INFLUENCE OF THE DISPERSION DEGREE OF MINERAL ADDITIVES ON THE YIELD AND COMPOSITION OF KUKERSITE SHALE SEMICOKING PRODUCTS

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Our earlier investigations have demonstrated that the mineral matter of oil shales considerably influences the yield and composition of their thermal decomposition products. However, up to now there are no data about the effect of the dispersion degree of mineral additives on the thermolysis process. Using model mixtures with calcium carbonate and silicon dioxide chemically precipitated on the surface of kerogen concentrate (Estonian kukersite) particles, it has been established that high-dispersed $CaCO_3$ and SiO_2 inluence the yield and composition of semicoking products to a notable higher degree than ground, relatively coarce-grained minerals.

Introduction

Proceeding from the mechanism of the effect of mineral compounds on the oil shale pyrolysis processes proposed earlier [1-3], it is reasonable to suppose that the sorption effect of mineral material is strongly dependent on its dispersion degree. In the case of fuel beneficiation a finer grinding of shale usually improves the characteristics of the process, but when a shale is thermally treated the effect is probably opposite: the role of secondary cracking reactions of the oil polar fractions retained on the solid residue surface will presumably grow.

We have no information on earlier investigations in this field. One of the possibilities to approach the problem is to use model mixtures where a superdispersed mineral material ($CaCO_3$ and SiO_2 in this work) is chemically precipitated on the particle surface of the shale processed.

Table 1. **Characteristics of Initial Model Mixtures and the Yield of Semicoking Products, wt. %**

Indices	Kukersite + CaCO₃									Kukersite + SiO₂						
	Sample number															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Initial mixtures																
Analytical moisture W^a	0.7	0.9	1.5	1.3	1.5	2.1	2.1	1.6	1.3	3.0	5.9	3.6	8.9	6.1	4.3	3.3
Ash A^d	47.2	43.9	38.8	33.7	29.0	24.5	21.8	18.5	14.3	79.1	66.2	52.6	37.4	28.2	20.9	9.1
Mineral carbon dioxide $(CO_2)^d_M$	34.2	29.4	22.5	18.9	15.6	11.1	7.5	5.6	0.5	*	*	*	*	*	*	*
Organic matter $100 - A^d - (CO_2)^d_M$	18.6	26.7	38.7	47.4	55.4	64.4	70.7	75.9	85.2	20.9	33.8	47.4	62.6	71.8	79.1	90.9
Semicoking products yield (dry material basis)																
Shale oil	11.1	14.8	19.6	25.1	29.0	36.5	41.8	40.5	44.9	7.3	10.5	24.1	28.2	32.9	38.4	52.5
Pyrogenetic water	2.1	2.3	2.2	5.6	4.1	5.0	3.1	5.9	6.6	1.8	3.6	4.3	3.3	5.0	6.7	4.7
Solid residue (semicoke)	81.9	77.3	71.2	62.5	51.9	47.1	36.5	32.5	33.6	87.5	79.1	63.2	50.8	48.5	40.7	23.2
Gas and losses (by difference)	4.9	5.6	7.0	6.8	15.0	11.4	18.6	21.1	14.9	3.4	6.8	8.4	17.7	13.6	14.2	19.6

* Only traces of mineral carbon dioxide have been detected.

The relative activity of carbonates in oil shale pyrolytic transformation reactions is usually lower than that of aluminosilicates [4, 5]. In our investigations, where concentrates of kukersite and Dictyonema shale (Estonia) were used as an organic component of model mixtures with natural limestone and dolomite ground to 100 μm, the same conclusions have been arrived at [6-8]. It has been established also that the effect of ground quartz on the yield and composition of kukersite semicoking products is negligible [9].

However, these results cannot be interpreted in terms of these mineral additives being inert independently of their dispersion degree.

Experimental

Characteristics of Middle Ordovician kukersite concentrate used in this work are presented in Table 1 (sample *16*). Model mixtures of the concentrate with high-dispersed $CaCO_3$ and SiO_2 were prepared in the following way:

A weighed portion of the kerogen concentrate was carefully blended with a portion of CaO (reagent grade) and distilled water, placed in a round-bottom flask with an agitator and stirred to get a uniform mixture. Thereafter gaseous CO_2 was bubbled through the suspension for 2 hrs. The solid product obtained was then separated from the reaction mixture on a vacuum filter, repeatedly washed with hot distilled water to remove the CaO residue, and dried. To prepare model mixtures of kerogen and SiO_2 a sample of the kerogen concentrate was suspended in water, and then a measured portion of liquid glass ($Na_2O \cdot nSiO_2$) was added to the mixture. Subsequently, on continuous agitation, 10 % hydrochloric acid was slowly added to the mixture in portion corresponding to the portion of liquid glass used. The solid product obtained was thoroughly washed with distilled water until washings became chlorine free, and then dried.

