Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 99-107

DISTRIBUTION AND COMPOSITION OF ORGANIC MATTER IN OIL- AND BITUMEN-CONTAINING ROCKS IN DEPOSITS OF DIFFERENT AGES

T. N. Yusupova, L. M. Petrova, R. Z. Mukhametshin, G. V. Romanov, T. R. Foss and Yu. M. Ganeeva*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre
Russian Academy of Sciences, 8 Arbuzova St., Kazan, Tatarstan 420088
*Tatar Geological-Exploration Department, Tatneft JSC, 6/10 Chernyshevskogo St., Kazan
Tatarstan 420503, Russia

(Received August 21, 1997; in revised form January 19, 1998)

Abstract

The core samples of oil- and bitumen-containing rocks from Tatarstan's deposits of different ages were studied by thermal analysis methods (DTA, TG, DTG). Based on the obtained data, a procedure was elaborated for determining the enclosed organic matter content and the index of its fraction composition.

A significant increase of the organic matter content in the core and its enrichment in high-molecular aromatic structures were shown to occur for the oil-containing rock samples when passing from the Devonian to Carboniferous and Permian deposits. The core samples of the Devonian oil-containing rocks may be divided into three groups: the samples taken from the zones where waste water flooding has been started relatively recently (1), or fresh water flooding has been carried on for a long time (2) and the samples of rock containing clay minerals as impurities. Thus, thermal analysis can be used in geochemical studies to identify the organic matter enclosed by oil- and bitumen-containing rocks.

Keywords: Devonian deposits, insoluble organic matter, oil-containing core, organic matter, thermal analysis, water-oil contact zones

Introduction

In Tatarstan, the exploited oil reserved in the large and medium fields become depleted. In this connection, the development of techniques to exploit both the less productive hydrocarbon deposits in the upper horizons and the numerous little fields jointly with a more complete recovery of residual oil at the basic production facilities may serve as an important reserve for the progress of oil industry. The prospects of additional oil recovery will depend, in many aspects, on

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

fundamental studies, aimed at understanding the mechanism of drive processes and eliminating the forces which retain oil in reservoir beds. Therefore, the study of oil-containing rocks in deposits of different ages in order to estimate the effects of such factors as various flooding conditions, water-oil contact (WOC) zones, occurrence depth, and different mineral compositions of reservoir rocks on the distribution of the enclosed organic matter and alterations in its composition is of most interest.

Among the instrumental techniques of physicochemical analysis, which provide a modern standard for systematic investigation of complicated natural organic substances, thermal analysis techniques have a special place. However, applications of thermal analysis techniques for studying oil-containing rocks have been covered relatively poorly in the literature [1–5].

The aim of this work was to estimate the sensitivity of thermal analysis parameters to changes in the chemical composition of the enclosed organic matter (OM) in the genesis process and after the flooding operations applied.

Experimental

The core samples of bitumen-saturated and oil-containing rocks from the terrigenous beds from the Tula, Bobricov and Tournaisian horizons of Carboniferous, Upper and Middle Devonian deposits have been investigated.

Simultaneous thermal analysis (DTA and TG) was carried out by means of a Q-1500D Derivatograph system (MOM, Hungary). Preliminary tests were performed to select the optimum conditions for the experiments. Open platinum crucibles were used in the experiments. The mass of oil-containing rock samples was in the range of 600–700 mg. The heating rate was constant and equal to 10°C min^{-1}. The atmosphere in the furnace was stationary. Alumina was used as inert substance.

A great advantage of simultaneous DTA-TG-DTG technique, in comparison with many other physical and chemical methods, is that it allows not only concentrated OM but also dispersed (finely dispersed) OM present in rocks in low concentration (below 0.25%) to be detected and examined. The thermal analysis results enrich our knowledge about the features of thermal destruction of OM and permit an insight into the qualitative and quantitative characteristics of OM changing during the transformation process.

Figure 1 shows the thermal analysis curves for an oil-containing rock sample. The small endothermic peak at 100–110°C is attributed to the release at absorbed water. The mass losses in the region 70–130°C correspond to the water content . The thermooxidative destruction of the OM in rock starts in the temperature region of 130–200°C and ends at 600–700°C [5]. The mass losses in the temperature region of 130–700°C correspond to the OM content in the rock. The two main stages of the thermooxidative destruction of OM may be clearly distinguished in the DTA and DTG curves. They are associated with the evaporation

