

Effect of Minerals on the Transformations of Organic Matter During Thermolysis in Benzene

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Abstract

The effect of minerals (montmorillonite, calcite, quartz) on the formation of group components of liquid products during pyrolysis of the kerogen of sapropel nature in benzene was investigated. It was established that the maximal amount of liquid products (with the mass concentration above 60 mass %) is formed in the presence of quartz and montmorillonite. It was established that carbonate and clayish rocks promote generation of high-molecular compounds in the pyrolyzate.

INTRODUCTION

Investigation of the interaction between inorganic and organic components in sedimentary rocks shows that in the majority of cases the effect of minerals manifests itself as adsorption and catalytic effects [1, 2]. In particular, for thermal destruction of organic matter (OM), these effects promote an increase in the yield of liquid products, a decrease in the concentration of tarry and pyrobitumen substances, prevalence of thermodynamically stable isomers of hydrocarbons. In this situation, as it was shown by the authors of [3], clayish minerals, especially montmorillonite and illite, as well as quartz under the conditions of dry pyrolysis ($T > 40$ °C), possess these properties to a larger extent than carbonate rocks do. At the same time, during thermolysis of OM in water, intensive formation of the pyrolyzate occurs in the presence of calcium carbonate [4].

EXPERIMENTAL

Kerogen of the shale oil of Cuonam horizon was chosen as the subject of investigation. The

Cuonam formation of bituminous sediments of the siliceous-carbonate-clayish and clayish-carbonate compositions is situated in the basins of the Olenek and Yudoma rivers (Yakutia) [5]. The bituminological analysis of these sediments showed that this horizon of the Cambrian age is generally bitumen maternal with high potential.

Kerogen was obtained from shale oil by means of consecutive separation of the chloroform, alcohol-benzene and “bound” (after acidic treatment) bitumoids. In order to study the hydrocarbon components of shale oil, the group composition of the chloroform-extracted bitumoid (the so-called bitumoid A) was determined. The yield of bitumoid A was 0.6 % of the weighed portion. The elemental composition of kerogen is represented by the following elements, concentration, mass %: C 72.29, H 7.61, O 11.41, S 7.02, N 1.67. The H/C atomic ratio is equal to 1.26, O/C – 0.12. On the basis of atomic ratios of hydrogen and oxygen to carbon according to van Krevelen, the kerogen is related to type II [6].

The effect of the inorganic constituent of sedimentary rocks on the formation of liquid products during thermolysis of the sapropel OM

was studied with montmorillonite ($\text{Na}_{0.7}\text{Al}_{3.3}\text{Mg}_{0.7}\text{Si}_2\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$), calcite (CaCO_3) and quartz (SiO_2) as examples. These minerals are among the main components incorporated into petroleum-enclosing rocks; therefore, they provide substantial changes in the petroleum natural substance. Montmorillonite is a representative of clayish rocks playing the part of oil-proof covers. Carbonate and sandy rocks composed mainly of calcite and quartz, respectively, serve as collectors of micropetroleum.

Thermolysis of kerogen was carried out in the isothermal and non-isothermal regimes: in an autoclave and in a flow reactor, respectively. The organic matter and minerals were ground before experiments till the particle size of 0.063–0.2 mm and dried at $T = 105^\circ\text{C}$ for 1 h. The ratio of kerogen to mineral mass was 1 : 1.

Thermal dissolution of samples in the steady regime was carried out in benzene in a sealed bomb made of stainless steel. The volumetric efficiency for benzene was 0.5. Benzene was chosen as the solvent due to the assumption that a fatty solvent medium allows more adequate reflection of the processes of petroleum formation and organic substance maturing. The bomb was placed in a thermostat furnace and kept there for 4 h at a temperature of 270, 320 and 370°C . The resulting pyrolyzate was separated from the solid residue by filtering and washing with hot benzene.

Thermolysis of the samples in the flow regime was carried out with a set-up described in [7]. A sample of OM was heated in the reactor from the room temperature to 500°C at the heating rate of $2.5^\circ\text{C}/\text{min}$, pressure in the system was 150 atm, benzene flow rate was $6\text{--}7\text{ cm}^3/\text{min}$. Liquid products of thermolysis were sampled at a temperature within the range from 200 to 500°C with a step equal to 25°C . Liquid products of each sample were united in three fractions (200–325, 325–450 and $450\text{--}500^\circ\text{C}$) on the basis of characteristic regions of the curve of pyrolyzate formation. Gaseous products formed in thermal decomposition of kerogen were not investigated.