Thermal decomposition of the mixtures prepared was performed in a Fischer retort using the standard procedure. The shale oils obtained were dephenolized using a 10 % aqueous solution of potassium hydroxide and thereupon separated into chemical group compounds 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.

Results and Discussion

As one can observe from the curves of shale oil, gas and pyrolytic water yields, kerogen basis, versus the quantity of mineral additive (Fig. 1) , the

influence of high-dispersed silica, unlike relatively coarse-grained quartz
[9], in depressing oil formation is quite pronounced, the influence on
formation of pyrolytic water and gas being less defined. Calcium
carbonate precipitated on the kerogen surface seems even to promote oil
formation in some concentration range. Both mineral additives slightly
favour the formation of pyrolytic water, as it was also the case with
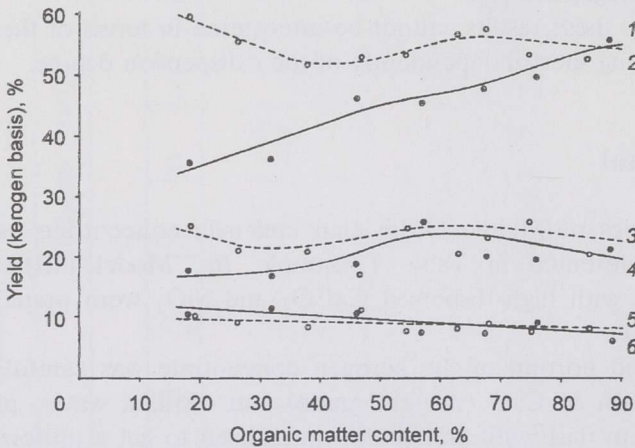grained calcite [7] and dolomite [8].

Fig. 1. Dependence of the yield of semicoking products (kerogen basis) on the
organic matter content in model mixtures: *1* and *2* - oil; *3* and *4* - gas; *5* and *6* -
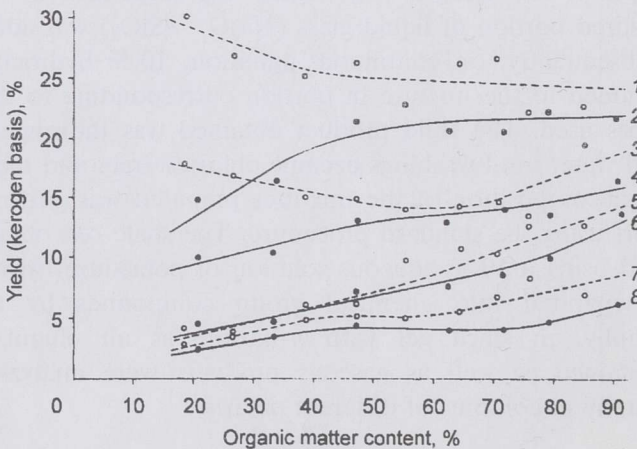pyrogenetic water. Mineral additives: *1*, *4* and *6* - SiO_2; *2*, *3* and *5* - $CaCO_3$

Fig. 2. Dependence of the yield of group components of semicoking oil (kerogen
basis) on the organic matter content in model mixtures: *1* and *2* - neutral
heteroatomic compounds; *3* and *4* - aromatic hydrocarbons; *5* and *6* - acidic
compounds; *7* and *8* - nonaromatic hydrocarbons. Mineral additives: *1*, *3*, *5* and *7*
- $CaCO_3$, *2*, *4*, *6* and *8* - SiO_2

Table 2. **Chemical Group Composition of Shale Oils Obtained, wt. %**

Group of compounds	Kukersite + CaCO$_3$									Kukersite + SiO$_2$						
	Sample number according to Table 1															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Hydrocarbons																
Aliphatic and naphthenic	6.3	7.3	8.5	10.0	8.7	9.1	11.5	16.4	15.9	8.8	10.4	11.4	10.1	8.6	9.5	10.2
Aromatic	28.2	30.6	29.6	28.2	26.7	25.3	24.8	21.5	22.7	29.4	29.7	26.9	28.0	30.8	27.6	28.4
Heteroatomic compounds																
Neutral and basic	51.7	48.2	49.3	50.3	47.1	46.7	47.8	34.0	34.7	45.4	44.6	45.6	45.0	42.2	46.2	37.8
Acidic (mainly phenols)	13.8	13.9	12.6	11.5	17.5	18.9	15.9	28.1	26.7	16.4	15.3	16.1	16.9	18.4	16.7	23.6