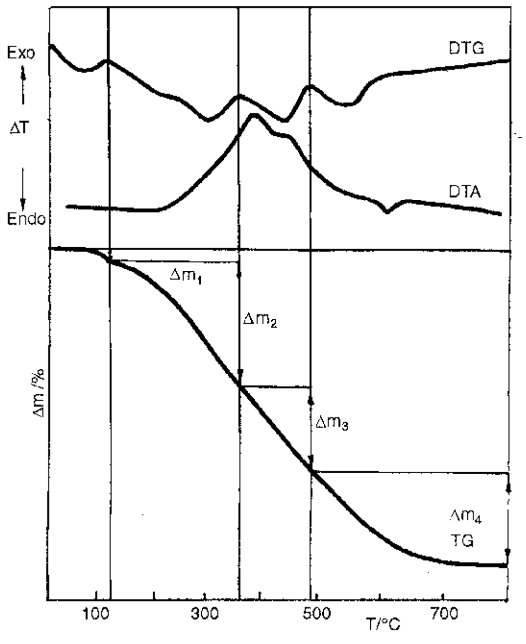

Fig. 1 Thermal analysis curves of an oil-containing rock sample taken from the Zelenogorsk area (sample N16 in Table 1)

and thermal oxidation of light and middle OM fractions (130–400°C) and the thermooxidative destruction of heavy OM fractions (400–700°C) [1–3]. The ratio of mass losses in the first stage of destruction (m_2) to the mass losses in the second stage (m_3) characterizes the fraction composition of OM. We named it as the index of the fraction composition of OM (F). It should be noted that the release of constitutional water from clays is superimposed on the thermooxidative destruction of the heavy fractions of OM in the temperature region of 500–700°C for rock samples containing clay minerals as impurities (Fig. 1).

Therefore, it is also necessary to study the rock samples after extraction of the OM with organic solvents in order to interpret the thermal analysis data more correctly. If carbonates are present in the sample, their content may be determined from the characteristic effects in the temperature region of 600–1000°C [6].

The thermal analysis data are given in Table 1.

Results and discussion

The data given in Table 1 illustrate the changes in the OM content in the rock and is the fraction composition index (F) through the cross section of the productive bed as shown in our previous paper [7, 8].

Table 1 Thermal analysis data for oil- and bitumen-containing rock samples taken from Tatarstan's fields

No.	Area, Well number	Coring interval/m	TA OM		TA mineral composition	
			m_2/%	m_3/%	m_1/%	m_4/%
		Devonian deposits				
1	Minnibayevo, 29589	1793-1745	0.98	0.44	–	–
2	Minnibayevo, 29589	1745-1749	0.73	0.33	–	–
3	Minnibayevo, 29589	1749-1752	0.95	0.33	–	–
4	Minnibayevo, 29612	1751-1756	0.62	0.28	–	–
5	Minnibayevo, 10891	1757-1764	1.00	0.40	–	–
6	Minnibayevo, 10891	1771-1777	0.70	0.30	–	–
7	Minnibayevo, 9504	1729-1730	0.71	0.29	–	–
8	Minnibayevo, 9504	1730-1734	0.77	0.33	–	–
9	Zelenogosk, 3711	1756-1764	0.77	0.33	–	–
10	Zelenogosk, 3711	1756-1764	0.52	0.40	0.14	–
11	Zelenogosk, 3711	1756-1764	0.18	0.15	0.30	–
12	Zelenogosk, 3711	1694-1699	0.62	0.28	–	–
13	Zelenogosk, 3711	1694-1699	0.95	0.65	–	–
14	Zelenogosk, 19912	1679-1686	0.99	0.75	–	–
15	Zelenogosk, 19912	1679-1686	1.03	0.72	–	–
16	Zelenogosk, 19912	1679-1686	0.40	0.27	0.10	–
17	Zelenogosk, 19912	1679-1686	0.64	0.40	0.10	–
18	Zelenogosk, 29238	1810-1815	1.10	0.73	–	0.20
19	Zelenogosk, 29238	1810-1815	0.90	0.63	–	0.20
20	Aznakayevo, 24587	1742-1749	0.93	0.73	–	–
21	Aznakayevo, 24587	1742-1749	1.00	0.80	–	–
22	Aznakayevo, 24587	1742-1749	0.39	0.48	0.60	–
23	Aznakayevo, 4435	1729-1736	0.58	0.42	0.40	0.30
24	Aznakayevo, 4435	1729-1736	1.15	0.75	–	0.10
25	Aznakayevo, 4435	1736-1742	0.95	0.65	–	–
		Devonian deposits, WOC zone				
26	Abdrakhmanovo, 14149	1749-1755	0.70	0.90	–	–
27	Abdrakhmanovo, 14149	1749-1755	0.86	1.80	–	–
28	Abdrakhmanovo, 14149	1749-1755	1.20	2.80	–	0.14
29	Bavly, 2587	1853-1858	1.00	1.30	2.00	–

