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ON THE MECHANISM OF THE EFFECT OF ALUMINOSILICATES
ON THERMAL DECOMPOSITION OF OIL SHALE KEROGEN

Kaarli UROV, Valentina VÖSSOTSKAJA. ALUMOSILIKAATIDE TOIMEMEHANISMIST PÕLEV-
KIVIDE KEROGEEINI TERMITSEL LAGUNEMISEL

Каарли УРОВ, Валентина ВЫСОЦКАЯ. О МЕХАНИЗМЕ ВОЗДЕЙСТВИЯ АЛЮМОСИЛИКАТОВ
НА ТЕРМИЧЕСКУЮ ДЕСТРУКЦИЮ КЕРОГЕНА ГОРЮЧИХ СЛАНЦЕВ

By the semicoking of model mixtures of kukersite shale concentrate ($A^d=9.4\%$) and a series of clay minerals it has been established that with increasing content of the latter in the raw material for processing the shale oil yield on kerogen basis does not decrease monotonously as in the case of non-catalytic minerals such as quartz, calcite, dolomite, etc., but remains relatively constant in the region of from about 40% to 70% of kerogen in the mixture (Fig. 1). This is probably caused by a mutual compensation of various effects due to mineral admixtures.

The sorption effect of mineral compounds (detaining the most polar part of shale oil on the solid residue surface followed by its more extensive secondary degradation as compared with the rest of oil [1]) results in decreasing the shale oil yield, organic matter basis (ΔT_1^0), that correlates with the relative mineral and organic (OM, %) content of the starting mixture:

$$\Delta T_1^0 = -s \left(\frac{100 - \text{OM}}{\text{OM}} \right) + a_1, \quad (1)$$

where s is the coefficient of the sorptive activity of mineral material and a_1 is a constant.

The catalytic effect of aluminosilicates that favours oil formation can be considered a logarithmic function:

$$\Delta T_2^0 = c \lg \left(\frac{100 - \text{OM}}{\text{OM}} \right) + a_2, \quad (2)$$

where c is the coefficient of the catalytic activity of mineral matter and a_2 is a constant.

With the increasing mineral content of the starting mixture the evolution rate of volatile products from the hot zone decreases and, as a result, a more exhaustive oil degradation takes place, while its yield diminishes as well. Let us express this effect as follows:

$$\Delta T_3^0 = -v \lg \left(\frac{100 - \text{OM}}{\text{OM}} \right) + a_3, \quad (3)$$

where v is the coefficient that takes into account the influence of the velocity of the evacuation of volatile substances on oil yield and a_3 is a constant.

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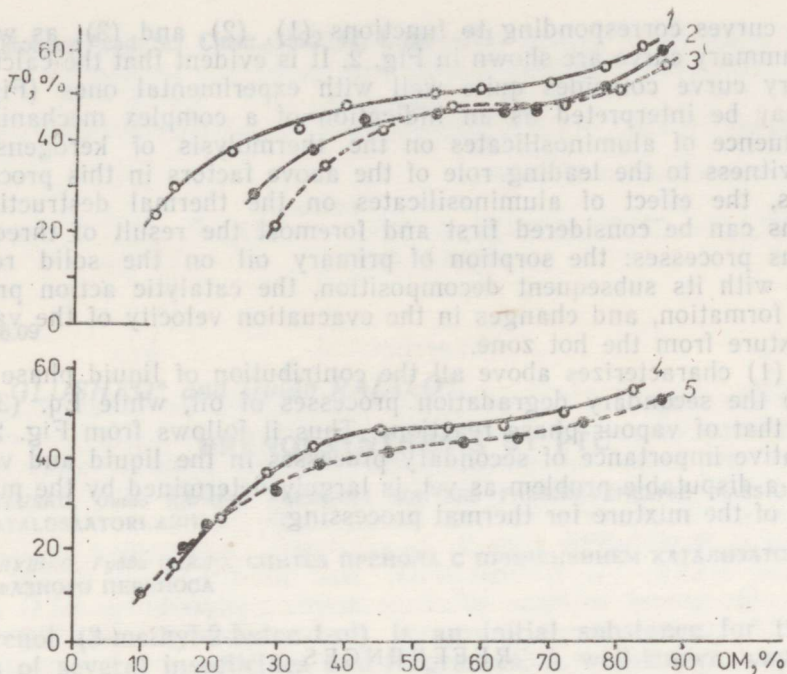


Fig. 1. Dependence of semicoking oil yield, kerogen basis, (T^0) on its content (OM) in the initial mixture for processing.

