

Research Article

Influence of Hydrothermal and Pyrolysis Processes on the Transformation of Organic Matter of Dense Low-Permeability Rocks from Domanic Formations of the Romashkino Oil Field

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The model experiments regarding the conversion of organic matters from carbonate rock samples of Dankov-Lebedyan deposits of Zelenogorskaya area and siliceous-carbonate rocks of Semiluki-Mendym deposits of Berezovskaya area of Domanic formations of Romashkino oil field were carried out. Two types of experiments were carried out: (1) the hydrothermal treatment of rocks at a temperature of 350°C in the presence of carbonic acid and a water content of 30%; (2) pyrolysis at temperatures of 350 and 600°C in the presence of hydrogen. The yield and quality of extracted hydrocarbons from the rocks depending on the mineral composition of rocks, content and composition of organic matter, and thermal stability of kerogen under hydrothermal influences were evaluated. Application of electron paramagnetic resonance in pyrolysis processes revealed the difference in mineral content of rocks (Mn^{2+} , SO_3^{2-} , and SO_4^{2-} ions) and free radicals R^* , as well as in vanadyl ion (VO^{2+}) concentration. It is established that an increasing temperature of pyrolysis promotes the formation of new free organic radicals in rock samples: in Domanic rocks of Semiluki-Mendym deposits at 350°C and in carbonate rocks of Dankov-Lebedyan horizon at 600°C. This indicates different ability of oil-generating potential of rocks with hydrothermal and pyrolysis technologies.

1. Introduction

The increased interest in high-carbon rocks, which are rich in organic matter (OM), is associated with their reserves and perspectives of shale oil production [1–5]. An analogue of the shale formations in Russia is the house deposits of the Volga-Ural oil and gas basin which stratigraphically belong to the Frasnian stage of Upper Devonian age. In the territory of Tatarstan, the Domanic formations are represented by typical domanicites with an organic content of Corg. 5–20% in Semiluki, Mendym, and Sargai horizons, as well as domanicoids starting from Tournaisian age up till Mendym horizon with an organic content of Corg 0.5–5%. The thickness of Domanic deposits in the Tatarstan area does not

prevail ten meters. The characteristic of Domanic formations is a high concentration of silica (till 37.23%). The Domanic bituminous rocks from Tatarstan territory belong to a least studied local oil-bearing horizons. The development of low-permeable carbonate rocks where pore spaces are clogged by clays and siliceous compounds is very difficult; in addition, if a reservoir formation has nonuniform lithology. Besides, the significant part of OM from high-carbon-enriched Domanic rocks falls on resins, asphaltenes, and kerogen. Kerogen is a nonsoluble part of organic matter, which contains mainly chemically strongly connected polymer components inside the rocks. These components are converted into hydrocarbons only under the temperatures of not less than 100°C [6–10]. The process of kerogen thermo