Table 1 Continued

No.	Area, Well number	Coring interval/m	TA OM		TA mineral composition	
			m_2/%	m_3/%	m_1/%	m_4/%
30	Bavly, 2587	1858-1863	0.50	2.00	2.00	–
31	Bavly, 2587	1858-1863	0.45	1.95	0.30	–
		Carboniferous deposits				
32	Minnibayevo, 118	1156-1164	1.70	1.90	–	–
33	Minnibayevo, 118	1156-1164	1.50	1.20	–	0.60
34	Minnibayevo, 118	1156-1164	1.70	1.20	–	1.80
35	Minnibayevo, 118	1156-1164	1.60	1.60	–	1.90
36	Minnibayevo, 26893	1195-1207	1.90	1.30	–	–
37	Minnibayevo, 29737	1190-1197	1.10	0.69	–	95.0
38	Minnibayevo, 29737	1190-1197	0.91	0.65	–	95.0
39	Minnibayevo, 29737	1190-1197	0.39	0.43	0.23	95.0
40	Arkhangelkoe, 7869	1175-1180	2.16	1.90	0.80	–
41	Arkhangelkoe, 7869	1180-1183	2.25	1.75	–	–

With the aim to reveal a relationship between the oil saturation of the rock samples and chemical composition of the enclosed OM, a graph is plotted in the co-ordinates of TA values (Fig. 2).

It can be observed that samples from Devonian deposits may be subdivided into three separate groups. Samples, the OM in which is characterized by the highest values of fraction composition index F (2.5–2.0) and low OM contents in the rock (0.9–1.4%), belong to the first group. The low oil saturation values are

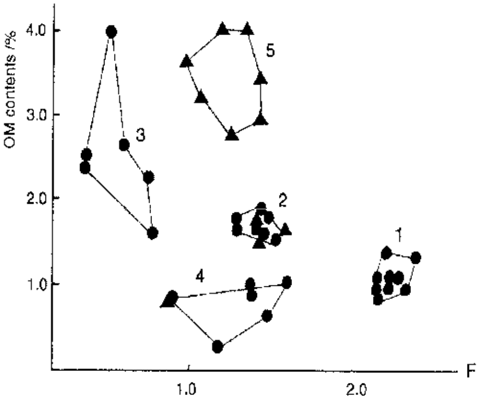

Fig. 2 Identification of organic matter in oil-containing rocks taken from Devonian (•) and Carboniferous (▲) fields, Tatarstan, by thermal analysis indexes

probably caused by the fact that in the process of drilling and core uplifting only a part of the oil adsorbed by the rock (immobile oil) is retained on the rock surface. To this day, the low oil saturation values (0.9–1.2 mass%, i.e. 12–20% by pore volume) have been attributed only to a weathering (evaporation) of the light OM fractions in the process of core storage in a nonhermetic packing. We investigated, specially by TA techniques, a core sample immediately after opening the hermetic film (polyethylene, paraffin) and after keeping this sample unsealed for 6 months. As a result of evaporation of the light OM fraction, the oil saturation decreased from 1.5 to 1.1% and the index F, naturally, also decreased from 1.9 to 1.5.

This clearly demonstrated that the lowest oil saturation values for the samples from Devonian deposits together with the highest fraction composition index values cannot be explained by the weathering. According to the history of development of the Romashkino field, the samples taken from the zones (Monnibayevo area) where the mineralized water flooding operation has recently been applied, were assigned to the first group.

The samples with much lower fraction composition index values (1.6–1.2) and increasing OM content in the rock (1.4–1.9%) belong to the second group. This group of samples was taken from the field zones which were flooded by fresh (oxygen enriched) waters for a long time (Aznakayevo, Zelenogorsk areas). The organic matter in these samples became partially oxidized resulting in an increase of oil share retained by the rock due to an enrichment by surface-active oxygen-containing structures. This has been confirmed by infrared spectroscopy data for the extracts [9].

Figure 2 shows TA data for the core samples from Devonian deposits taken from a WOC zone (the third group). Because of a greater degree of oil oxidation (F is very low, 0.2–0.7), the share of the immobile oxidized oil in core samples increases to 1.6–4.0%. Thus, a regular increase in the OM content in oil-containing rock samples with a rising degree of oil oxidation is well observed.

