3a), possibly due to too narrow a range of changes in the organic content of the samples investigated. However,

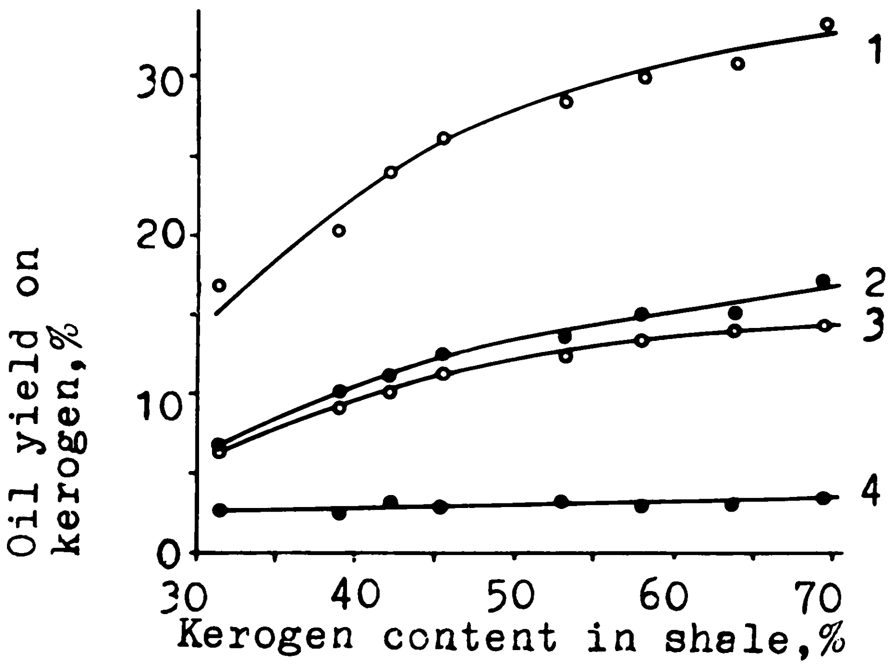

Fig.2. Dependence of the yield of semicoking oil and its constituents on the organic content in the Kapali shale (1 - total oil, 2 - heteroatomic compounds, 3 - aromatic hydrocarbons, 4 - non-aromatic hydrocarbons)

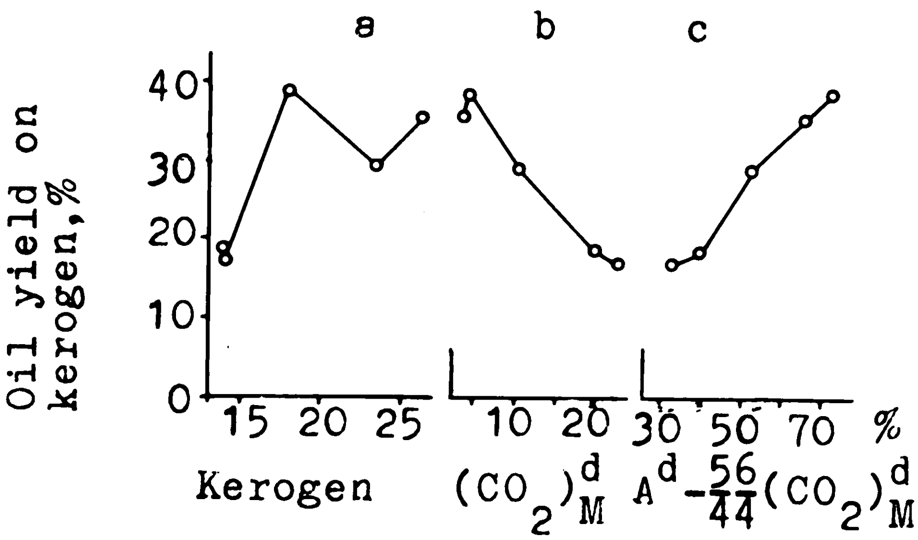

Fig.3. Dependence of the yield of semicoking oil from the Byelorussian shale on the content of kerogen (a), carbon dioxide of carbonates (b) and noncarbonaceous mineral matter (c) in the shale

the effect of carbonates whose content is characterized by the carbon dioxide content of carbonates (Fig.3b), and noncarbonaceous mineral matter (by the difference between the ash content of sample and that of CaO in ash, Fig.3c) on the yield of oil is more pronounced.

