Temperature influence on the composition of high-carbonic Domanic rocks organic matter during hydrothermal treatment in CO_2 atmosphere

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Temperature influence on the composition of high-carbonic Domanic rocks organic matter during hydrothermal treatment in CO_2 atmosphere

G Kayukova[1,2], A Mikhailova[2], Z Nasurova[1], O Sotnikov[3], E Nazimov[3]

[1]Kazan Federal University, 18 Kremlevskaya Str., Kazan, Russia
[2]A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russia
[3]Institute TatNIPIneft PJSC "Tatneft", 75 Lenin St., Almetyevsk, Russia

E-mail: galina.kayukova@rambler.ru

Abstract. Depositions of the Domanic type in the territory of Tatarstan are stratigraphically associated with carbonate-siliceous deposits of the Upper Devonian part of the section. These deposits, enriched with organic matter, are characterized by the ability to generate liquid and gaseous hydrocarbons and accumulate them in the form of deposits of unconventional type. In this paper, the results of geochemical studies of rock samples from the depth interval 1705-1728 m of the Semi-Bug-Buregian deposits of the Berezovskaya area of the Romashkino oil field are presented. It is shown that the rocks, in spite of the narrow core sampling interval, differ in the content of quartz and calcite, as well as in the admixture of minerals such as muscovite, pyrite and albite. The content of organic matter according to thermal analysis data varies from 1.97 to 35.48 %, a significant part of which falls on an insoluble organic matter - kerogen. The influence of hydrothermal processes on the production capacity of the organic matter of these rocks is shown to generate hydrocarbons at temperatures of 200, 250, 300 and 350°C in a carbon dioxide medium. The yield and quality of the products obtained is estimated. The results of the research give grounds to believe that: firstly, the rocks of the Berezovskaya area of the Romashkino oil field have not fully realized their oil potential and the hydrothermal effect on them contributes to the thermal maturation of organic matter in the rock; second, at these temperatures, more intensive recovery of free hydrocarbons from the rock occurs. Thus, the hydrocarbon potential of the house rock is determined by the composition and content of liquid bituminous components that are in a free state in the rock, as well as the products of destruction of tar-asphaltene substances and macromolecules of insoluble kerogen and, consequently, it can be successfully realized with further optimization of hydrothermal processes directed to increase the quantity and improve the quality of the extracted fluids.

1. Introduction

Domanic deposits in the territory of Tatarstan are stratigraphically associated with carbonate-siliceous deposits of the Upper Devonian part of the section. These deposits, enriched with organic matter, are characterized by the ability to generate liquid and gaseous hydrocarbons and accumulate them in the form of unconventional reservoirs. There is a big interest in high-carbon containing rocks, which are enriched with organic matter (OM), because of its reserves and perspective of shale oil production [1-7]. The share of shale oil in world energy balance is significantly increasing. The uniqueness of discovering hydrocarbon reservoirs in shales is not only about new rock types containing huge hydrocarbon accumulation, but also they are the main oil and gas pay zones in their location region and bedded around their formation. Domanic deposits of Volga-Ural petroleum province of Russia are presently considered as an analogue of shale formations [7]. The main part of Domanic formation section takes bituminous rocks with high content of OM from Semikul and Mendim deposits of upper Devonian, which are considered as underexplored oil bearing horizons in territory of Tatarstan and currently are not explored [2-3, 6]. A large part of Domanic OM take bituminous resin-asphaltene components and kerogen. According to modern concepts kerogens are natural geopolymers with irregular structures and are regarded as potential source of petroleum generation [8-9]. Kerogen has solid state, stable chemical structure, specific composition and generally is not dissolved in mineral and organic acids. The Investigation structure of kerogen can be done in laboratory or industrial scale by modeling hydrocarbon formation processes [10]. Thereby, studying Domanic shale is very important, initially for general understanding of oil generation, migration and accumulation issues. Secondly, for solving problems regarding discovery of industrial reservoirs directly in Domanic formations. Thirdly, to reveal the production perspectives of Dominic hydrocarbon resources by modern secondary production techniques.