The core samples from Devonian deposits containing clay minerals as impurities constitute a special domain (the forth group). The organic matter in these samples is characterized by rather low values of F (0.7–1.6) and low values of its content in the rock (0.4–1.1%) [9]. Many authors believe that clay minerals are the most active components of the dispersed rocks determining the reservoir permeability, water saturation and diffusion-adsorption behaviour [10–12]. As we have reported earlier, a decrease in the characteristic temperatures of thermooxidative destruction of OM is typical of samples containing clay minerals as impurities [13–14].

The fifth group (Fig. 2) is constituted by samples from Carboniferous deposits. These samples are characterized by increased oil saturation values (2.6–4.0%). The F values vary in the range of 0.9–1.5 for the Carboniferous system samples, which evidences a change in the chemical composition of OM towards the enrichment in heavy fractions. As a result, the amount of oil retained in the rock becomes greater. It should be noted that the mineral part of core samples belonging to the fifth group consists mainly of sandstone or contains some carbonate impurities (Table 1). However, samples from Tournaisian deposits, whose mineral part consists of 95% carbonates belong to the second group, i.e. when F values are equal to 0.9–1.4, the oil saturation values are considerably lower (1.4–1.7%) than for the samples from Tula and Bobricov horizons (sandstone rock) [15].

TA data for natural bitumen-saturated rocks have been reported earlier [16]. It was shown that the OM fraction composition index and the oil saturation values vary in the ranges of 0.25–0.90 and 5.3–12.8%, respectively. Such characteristic bitumen features as high viscosity and density values, low mobility in bed conditions, high content of resin-asphaltene substances, sulphur compounds and metal complexes have been described. The typical features of natural bitumens changed under the influence of geological, geochemical and biochemical transformation processes were found. The natural bitumen samples form the large domain if the TA data are plotted in Fig. 2. This group includes also the natural bitumen samples from Kazakhstan for which TA data have been reported [17].

Thus, the investigation of the qualitative and quantitative characteristics of the OM directly in pore rock medium demonstrates that the oil saturation of core samples depends essentially on the chemical composition of the OM namely, it grows with increasing proportion of the heavy fractions as a result of the hypergenic oil transformation and oxidation during prolonged fresh water flooding or in WOC zones. The mineral composition of rocks determines also the oil saturation of core samples, so the oil saturation is reduced in pure carbonate samples and samples containing clay minerals when all other factors are the same.

Extracts of oil-containing rocks are used to study the chemical composition of the enclosed organic matter by other physical and chemical techniques. We have investigated factors influencing the composition of the extract and completeness of extraction of the organic matter from the rock. A device for the extraction of oil- and bitumen-saturated rocks has been worked out earlier [18]. It excludes the periodic solvent addition and rock contact with an environment what leads to formation of new oxidized structures. Methylene chloride and alcohol-benzene mixture were used sequentially as solvents. Solvent evaporation was carried out in the reverse sequence in order to conserve the light fractions of the extracted organic matter. It should be noted that some transformations take place during extraction in spite of all precautionary measure. For OM derived from rock and crude oils, F has the same physical sense as the mass ratio of the sum of the light and middle fractions to the heavy fractions.

If F is determined for an oil and then this oil is put on sand in an amount of 1–2% and F is determined again, the first and second values of F should be strictly identical. This fact was illustrated also by the authors of [19] by the example of the TG analysis applied for studying an oil distillation process for some different types from the USA, Canada and Latin America. However, we have not observed such accordance in our experiments for the oil in core samples (extracts of oil-containing rocks, OM in pore rock medium) (Fig. 3). It was stated that ranges of variation of F for OM in the rock and for extracts are different. This is seen best of all for the samples from Devonian deposits and especially in the range of the highest F values (for samples from zones flooded by waste waters). This distinction between the thermal analysis results is due to the loss of light hydrocarbons in the extraction process. A special experiment on the extraction Devonian oil from its solution in benzene points to a 15% loss of light hydrocarbons from the product mass. The reported factors have significantly smaller effect on the Carboniferous deposits, therefore their oil extracts are closer in composition to the organic matter in the rock.