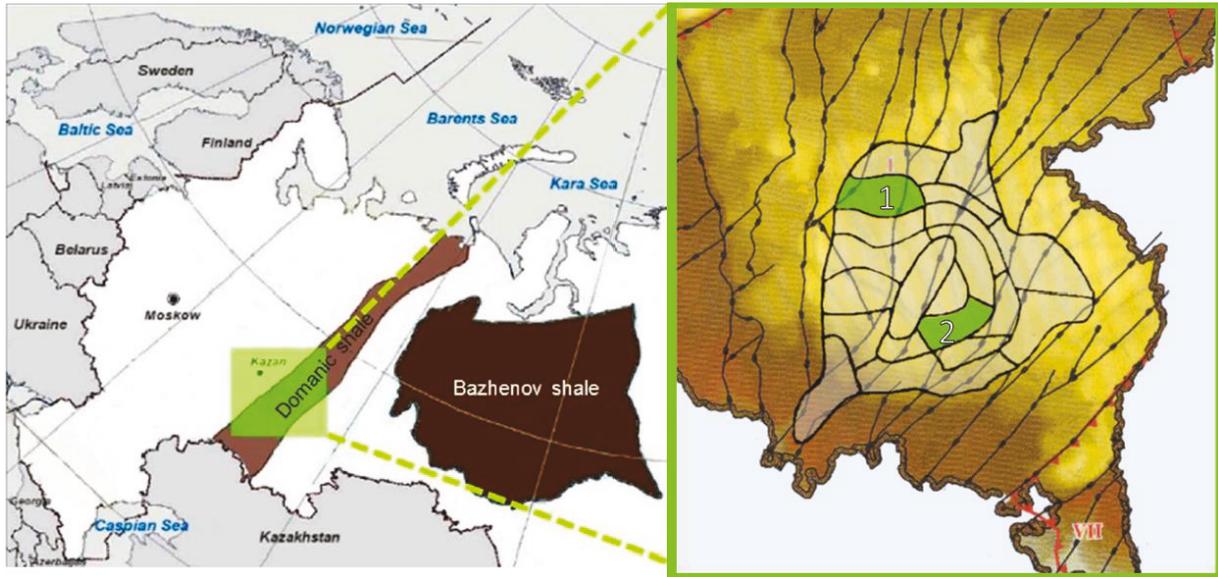


FIGURE 1: Location maps of the Volga-Ural basin. 1 = Berezovskaya area; 2 = Zelenogorskaya area.

destruction, as well as its extraction due to artificial maturity of kerogen, may serve as an evaluation technique for oil-generating potential of bituminous source rocks [7, 9–12].

However, “tight oil” allocates in dense low-permeable reservoir rocks; the characteristics of them are similar to conventional oils. But they need special production technologies, including horizontal drilling of wells and hydrofracturing operations [5].

The hydrothermal processes are widely applied in natural conditions, where maturity of organic matter occurs as a result of its interaction with hydrothermal fluids, the main component of which is water [13]. In the development of high-carbon-enriched rocks, as well as heavy oil reservoirs by hot water, steam, and gases, which were in OM reservoirs, containing mobile hydrocarbons (oil, bitumen, and bitumoid) and nonsoluble, immobile OM–kerogen will be considered in physical and chemical conversions [14]. One of the means to obtain information about the nature of hydrocarbon accumulations in Domanic deposits and the possibility of their extraction is studying the composition of rocks and modeling the hydrocarbon formation processes under various hydrothermal and pyrolytic influences. In order to simulate the influence of geological factors on OM many authors made numerous experiments on aqueous pyrolysis of individual compounds and carbonic sedimentary rocks [13–17]. However, while producing shale oil from Domanic source rocks, these observations were not enough. Hence, obtaining new thoughts about the composition and properties of hydrocarbons from dense low-permeable rocks is very important and relevant task in studying oil formation processes, as well as in developing scientific bases for designing new shale oil recovery techniques.

The object of study is investigating the processes of organic matter conversions from Domanic rocks with various lithology-facial composition during hydrothermal

and pyrolytic processes in easily recoverable petroleum hydrocarbons.

2. Materials and Methods

2.1. The Object of Study. The object of comparative studies was two samples of rocks from the Domanic formations of the Romashkino deposit, differing in the lithologic facies type, the content of OM and its composition: (1) from the Dankov-Lebedyan carbonate deposits of Zelenogorsk area from the depth interval 1379–1385.5 m (m.v. 4.8–4.9 m); (2) from the siliceous-carbonate deposits of the Semiluki-Mendym (Domanic) horizon from the depth interval 1712.5–1718.5 (m.v. 2.75 m) of the Berezovskaya area, as well as samples of these rocks after hydrothermal and pyrolytic effects on them.

The given rock samples were studied after hydrothermal and pyrolytic influences as well. The samples had a distinction in lithology facies, OM content, and its composition.