The resulting fractions were separated on the basis of solubility into kerogen pseudo-components: pre-pyrobitumen (a mixture of carbenes and carboids), pyrobitumen, tar, oil.

TABLE 1

Conversion of kerogen into liquid products during thermolysis, mass %

Sample	Regime			
	Stationary		Flow	
	Temperature, $^\circ\text{C}$			
	270	320	370	200–500
Kerogen	4.54	14.2	25.9	51.4
Kerogen + calcite	5.40	13.8	25.6	51.7
Kerogen + montmorillonite	6.03	17.4	33.3	60.4
Kerogen + quartz	5.47	18.1	38.2	61.7

Pre-pyrobitumen insoluble in benzene under normal conditions were separated by filtering the pyrolyzate with paper filters. Pyrobitumen was isolated with Golde cold procedure by means of precipitation in hexane taken in excess. The components of the liquid product soluble in hexane (petrolene) were separated into tar and hydrocarbon groups (saturated, aromatic). Separation was carried out by means of liquid adsorption chromatography on aluminium oxide. Elution was carried out with hexane, a mixture of hexane with benzene at a ratio of 3 : 1, tar species were consecutively washed out with a mixture of ethanol with benzene (1 : 1). The eluates were combined in groups on the basis of R_f values determined by means of thin layer chromatography with Silufol plates with a UV 254 luminophor and on the basis of UV spectral data.

RESULTS AND DISCUSSION

Thermolysis of OM at a temperature of 270°C in the steady regime results in insignificant generation of liquid products by kerogen: not more than 6 mass % (Table 1). Evidently, this is connected with rather mild thermolysis conditions under which destruction of the kerogen matrix proceeds only to a small extent. The presence of minerals causes only insignificant increase in the formation of liquid products. Temperature rise to 320°C causes a 3 times increase in the conversion of kerogen into liquid products, while rise up to 370°C – more than 6 times. The largest yield of liquid products is observed in the presence of quartz and montmorillonite. High conversion of the OM

into liquid products in the presence of quartz is likely to be connected with the fact that quartz, within the row of minerals chosen, possesses the lowest thermal capacity (0.80 kJ/(kg · K)). In the case of calcite and montmorillonite, the corresponding values are 0.88 and 0.92 kJ/(kg · K), respectively [8].

Evidently, low thermal capacity and chemical inertness of quartz distributed within the bulk OM ensure more rapid heating of the system, which causes early generation of liquid products. Forming local heating sites, quartz promotes additional dissolution of kerogen in the newly formed micropetroleum. In the case of a clayish mineral, the catalytic effect on thermal destruction of kerogen is exhibited. It is known that due to negatively charged centres and Van der Waals forces the surface of natural aluminosilicates actively adsorbs organic carbocations; hydrogen disproportionation, hydrogenation, isomerisation can proceed on the surface of clayish minerals. This also results in an increase in the yield of the liquid part of the pyrolyzate [9].

An increased (by more than 60 %) formation of the pyrolyzate in the presence of the clayish and sandy components of sedimentary rocks is observed also in the flow regime.

It should be noted that the degree of generation of oil-like substances from the initial kerogen and from a mixture of kerogen with calcite is almost the same in the stationary regime and in the flow one. The presence of carbonate rocks during thermolysis of OM in benzene is likely to have no effect on the yield of pyrolyzate.

The main part of the OM passes into the liquid phase within temperature range 325–

450 °C. Mass concentration of the liquefied kerogen within this range is 67.6–81.7 mass % (Table 2). This region of kerogen decomposition is the most interesting one for the investigation of petroleum formation processes because it is this temperature range that embraces the generation of the main portion of liquid products (the so-called petroleum window). According to the data of thermogravimetric analysis of this kerogen, the maximal temperature of its decomposition is 440 °C, the coefficient of sample mass loss K_{Π} is 47 %. However, we established experimentally that the maximum of OM decomposition shifts by 40–50 °C to the low-temperature range for thermolysis in the flow regime in benzene [10].

Low conversion of kerogen within other temperature ranges is explained by the absence of clearly expressed destructive processes in the kerogen matrix. It is probable that the low-temperature region involves desorption of the components formed during the formation of the biogeopolymer kerogen. Under the conditions of flow thermolysis, benzene is in the supercritical state, which promotes additional release of natural bitumoid from kerogen. Insignificant yield of liquid products within the high-temperature region is due to depletion of the generation potential of the matter under investigation, that is, the major part of labile OM has already been transformed into liquid products, so further temperature rise leads only to the formation of gas and coke.