2. Materials and Methods

The object of geochemical study were samples from Romashkino oil field of Semiluksko-Mendim (Domanic) deposits, Berezev area. The interval of coring sample 1705-1728 m. The data, gained by Simultaneous Thermogravimetry and Differential Scanning Calorimetry allows to evaluate the content of organic matter in rocks and its thermal stability in the range of 20-1000 °C (Table 1). For the modeling of hydrothermal experiments Domanic rocks are used, constituting clay and limestone of the same interval mentioned before. However, the content of OM in the given rock sample is very high – 35.48 %, from this 25.43 % stands for kerogen. The hydrothermal conversion experiments of OM of Domanic rocks are carried in laboratory autoclaves with a volume of 1 L (Parr Instruments, USA) at temperatures 200, 250, 300 and 350 °C during 5 hours in CO_2 environment. The water content in system is 30 wt % of rock sample taken for the experiments. The initial pressure of the system was 2 MPa. During the process, depending from temperature, the vapor pressure of mixtures rises up to 17 MPa. The organic matter content in given samples was evaluated by loss of mass in 200-600 °C temperature range. For rock samples more than 650 °C, the mass loss is explained by thermal cracking of carbonates. And the mass losses for temperatures 20-150 °C are related with evaporation of light fractions and cleaning free and adsorbed water in clay-carbonic minerals [11], [12].

3. Results and Discussions

Table 1. The thermal analysis data of Domanic (Berezev area) rock samples from different coring intervals.

Sample	Coring interval, m	Mass loss of rocks in temperature ranges of 20-1000 °C						
		20-200	200–400	400–600	600–800	800-1000	∑ OB	F_{OB}**
1	1705.0-1712.5 (3.56-3.59)	0.34	1.26	4.48	9.04	7.74	5.74	0.28
2	1712.5-1718.5 (2.67-2.73)	0.27	2.17	9.56	11.77	3.12	11.73	0.23
2*		0.50	1.43	8.76	11.04	5.44	10.19	0.16
3	1712.5-1718.5 (4.84-5.00)	0.14	0.50	1.47	7.48	32.04	1.97	0.34
3*		0.15	0.16	0.99	10.16	29.30	1.15	0.16
4	1718.5-1724.5 (4.00-4.09)	0.34	2.68	11.12	12.53	10.47	13.80	0.24
5	1718.5-1724.5 (5.19-5.28)	0.48	2.65	8.01	10.85	1.79	10.66	0.33
6	1724.5-1728.0 (2.77-2.85)	0.25	0.82	4.18	10.35	20.86	5.00	0.20
6*		0.19	0.32	3.62	9.05	24.01	3.94	0.09

*Rocks after extraction; **$F_{OB}=\Delta m_1(200\text{-}400^oC)/\Delta m_2(200\text{-}600^oC)$

Analyzing samples from Romashkino oil field of Berezev area of Semilukskoe horizon, Domanic deposits revealed heterogenic rock composition in small coring interval. The content of OM in rock samples varies from 1.97 to 13.80 %. The minimal OM amount is observed in samples 3 and 6. The former constitutes for dark gray clays and the latter for transition of dark gray clays to limestone. Oppositely, samples 2 and 4 are rich in OM. The former is also constitutes for dark gray clay, but sample 4 is recrystallized limestone transiting from gray to dark gray color. The given samples are characterized by enough high content of kerogen. This is explained by mass loss in temperature range of 400-600 °C from 1.47 to 11.12 %. Based on fractional value $FOM=\Delta m_1(200\text{-}400\ °C)/\Delta m_2(200\text{-}600\ °C)$ after extraction, the OM content in rocks decreases, which is mostly realized in samples 3 and 6, which shows free hydrocarbon content is high enough. Table 2 provides the thermal analysis data before and after hydrothermal treatment at various temperatures.

Table 2. The thermal analysis data before and after hydrothermal treatment at various temperatures.