Romashkino is one of the largest oil fields in the world [18–20]. It is located in the southeast of Tatarstan Republic in the central part of the South Tatarian arch—one of the largest structural elements of Volga-Ural oil and gas province (Figure 1). The reservoir is characterized by asymmetric plateau-like upheaving composed of Paleozoic carbonate and terrigenous deposits, the thickness of which reaches 2 km. By applying the edge water flooding, the given reservoir was artificially separated by injection wells into 21 independently developed areas, considering the geological structure. Among them, Berezovskaya and Zelenogorskaya areas are the objects of current investigation.

The oil-bearing capacity of Romashkino oil field is concentrated in 22 horizons, where the most important reservoirs are in Pashian and Timan horizons. These reservoirs belong to terrigenous deposits of Frasnian strata of Upper

Devonian age and dipped on granite-gneissic rocks with crystalline basement. There are industrially developed oil reservoirs in the sandstones of coal measures (Tournaisian age up), as well as in the limestone deposits of Upper Devonian. There are Domanic deposits (house formations rocks) enriched with organic matters around Frasnian strata of Upper Devonian age, which are considered as a source of oil in Romashkino and other reservoirs of Tatarstan.

The last investigations give reasons to imply that the oil-generating potential of Domanic deposits from Romashkino oil field is not finished yet as a burial depth, and hence, the thermal history is not enough to cover the intensive generation of hydrocarbons that is crucial for “oil window” [4, 11, 21, 22]. Consequently, hydrothermal and pyrolytic influences on the tight rocks will provide artificial thermal maturity of kerogen with the formation of oil in liquid phase, thus increasing the oil recovery factor of reservoirs.

2.2. Hydrothermal Experiments. Laboratory experiments on the conversions of the organic matter of the rock samples were carried out in a Parr Instruments (USA) laboratory autoclave of volume 1 L at the temperature of 350°C for 5 hours in the steam-gas medium at the initial CO₂ pressure in the system of 2 MPa. Hydrothermal experiments were carried out with the original rock samples without preliminary extraction of free hydrocarbons. The mass of the rock taken into experiment was 200 g. The water content in the reaction system was 30% by mass of the rock taken. During the experiment the pressure was elevated from 6.3 up to 17 MPa.

To extract hydrocarbons from the rock samples, we used the method of extraction with addition of solvents mixture, namely, chloroform, benzene, and isopropanol taken in equal ratios. Initial rock samples were analyzed with the use of a complex of physicochemical methods. We followed the methods of Kayukova et al. [14].

Rock samples analysis revealed the presence of the organic matter and thermal effect availability. It was performed on a synchronous thermal analysis instrument STA 443F3 Jupiter (Netzsch, Germany) with the Netzsch Proteus Thermal Analysis software. Measuring conditions were as follows: oxidizing medium (air), heating rate = 10°C/min, and temperature range = 20–1000°C. TG-DTA curves were processed by the Netzsch Proteus Thermal Analysis software computer standard.

XRD data were collected using a Shimadzu XRD-7000S in a θ - 2θ configuration using the Bragg-Brentano method. The diffractometer used a Cu K α radiation ($\lambda = 1.54060$ nm) and operated at 40 kV and 30 mA. Data handling was performed by the DIFFRACplus Evaluation Package with the EVA search/match module (version 4.0). The PDF-2 ICDD database was used.

Analysis of the group composition of bitumen samples was carried out in accordance with the common technique (SARA-analysis). Asphaltenes were precipitated under the effect of a 40-fold amount of an aliphatic solvent—hexane. Hexane is chosen to preserve the light fractions of bitumoids. Maltenes were separated by means of liquid-adsorption chromatography on aluminum oxide having been calcined

at 420°C into saturated hydrocarbons via their elution with hexane as an adsorbent, aromatic compounds via their elution with toluene, and resins, which were extruded from the adsorbent with the help of solvents mixture, namely, benzene and isopropyl alcohol taken in equal proportions.