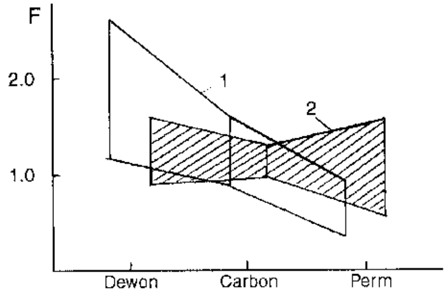

Fig. 3 Variation ranges of the fraction composition index (F): organic matter (1) and extracts (2) from oil-containing rocks, Tatarstan's fields of different ages (based on thermal analysis data)

There is also another aspect of the distinction between core oils and rock OM. Si, in the course of the extraction of core oils from the rock samples taken directly from the WOC zone (these data are not shown in Fig. 3), a significant part of OM (sometimes up to 50%) transformed to compounds of carbene and carboid types is retained on the rock without dissolution in the organic solvent. The values of F are essentially lower in this case (0.2–0.4 in comparison to 0.4–1.0 for extracts). The presence of insoluble organic matter has also been observed also in samples of bitumen-containing rocks from Permian deposits [16].

Conclusions

A procedure was developed for the determination of organic matter content and its fraction composition index by means of thermal analysis (DTA, TG, DTG) of oil- and bitumen-containing rocks.

Thermal analysis techniques were shown to be suitable for geochemical studies in order to identify the organic matter enclosed in oil- and bitumen-containing rocks. Thermal analysis allows to obtain a comprehensive knowledge about the enclosed organic matter by taking into account the presence of insoluble organic matter and without any additional treatment (temperature, dissolution). It permits establishment of more correct natural laws of changes in the distribution of organic matter and its chemical composition depending on the degree of transformation of OM, the secondary and tertiary stimulation operations applied in the fields to enhance oil recovery, and the mineral composition of reservoir rocks.

References

1 K. Rajeshwar, Thermochim. Acta, 63 (1983) 97.
2 K. N. Iha and B. Verkochy, SPE Reservoir Engineering, July, 1986.
3 B. Verkochy and K. N. Iha, J. Canad. Petrol. Technology, 3 (1986).
4 D. Vucelic, V. D. Krsmanovic, V. Vucelic, M. Kicanovic and D. Vitorovic, J. Thermal Anal., 36 (1990) 2465.
5 G. V. Romanov, V. I. Semkin, T. N. Yusupova et al., Manuscript is deposited in VINITI 17. 12. 85. N 8695-B.
6 N. D. Topor, Differentsialniy termicheskiy analiz mineralov, Izd. Nedra, Moskva 1964.
7 T. N. Yusupova, G. V. Romanov, L. M. Petrova and V. I. Semkin, Internat. Confederation for Thermal Analysis, 10th Congress Hatfield, August 1992. Workbook Supported by Perkin Elmer, p. 333.
8 T. N. Yusupova, L. M. Petrova, R. Z. Mukhametshin et al., Internat. Conf. 'Problems of complex development and production of hard-accessible oils and natural bitumens', Abstracts, Kazan, (1992) 179.
9 L. M. Petrova, T. N. Yusupova, G. V. Romanov et al., Internat. Symp. 'Non-traditional sources of hydrocarbon raw materials and problems of its development', Abstracts, St.-Petersburg, (1992) 201.
10 V. M. Berezin, V. V. Gizatullina and V. S. Yarygina, Tectonics and oil-gas content of Bashkiria. Ufa, 5 (1983) 43.
11 I. Kh. Timiryasova, V. A. Pokrovsky and L. I. Slavnaya, Oil field practice and oil transport, 10 (1984) 1.
12 M. I. Gerber, Geochemical Collection, 4 (1957) 131.
13 R. A. Manapov, T. N. Yusupova, G. V. Romanov et al., Internat. Conf. 'Problems of complex development and production of hard-accessible oils and natural bitumens', Abstracts, Kazan, (1994) 2114.
14 U. G. Romanova, R. A. Manapov and T. N. Yusupova, Internat. Conf. 'Mössbauer spectroscopy for oil-containing clay rocks of Tatarstan', Abstracts, Rimini (Italy), (1995) 10.
15 G. P. Kayukova, G. P. Kurbskyi, T. N. Yusupova et al., Geologiya nefti i gaza (Russ.), 5 (1993) 37.
16 G. P. Kayukova, G. P. Kurbskyi, T. N. Yusupova et al., Geochimiya (Russ.), 12 (1993) 1748.
17 N. K. Nadirov, G. A. Musayev, G. V. Romanov et al., Neftechimiya (Russ.), 6 (1991) 781.
18 V. I. Semkin, G. V. Romanov and T. N. Yusupova, Oficialnyi patentnyi Bulleten 'Izobreteniya' (Official patent Bulletin 'Inventions') [in Russ.], Moscow, 1992. N34. Inventor's certificate N 1761177A1.
19 Vossoughi Shapour and El Shoubary Yousef, World Congr. III Chem. Eng., Tokyo, 1986, Vol. 1, p. 476.