samples	The mass loss of rocks in temperature range of 20-1000 °C						
	20-200	200–400	400–600	600–800	800-1000	∑ OB	F_{OB} **
Initial rock							
1	0.96	10.05	25.43	11.32	0.45	35.48	0.39
1*	0.76	9.33	24.99	12.94	0.36	34.32	0..37
After thermal treatment T 200 °C, P 7.6 MPa							
1.1	0.76	13.04	18.41	18.85	0.18	31.45	0.71
1.1*	0.61	11.35	18.21	18.80	0.41	29.56	0.62
After thermal treatment T 250 °C, P 8.3 MPa							
1.2	0.49	12.40	16.14	13.43	0.21	28.54	0.77
1.2*	0.28	10.19	15.06	10.54	0.45	25.25	0.68
	After thermal treatment T 300 °C, P 10.5 MPa						
1.3	0.89	11.17	15.28	13.50	0.32	26.45	0.73
1.3*	0.35	9.30	12.45	12.54	0.35	21.95	0.75
After thermal treatment T 350 °C, P 17.0 MPa							
1.4	1.02	8.34	16.36	13.36	0.13	24.69	0.73
1.4*	0.46	8.31	10.58	12.57	0.38	18.89	0.79

*rock sample after extraction; **$F_{OB} = \Delta m_1(200\text{-}400\ ºC)/\Delta m_2(200\text{-}600\ ºC)$

According to thermal analysis of initial rock samples, the low value of fractional composition FOM = 0.39 is observed, that proves the small amount of mobile hydrocarbon and large content of kerogen are in rocks. Increasing the given value for rock samples after hydrothermal treating indicates about formation of light hydrocarbons due to destruction of high molecules in free bituminous components, which are in both rocks and insoluble kerogens. After experiments and extraction, the OM content decreases, because of new formed hydrocarbons. The kerogen content doesn't change much and stays actually the same as in experiment at 350 °C. However, the mass loss of rock samples in 200-400 °C range is less, which indicates less destruction of OM with free hydrocarbon formation. The hydrothermal treatment of rock samples comparatively at lower temperatures, i.e. 250, 200 °C results to intensive extraction of free hydrocarbons existing in the structure of kerogen as liquid phase [13]. It is important to mention that kerogen from Domanic rocks of Berezev area are not destructed totally even at 350°C (11.35 vis. 25.43 %). The extraction yield from Domanic rock samples after hydrothermal treatment at all investigated temperature ranges is increasing according to initial rocks (Table 3). The saturate content is high in the products of group composition of experiments. The aromatic compounds, as well as resins are decreasing. The products of asphaltenes consist of two fractions, containing normal asphaltenes (Fraction A), which are dissolved in aromatic solvents and their modification products – not dissolving carbene-carboid types (Fraction B).

Table 3. The group composition of extracts from rock samples of Berezev area before and after hydrothermal experiments at various temperature ranges in CO medium.

Sample	Content of bitumoid, wt %	*Group composition, wt %				
		SH	AC	Resins	Asphaltenes	Carbene-Carboids
Initial rock						
1	0.25	18.58	38.94	28.32	14.16	-
Rock after experiment T 200°C, P 7.6 MPa						
1.1	1.90	29.22	25.80	24.89	18.72	1.37
Rock after experiment T 250°C, P 8.3 MPa						
1.2	2.28	32.46	28.24	22.98	14.21	2.11
Rock after experiment T 300°C, P 10.5 MPa						
1.3	3.85	31.86	24.11	24.05	13.84	6.14
Rock after experiment T 350°C, P 17.0 MPa						
1.4	4.56	35.69	23.45	24.48	12.07	4.31

SH – saturate hydrocarbons, AC – aromatic compounds

In the work [14] from rock samples of Domaic deposits (Sarmanov area, Romashkino Oil Field) we have determined the main relations, characterizing hydrothermal treatment processes to OM and kerogens. These dependencies show the transformation of structural elements in kerogen, by aliphatic bonding with further transition to free micro oil of large fragments, containing naphthenic and aromatic hydrocarbons. Hydrothermal treatment breaks molecular aggregates of asphaltenes as well. This is explained by dealkylation reaction, which brings compaction of carbon skeleton, increasing the degree of structurization and carbonization. The existence of two solid disperse phases that varies by their structure and dissolving in organic solvents, in the products of hydrothermal experiments is also a result of dealkylation reaction. The element analysis of asphaltenes (Fraction A) and carbene-carboids (Fraction B) after hydrothermal treatment indicates a significance increase in sulfur content, most part of which is concentrated in carbene-carboid compositions. In this fraction a hydrogen is decreasing noticeably, but carbon content is increasing. This reflects to declining the proportion value H/C_{at}. The nitrogen content also increases in asphaltenes of initial rocks. Besides the most part takes place in asphaltenes of fraction A. In experimental products of asphaltenes (Fraction A) the free radical concentration relative to vanadium (V^{+4}) concentration, which is in vanadyl-porphyrin complex composition, is increased as temperature rises [15]. This indicates to more carbonization of its structure. This reflects to increasing value of R^*/V^{+4} (from 0.35 to 0.55, 0.51, 0.74 and 0.8), as temperature rises. The abnormal high values (2.42, 3.2, 2.39 and 3) belong to carbene and carboid type compounds, which are differed from asphaltenes by low content of alkyl radicals, vanadyl-porphyrin complexes and other functional groups.