The structural-group composition of the bitumen samples and reactions products was investigated by IR Fourier spectroscopy method. IR-spectra were taken on an IR Fourier spectrometer Vector-22 (Bruker) within the range of 4000–400 cm⁻¹ with the resolving power of 4 cm⁻¹. For the comparative correlation of data, spectral coefficients characterizing the structural-group composition of the products investigated were used. Spectral factors are the ratios of the optical densities of the absorption bands at 1710 (oxidation products), 1600 (arenas), and 1380 and 720 cm⁻¹ (alkanes): $C_1 = D_{1600}/D_{720}$ (aromaticity index), $C_2 = D_{1710}/D_{1465}$ (state of oxidation), $C_3 = D_{1380}/D_{1465}$ (of branching degree), $C_4 = (D_{720} + D_{1380})/D_{1600}$ (of wax content), and $C_5 = D_{1030}/D_{1465}$ (degree of sulfuring).

The investigation of the hydrocarbon composition of the rock extracts was performed on the “Crystal 2000M” apparatus by capillary gas chromatography method in the mode of temperature programming within the range of 100–300°C. In the temperature interval from 100 to 150°C, the temperature increased at the rate of 10°C/min and within the 150–300°C diapason at that of 3°C/min, respectively. Hydrogen was used as the gas carrier. The evaporator temperature was 310°C, and the detector temperature was 250°C.

2.3. Pyrolysis Experiments. The pyrolysis experiments in water environment were carried out in order to simulate the maturity of kerogen of investigated rock samples with further liquid oil formation. The experiments were conducted in a flow-through cell pyrolytic cell (CDS 1500, Valved interface) in two steps: at 350°C and 600°C during 30 min each. The first temperature is transitional between evaporation mode and kerogen destruction mode, while the second temperature corresponds to the completion of thermal destruction process. For pyrolytic investigations, the rock samples were dispersed to a homogenous condition and then loaded into a quartz tube of flow-through cell with 2 mm diameter (CDS 1500, Valved interface) located inside the platinum wire spiral in an electric furnace SUOL (MR 0.15 2/12180 B; 950 W). The hydrogen was provided into the reaction chamber through a gas supply line connected with hydrogen generator. The transformation process of organic matters in pyrolytic conditions directly in rock samples was observed by EPR method [23–25].

Paramagnetic properties of the initial and thermally activated rock samples were measured by EPR method on CMS-8400 X-band spectrometer at room temperature and a frequency of 9.43 GHz with a magnetic field sweep 360 mT (from 40 to 400) for the registration of Fe³⁺ ions, 140 mT (from 263 to 403) for the registration Mn²⁺ ions and vanadyl complexes (VO²⁺), and 10 mT (from 329.3 to 339.3) for the registration vanadyl complexes (most intense line), sulfate ions (SO₃⁻, SO₂⁻), and stable organic free radicals (R*, C₃₅₀, C₆₀₀). The content of stable free radicals and ions was