Table 3. Composition of Semicoking Gases (Air-Free Basis), vol. %

Compounds	Kukersite + CaCO₃								Kukersite + SiO₂					
	Sample number according to Table 1													
	1	2	3	4	5	6	7	8	10	11	12	13	14	15
H_2S	7.5	9.2	8.8	9.5	8.9	5.7	7.9	12.0	15.1	9.2	12.9	16.6	8.3	10.8
CO_2	24.1	24.3	23.7	27.6	32.9	26.7	33.4	31.8	41.0	38.0	36.8	18.4	30.1	32.1
CO	12.7	12.4	12.3	11.9	11.5	11.6	11.9	10.4	6.6	10.6	11.3	9.0	9.6	9.1
H_2	8.3	6.4	5.7	5.9	3.7	3.2	4.3	4.0	0.9	1.8	3.0	6.2	0.8	1.1
CH_4	17.6	14.9	20.9	19.3	17.0	31.2	19.4	14.8	12.9	15.3	12.1	20.2	17.3	15.1
C_2H_6	10.9	11.9	9.3	9.0	9.4	7.6	9.3	9.5	8.4	8.2	8.6	11.5	11.0	10.2
C_2H_4	3.1	3.3	2.4	2.2	2.7	2.0	2.3	2.6	3.1	2.6	2.3	3.5	2.8	2.5
C_3H_8	5.6	7.2	6.5	5.5	5.4	4.0	4.1	5.1	3.9	5.2	4.5	5.1	5.6	5.5
C_3H_6	5.5	5.0	5.7	4.7	4.6	4.2	3.8	4.0	3.9	4.4	4.3	4.9	9.3	7.7
C_4H_{10}	2.0	2.6	2.0	2.3	1.5	1.8	1.8	2.2	1.4	1.8	1.6	1.7	2.3	2.3
C_4H_8	0.5	0.9	0.5	0.3	0.2	1.0	0.3	1.6	1.4	1.4	1.3	1.4	1.6	1.7
C_5-C_6	2.2	1.9	2.2	1.8	2.2	1.0	1.5	2.0	1.4	1.5	1.3	1.5	1.3	1.9

Data on the chemical composition of the oils and gases obtained are presented in Tables 2 and 3 as well as in Fig. 2. One can see that whereas high-dispersed calcium carbonate even promotes to some extent the formation of neutral heteroatomic (mostly oxygen-containing) compounds, a notable decrease in the yield of these compounds takes place in the case of silicone dioxide when concentration of the mineral additive increases. A similar pattern, but to a lesser degree, of $CaCO_3$ and SiO_2 effects on aromatic hydrocarbons has been observed.
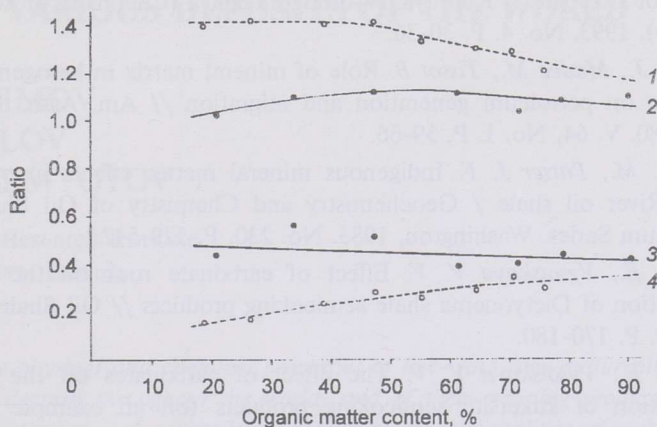

Fig. 3. Characteristics of aliphatic hydrocarbons of oils: *1* and *2* - carbon preference index (CPI); *3* and *4* - concentration ratio *n*-1-alkenes : *n*-alkanes. Mineral additives: *1* and *4* - $CaCO_3$; *2* and *3* - SiO_2

As for aliphatic hydrocarbons present in oils, their composition in respect to carbon preference index and alkenes : alkanes ratio undergoes no remarkable changes under the influence of a mineral additive (Fig. 3).

On the whole, one can conclude that high-dispersed $CaCO_3$ an SiO_2 influence the yield of kukersite semicoking products and their composition to a considerably greater extent than the ground, relatively coarse-grained minerals. In the case of shales where the organic matter, unlike that of kukersite, is also highly dispersed, this phenomenon can be expected to become more pronounced.

Acknowledgments

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