For geochemical research, the most interesting aspects are those concerning the effect of mineral constituents of sedimentary rocks on the generation of definite groups of petroleum-like components by kerogen. One can see in the data presented in Table 3 that the group composition of the products of kerogen thermolysis differs from that of the products of thermolysis of kerogen in mixture with minerals.

The group composition of pyrolyzates obtained by thermolysis shows that kerogen generates mainly high-molecular compounds (pyrobitumen and tar). It is also clear that the content of tar and low-molecular HC increases with an decrease in pyrobitumen concentration.

For kerogen thermal destruction in stationary regimes, the highest degree of tar

TABLE 2

The degree of kerogen conversion into liquid products during thermolysis in the flow regime, mass %

Sample	Fraction, °C		
	200–325	325–450	450–500
Kerogen	7.2/14.1	49.2/81.7	51.4/4.2
Kerogen + calcite	1.1/2.2	42.6/80.3	51.7/17.5
Kerogen + montmorillonite	4.7/7.8	47.0/70.0	60.4/22.2
Kerogen + quartz	10.0/16.2	51.7/67.6	61.7/16.2

* The first value is for cumulative conversion, the second one for the yield of liquid products.

TABLE 3

The group composition of liquid products obtained from kerogen at different thermolysis temperatures, mass %

Sample	Paraffin- naphthene HC	Aromatic HC			Tar	Pyrobitumen	Pre-pyrobitumen
		mono	bi	poly			
Bitumoid A	25.3	9.4	7.8	4.2	38.5	14.8	—
<i>T = 270 °C</i>							
Kerogen	11.5	4.5	13.5	9.8	36.0	25.0	—
Kerogen + calcite	10.5	4.8	7.7	3.8	40.4	32.8	—
Kerogen + montmorillonite	6.4	2.6	9.7	1.7	18.7	60.7	—
Kerogen + quartz	18.7	12.4	5.2	22.6	28.4	12.7	—
<i>T = 320 °C</i>							
Kerogen	7.7	3.5	13.0	10.4	33.1	32.3	—
Kerogen + calcite	8.3	3.8	7.3	3.8	37.5	39.3	—
Kerogen + montmorillonite	9.5	3.0	8.3	3.0	29.9	46.3	—
Kerogen + quartz	5.4	21.3	8.2	18.1	13.2	33.7	—
<i>T = 370 °C</i>							
Kerogen	4.6	3.8	11.1	11.7	31.3	37.6	—
Kerogen + calcite	6.8	3.4	6.1	3.6	32.7	47.4	—
Kerogen + montmorillonite	11.1	3.6	7.2	3.8	40.5	34.0	—
Kerogen + quartz	1.1	5.8	27.3	4.9	36.6	24.3	—
<i>T = 200–500 °C</i>							
Kerogen	10.6	7.6	8.9	12.4	25.6	19.5	15.5
Kerogen + calcite	2.0	4.0	1.5	13.2	46.9	16.6	15.9
Kerogen + montmorillonite	2.0	34.6	17.1	5.7	20.9	13.0	6.7
Kerogen + quartz	10.0	16.8	10.9	15.0	17.8	19.8	9.6

and pyrobitumen generation is achieved with calcite and montmorillonite: more than 40 and 60 mass %, respectively. The most intensive formation of HC is observed in the case of the initial kerogen and a mixture of kerogen with quartz. The content of aromatic HC in pyrolyzates is almost independent of temperature in all the cases except quartz.

The data on the total content of group components obtained by thermolysis in the flow regime provide evidence of increased generation of high-molecular fragments of OM by kerogen: pyrobitumen, tar, polyaromatic HC (Table 4). As we have already indicated above, the maximal thermal destruction of the kerogen matrix occurs within temperature range 325–450 °C. In all the cases, the concentration of group components increases several times; especially noticeable increase is exhibited by the high-molecular structural blocks of kerogen –

pyrobitumen and pre-pyrobitumen. High content of these compounds points to the advantages of the high-temperature flow set-up in comparison with other methods of OM thermolysis because the former allows one to obtain compounds without their noticeable secondary transformations. Comparing the character of component distribution over fractions one may state the following regularities. For thermolysis of the initial kerogen and a mixture of kerogen with quartz, the concentration of low-molecular HC increases with temperature rise, while in the presence of calcite the concentration of aromatic compounds decreases.