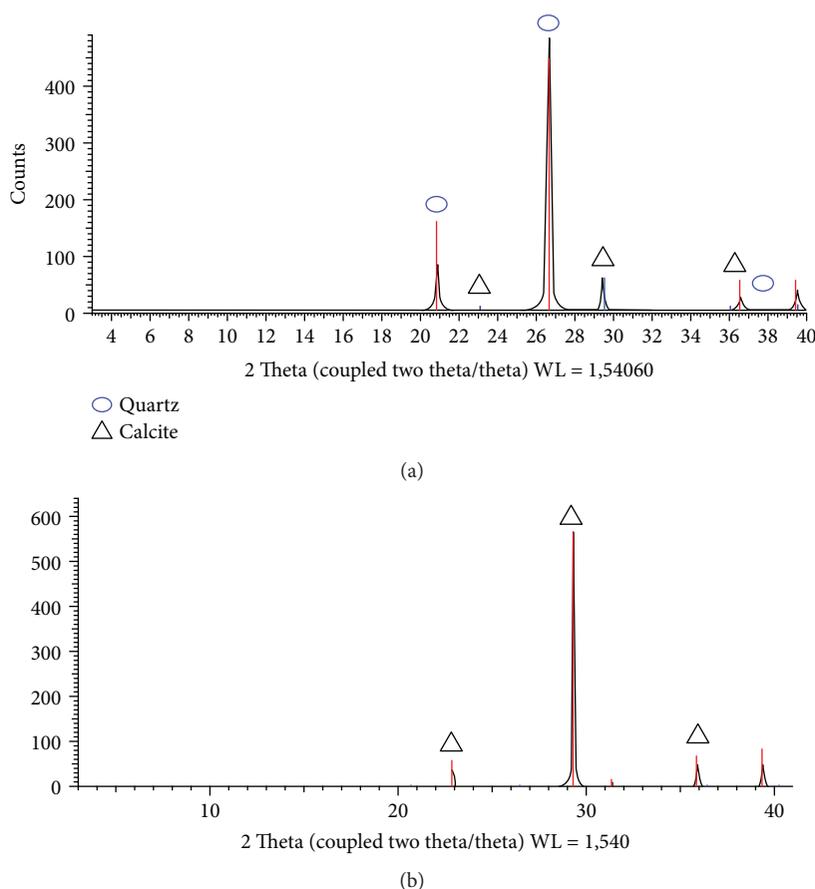


FIGURE 2: XRD patterns of rock samples: (a) Berezovskaya area; (b) Zelenogorskaya area.

measured in arbitrary units (the amplitude of EPR signal corrected for line width, obtained values were correlated to the weight of samples).

3. Results and Discussion

3.1. Characteristics of Rocks. According to the data of X-ray diffraction and thermal analysis [26–28], the samples studied differ in mineral composition, OM content in rocks, including insoluble kerogen, which is typical for different sedimentation environments. Thus, the rock sample from the Berezovskaya area contains 88.87% of quartz and 11.13% of calcite, and the sample from Zelenogorskaya contains 99.76% of calcite and only 0.24% of quartz. This follows from the diffractograms shown in Figure 2.

The carbonate material content was determined both by the character of the diffractograms and by the curves of DTA and DSC of thermal analysis (Figure 3). The investigated samples of rocks differ in mass loss with an increase in temperature from 20 to 900°C and the presence of thermal effects associated with the decomposition of organic matter in rocks and the dissociation of carbonate minerals. The content of OM was estimated from the mass loss of rock samples in the temperature range 200–600°C, since at temperatures of 20 to 200°C, mainly adsorbed water is removed and evaporation of volatile hydrocarbons from the rock; losses above

650°C are related as mentioned above, with the destruction of carbonate minerals [26].

The endothermic effect in the temperature range 650–800°C on the DSC curve of the carbonate rock sample from the Zelenogorskaya area (Figures 3(b) and 3(d)) is explained by the thermal dissociation of carbonates [25]. The thermal analysis was carried out both with initial samples of rocks and with extracted samples of rocks, that is, after removal of free hydrocarbons from them by extraction with organic solvents.

In the sample of the Berezovskaya area, according to the data of thermal analysis (Table 1), the content of OM is 35.48%. As a result of its hydrothermal treatment, the content of OM is reduced to 24.89%, the subsequent extraction of it leads to a nearly twofold decrease in OM, up to 18.89%, compared to the initial rock. The main weight loss of the rock sample occurs in the temperature range 400–600°C, due to the destruction of high molecular weight bituminous components and insoluble kerogen, that is, that part of the organic matter that has not been converted in natural maturation processes to the stage of petroleum generation.