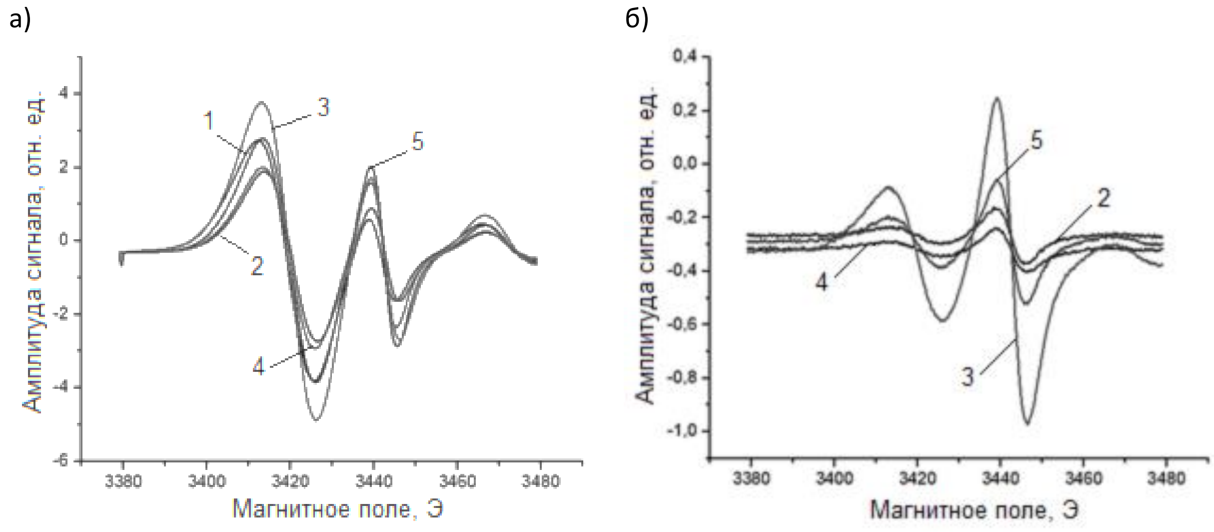

Figure 1. EPR spectrum of asphaltenes (left) and carbene-carboids (right) from Domanic (Berezev area) deposits: 1 - initial rock; 2 - product of experiments at 200 ºC, 3 -products at 250 ºC , 4 - products at 300 ºC, 5 – products at 350 ºC

Thus, the kerogen destruction after hydrothermal experiment and increasing high molecular component in the products indicate Domanic rocks from Romashkinskoe Oil Field are not suffered by high temperature effects in the genesis process and consequently their oil generating potential may be practiced by application of hydrothermal technologies.

4. Conclusion

Depositions of the Domanic type in the territory of Tatarstan are stratigraphically associated with carbonate-siliceous deposits of the Upper Devonian part of the section. These deposits, enriched with organic matter, are characterized by the ability to generate liquid and gaseous hydrocarbons and accumulate them in the form of deposits of unconventional type.

The effect of hydrothermal processes to yield-producing ability of OM to generate carbohydrates at temperatures 200, 250, 300 and 350 ºC in CO surrounding is revealed. The results of experiment indicate that oil generating potential of rocks from Domanic horizon, Berezev area, Romashkino Oil Field are not totally implemented. The hydrothermal influences on these rocks result to thermal maturity of OM. In the given temperature ranges free hydrocarbons may be extracted more intensively from rocks. The hydrocarbon potential of Domanic rocks are defined by composition and liquid bituminous content. As well as destruction products of resin-asphaltene compounds and macromolecule of kerogens. Hence, oil generating potential of Domanic rocks may be successfully realized by further optimizing hydrothermal processes, directed to enhancing hydrocarbon recovery.

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