At the same time it is observed that carbonates have a suppressing effect on oil formation, while the effect of the noncarbonaceous part of mineral matter is favourable. However, it would be incorrect to extrapolate the last curve into a region of higher concentrations of these mineral components; it is possible that starting from a certain amount of noncarbonaceous minerals, the most significant role will be played by the adsorption factor, and the oil yield on kerogen will decrease again.

Statistical analysis demonstrates that usually mineral substances reveal a suppressing effect on oil formation: on the basis of data on oil shales from 82 deposits and outcrops, the semicoking oil yield on kerogen (T^k,%) correlates positively with the kerogen content (K^d,%) of shale:

$$T^k = 0.32\ K^d + 27.5$$

At a high mineral content of shale the oil yield decreases mainly due to polar compounds more strongly retained by the solid residue (Fig.2, Table 1). Obviously it is no coincidence that the semicoking gas from sample 1 contained 21.2, but that from sample 2 39.9 vol.-% of CO_2, whose formation is most probably associated with the secondary cracking of adsorbed oxygen compounds.

Table 1. Semicoking oil from two samples of Kashpir oil shale (K^d respectively 15.5 and 1.5%)

	Sample 1	Sample 2
Yield on kerogen,%	26.8	12.7
Density ρ_4^{20}	0.974	0.961
C,%	79.5	79.4
H,%	9.6	10.6
Non-aromatic hydrocarbons,%	13	40
Aromatic hydrocarbons,%	44	25
Heteroatomic compounds,%	43	35

In order to elucidate the influence of mineral matter of different types on the yield of oil, artificial mixtures of the kerogen concentrates of kukersite (K^d=90.4%) and dictyonema shale of Estonia (K^d=56.1%), the carbonate rock from the kukersite bed (%: calcite 77, dolomite 6, quartz 5) and the argillaceous mineral matter of dictyonema shale (%: hydromica 52, chlorite 3, quartz 34) were used.

On the basis of the dependences obtained (Fig.4 and 5) the following may be concluded: 1.The same mineral matter influences the pyrolysis of different kerogens differently. Thus, if carbonates strongly suppress the formation of oil from the kerogen of dictyonema shale, then their presence influences the kukersite shale kerogen little. 2.The carbonaceous mineral matter in both cases has a suppressing effect on oil formation, although the dependence of oil yield (kerogen basis) on the content of carbonates is not so pronounced. 3. The effect of the argillaceous matter content is, in comparison with carbonates, more pronounced.

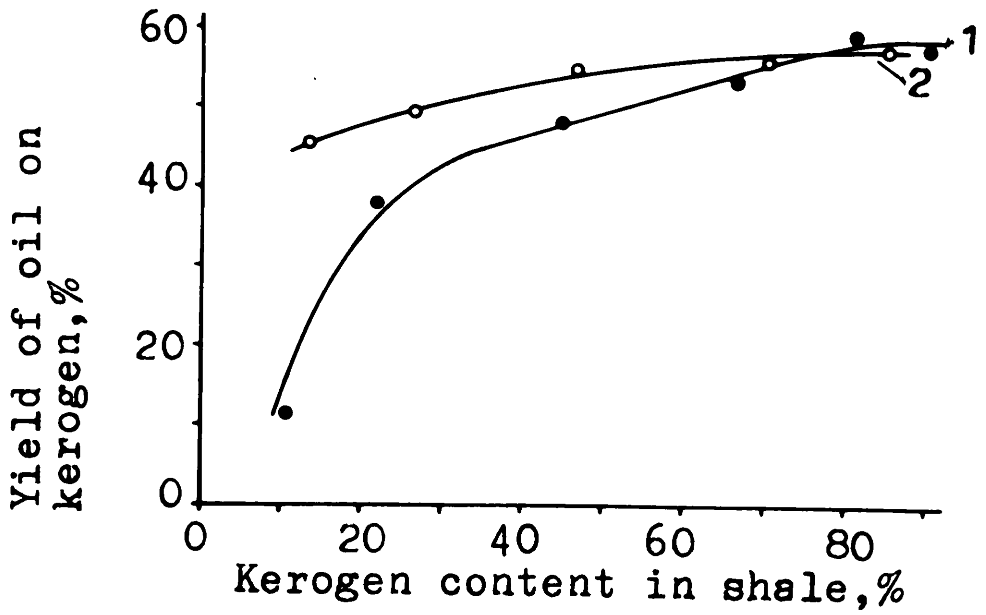

Fig.4. Dependence of the semicoking oil yield (kukersite shale kerogen basis) on the content of kerogen in the mixtures with argillaceous (1) and carbonaceous (2) rock

On the other hand, in some cases, the argillaceous mineral material may contribute to oil formation: with the decrease in its content below a certain level the oil yield begins to decrease again (Fig.5, curve 1). This gives evidence of a complicated nature of the effect of argillaceous minerals on the kerogen destruction processes. Here the suppressing adsorption effect on oil formation is obviously associated with the catalytic effect of alumosilicates, favouring the redistribution of hydrogen between the volatile products and nonvolatile residue and, as a result, also oil formation. This means that at a very high organic content its influence weakens due to a low concentration of alumosilikates, but at a low kerogen content it is disguised by the dominating adsorption processes.