According to the thermal analysis data, the OM content in the sample of the Zelenogorskaya area is 1.05%. After the hydrothermal experiment and extraction from the rock of free hydrocarbons, the content of OM in it is reduced to zero

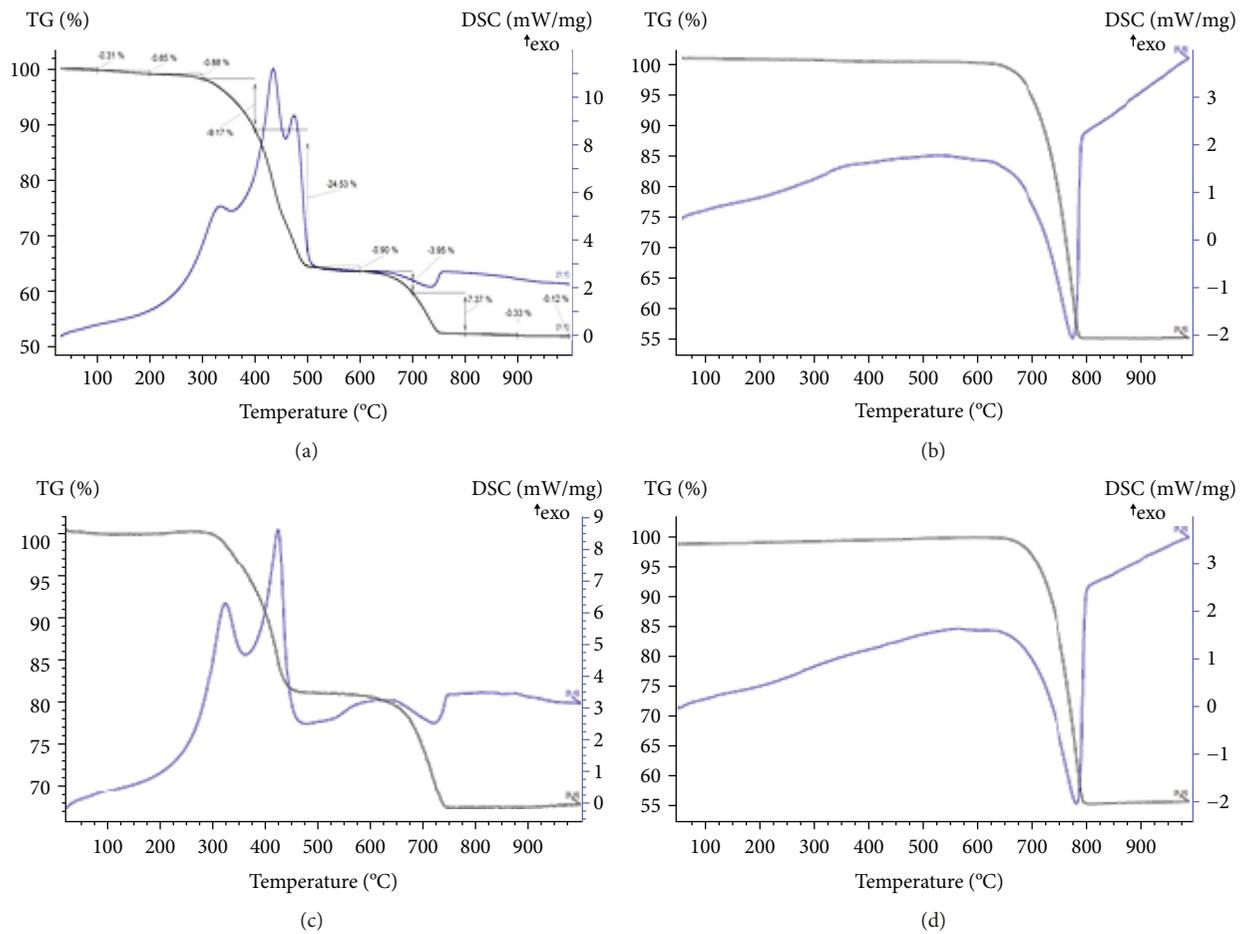


FIGURE 3: TG and DSC curves for thermal analysis of rock samples before and after hydrothermal experiments: Berezovskaya area before (a) and after (c) experiment; Zelenogorskaya area before (b) and after (d) experience.