High concentrations of mono- and diaromatic HC are observed in the presence of montmorillonite, especially in the fraction 325–450 °C. Within this temperature range, intense formation of polyaromatic HC also occurs under

TABLE 4

Effect of minerals on the group composition of liquid products obtained by thermolysis of kerogen with different minerals in the flow regime, mass %

Temperature, °C	Paraffin- naphthene HC	Aromatic HC			Tar	Pyrobitumen	Pre-pyrobitumen
		mono	bi	poly			
<i>Without minerals</i>							
200–325	10.0	5.4	66	17.3	26.3	21.0	13.4
325–450	9.5	7.6	9.5	12.9	24.7	27.9	7.9
450–500	12.4	9.7	10.5	6.9	25.7	9.7	25.1
<i>With calcite</i>							
200–325	2.0	5.1	2.0	12.7	35.6	12.5	30.1
325–450	0.8	4.4	1.4	24.6	36.0	23.8	9.0
450–500	3.1	2.5	1.1	2.2	69.1	13.4	8.5
<i>With montmorillonite</i>							
200–325	2.9	23.3	11.5	8.1	31.4	12.7	10.1
325–450	1.8	41.1	21.2	3.5	9.1	19.1	4.2
450–500	1.3	39.5	18.6	5.5	22.1	7.2	5.8
<i>With quartz</i>							
200–325	6.5	9.3	6.5	28.5	18.3	19.1	11.8
325–450	8.3	10.4	9.2	9.8	25.2	27.5	9.6
450–500	15.3	30.8	17.1	6.6	9.9	12.9	7.4

the influence of calcite. In other cases, the concentrations of these compounds decrease with further heating of the samples. Generation of tar and pyrobitumen by kerogen under increased temperature comes down in almost all the samples; however, in the case of calcite, tar content of the fraction 450–500 °C increases by a factor of 2 in comparison with other fractions. The fraction of tar remains almost unchanged within all the temperature ranges, which is an evidence of the constant rate of generation of these components. Attention should be paid to the similarity between kerogen without minerals and kerogen with quartz in the character of HC and tar distribution within all the temperature intervals, and also one should note that comparable amounts of high-molecular components are present in the main fraction (325–450 °C). The latter fact is first of all due to the physical characteristics of quartz (for example, low thermal conductivity) affecting the formation of liquid products from kerogen.

Pre-pyrobitumen group includes thermally unstable compounds which were not detected in the pyrolyzates obtained in the stationary regime. Residing in the reaction zone for a long

time, these compounds are likely to undergo complete destruction when thermolysis of OM is carried out in an autoclave. In the flow regime of kerogen thermal destruction, the formation of pre-pyrobitumen proceeds with high intensity at temperatures up to 325 °C, then in the presence of minerals the content of pre-pyrobitumen decreases with an increase in temperature; in the case when the mineral constituent is absent, the content of pre-pyrobitumen increases several times.

CONCLUSIONS

The largest amount of liquid petroleum-like products is formed in thermolysis of kerogen of the II type in benzene in the presence of quartz and montmorillonite.

The group composition of pyrolyzates differs: mainly high-molecular products are formed during kerogen thermolysis in the flow regime without any minerals and in mixture with calcite, while the content of low-molecular compounds, especially aromatic ones, increases under the action of montmorillonite and quartz.

High content of tar and pyrobitumen is observed in the presence of calcite and montmorillonite in the pyrolyzates obtained by thermolysis in the stationary regime.

REFERENCES

- 1 J. Espitalie, S. Makadi, J. Trichet, *J. Org. Geochem.*, 6 (1984) 365.
- 2 J. M. Hunt, *Petroleum Geochemistry and Geology*, W. H. Freeman, San Francisco, 1974.
- 3 V. V. Vysotskaya, K. E. Urov, *Goryuchiye Slantsy*, 2 (1987) 170.
- 4 T. I. Eglinton, S. J. Rowland, C. D. Curtis, A. G. Douglas, *J. Org. Geochem.*, 10 (1986) 1041.
- 5 V. E. Savickiy, A. E. Kontorovich, V. M. Evtushenko, *Kembriy Sibirskoy platformy*, Nedra, Moscow, 1972.
- 6 B. T. Tisso, D. Velte, *Obrazovaniye i rasprostraneniye nefti*, Mir, Moscow, 1981.
- 7 Yu. V. Korzhov, A. K. Golovko, YU. F. Patrakov, *Geokhimiya*, 7 (1995) 1030.
- 8 A. K. Romankov, *Primery i zadachi po kursu protsessov i apparatov khimicheskoy tekhnologii*, Vyssh. shk., Moscow, 1986.
- 9 T. T. Klubova, *Glinistye mineraly i ikh rol' v genezise, migratsii i akkumulyatsii nefti*, Nedra, Moscow, 1973.
- 10 V. V. Saveliev, in: *Materialy Vseros. konf. "Genezis nefti i gaza"*, GEOS, Moscow, 2003, p. 280.