Mineral admixtures: 1 — palygorskite, 2 — kaolinite, 3 — halloysite, 4 — montmorillonite (bentonite), 5 — montmorillonite (activated gumbrine).

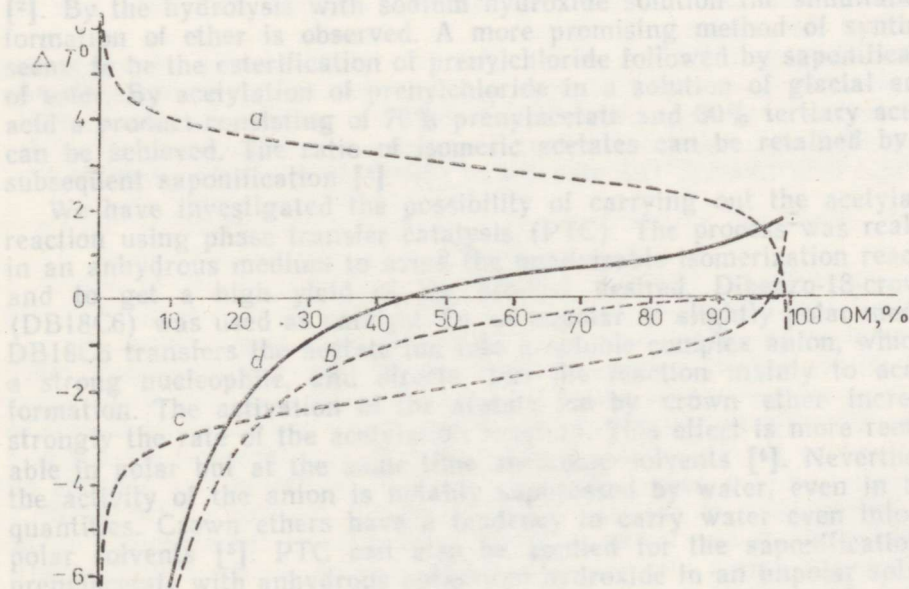


Fig. 2. Curves corresponding to functions (1), (2), and (3) and their summary curve: a — function (2) when $c=1.0$ and $a_2=3.0$; b — function (1) when $s=0.8$ and $a_1=0$; c — function (3) when $v=1.2$ and $a_3=-2.0$; d — summary curve of a, b, and c.

The curves corresponding to functions (1), (2), and (3), as well as their summary curve are shown in Fig. 2. It is evident that the calculated summary curve coincides quite well with experimental ones (Fig. 1). This may be interpreted as an indication of a complex mechanism of the influence of aluminosilicates on the thermolysis of kerogens and bears witness to the leading role of the above factors in this process.

Thus, the effect of aluminosilicates on the thermal destruction of kerogens can be considered first and foremost the result of three synchronous processes: the sorption of primary oil on the solid residue surface with its subsequent decomposition, the catalytic action promoting oil formation, and changes in the evacuation velocity of the vapour-gas mixture from the hot zone.

Eq. (1) characterizes above all the contribution of liquid phase reactions to the secondary degradation processes of oil, while Eq. (3) describes that of vapour phase reactions. Thus it follows from Fig. 2 that the relative importance of secondary processes in the liquid and vapour phases, a disputable problem as yet, is largely determined by the mineral content of the mixture for thermal processing.

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$$\Delta T_1 = -s \left(\frac{100 - OM}{OM} \right) + a_1 \quad (1)$$

where s is the coefficient of the sorptive activity of mineral material and a_1 is a constant.

The catalytic effect of aluminosilicates that favours oil formation can be considered a logarithmic function:

$$\Delta T_2 = -c \left(\frac{100 - OM}{OM} \right) + a_2 \quad (2)$$

where c is the coefficient of the catalytic activity of mineral matter and a_2 is a constant.

With the increasing mineral content of the starting mixture the evolution rate of volatile products from the hot zone increases and, as a result, a more exhaustive oil degradation takes place while its yield diminishes as well. Let us express this effect as follows:

$$\Delta T_3 = -v \lg \left(\frac{100 - OM}{OM} \right) + a_3 \quad (3)$$

where v is the coefficient that takes into account the influence of the velocity of the evacuation of volatile substances on the yield and a_3 is a constant.

Fig. 2. Curves corresponding to functions (1), (2), (3), (4) and their summary curve (5) when $s=0.8$ and $c=0.05$ and $v=0.05$ and $a_1=0.5$, $a_2=0.5$, $a_3=0.5$ and $a_4=0.5$.