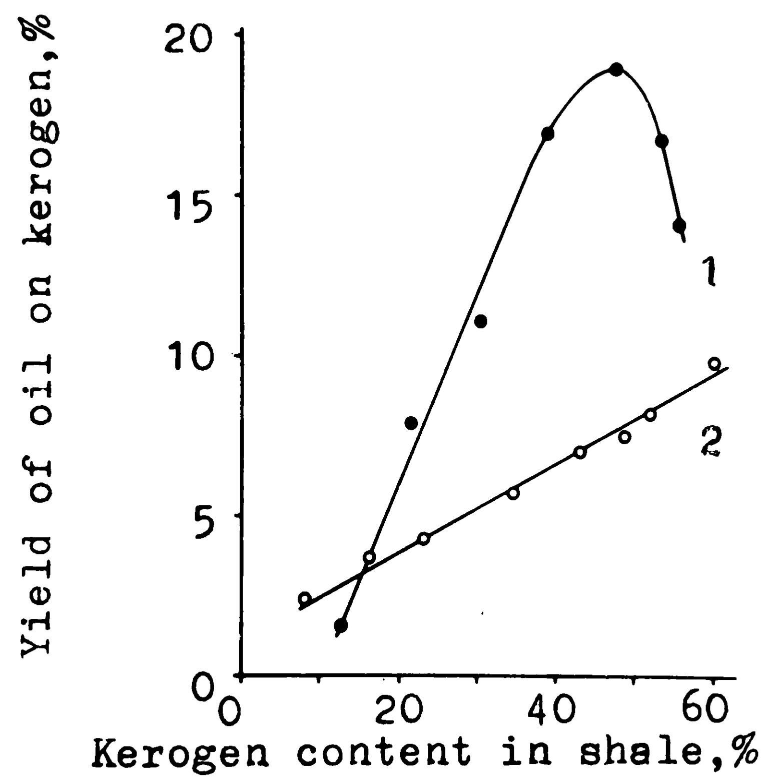

Fig.5. Dependence of the semicoking oil yield (dictyonema kerogen basis) on the content of kerogen in the mixtures with argillaceous (1) and carbonaceous (2) rock

Thermographic analysis of the model mixtures under study (a Q-1500 derivatograph, platinum crucibles with a lid, air flow) demonstrated that mineral matter shifts the thermal transformation of kerogen into a region of higher temperatures. Thus, with increasing argillaceous rock content in the mixture with kukersite concentrate from 29.5 to 64.8% the first exothermal maximum in the DTA curve is shifted from 310 to 375°C, the first major endothermal peak is shifted from 380 to 425°C. The corresponding, although smaller, changes are observed in the DTG curves.

High-rate thermal destruction of model mixtures was carried out by passing the fine-grained material through the pre-heated (up to 500-625°C) tube in a stream of pre-heated N_2 or CO_2 for 0.1-0.2 sec. The rate of heating was about 10^5 °/min.

Table 2. High-rate pyrolysis of two mixtures of the kerogen concentrate of dictyonema shale and its mineral matter, %

	Sample 1	Sample 2
Kerogen content in the mixture	19.5	59.2
Oil yield on kerogen	25.1	21.8
Content in oil: C	81.0	77.6
H	7.9	7.5
Non-aromatic hydrocarbons	12	8
Aromatic hydrocarbons	31	25
Heteroatomic compounds	57	67

It follows from the data in table 2 that, in this case, mineral substances cause no decrease in the oil yield on kerogen. The oils contain, in comparison with standard oil, more heteroatomic compounds (57-75% as against 46-52%), its density being higher (1.03-1.07 as against 0.84-0.99). This allows optimization of the thermal decomposition processes of oil shales with respect to the yield and composition of the pyrolysis products by combining the effects of two factors: the degree of enrichment of shale with kerogen and the rate of its heating.