TABLE 1: The data of the study of rock samples by the method of thermal analysis.

Object	Mass loss of the rock samples (wt %)					Σ OM	F*
	20–200°C	200–400°C	400–600°C	600–800°C	800–1000°C		
(1) Berezovskaya area							
Semiluki-Mendym (Domanic) sediments, depth 1712.5–1718 m							
Initial sample	0.96	10.05	25.43	11.32	0.45	35.48	0.39
After extraction	0.76	9.33	24.99	12.94	0.36	34.32	0.37
After thermal treatment	1.02	8.34	16.35	13.36	0.13	24.69	0.73
After extraction	0.46	8.31	10.58	12.58	0.38	18.89	0.79
(2) Zelenogorskaya area							
Dankov-Lebedyan (carbonate) deposits, depth 1379–1385.5 m							
Initial sample	0.31	0.63	0.42	43.13	0.12	1.05	1.50
After thermal treatment	0.24	0.38	0.34	43.47	0.20	0.72	1.12
After extraction	0	0	0	43.13	0.23	0	0

*F_{OM} = Δm₁ (200–400°C)/Δm₂ (400–600°C)

values. Differences in the rock composition of rocks are reflected in the values of the fractional index $F_{OM} = \Delta m_1 (200-400^\circ\text{C})/\Delta m_2 (400-600^\circ\text{C})$ [29], which is the ratio of the rock mass loss in the indicated temperature intervals.

According to the Rock-Eval data, the TOC content in the initial sample of carbonate rock from the deposits of the

Zelenogorskaya area is 3.03 wt %. After hydrothermal testing and extraction, TOC is reduced to 1.03 wt %. The content of free hydrocarbons (S_1) and kerogen (S_2) in the rock is also reduced: S_1 from 2.29 to 0.04 mg/g of rock and S_2 from 1.49 to 0.05 mg/g of rock. The rock samples were studied by Rock-Eval method after extraction [30].

TABLE 2: SARA analysis of the Bitumoids before and after Experiments.

Object	Amount (wt %)	*Group composition (wt %)				Carbene-carboides
		S	A	R	As.	
(1) Berezovskaya area						
Semiluki-Mendym (Domanic) sediments, depth 1712.5–1718 m						
Initial sample	0.25	18.58	38.94	28.32	14.16	—
After thermal treatment	4.56	35.69	23.45	24.48	12.07	4.31
(2) Zelenogorskaya area						
Dankov-Lebedyan (carbonate) deposits, depth 1379–1385.5 m						
Initial sample	0.63	39.69	26.72	17.56	16.03	—
After thermal treatment	0.97	56.38	13.83	14.63	9.04	6.12

*S = saturated hydrocarbons; A = aromatic hydrocarbons; R = resins; As. = asphaltenes.

In a sample of high-carbon rock from the Domanic carbonate-siliceous deposits of the Berezovskaya area, the TOC is 19.87 wt %, after experience the TOC decreases to 13.70 wt %. Similar to carbonate rock after hydrothermal treatment, the content of free hydrocarbons and kerogen in the rock decreases: S_1 from 7.69 to 2.23 mg/g of rock and S_2 from 120.26 to 76.64 mg/g of rock. Thus, the data of Rock-Eval, as well as the data of thermal analysis, show that at a temperature of 350°C there is a partial destruction of kerogen and more intensive extraction of free hydrocarbons from the rocks.

3.2. Characteristic of Products of Hydrothermal Experiments.

The yield of liquid hydrocarbon fluids (bitumoids) from the original rock samples (samples 1 and 2), irrespective of the content of OM in them, is extremely low: 0.25 and 0.63%, respectively (Table 2). As a result of the influence of hydrothermal processes, after processing rocks in a carbon dioxide environment at a temperature of 350°C in the presence of an aqueous phase, the yield of extracts from rocks increases from 0.63 to 0.96% from the Zelenogorskaya area sample, i.e., in 1.5 times, and from 0.25 to 4.56% from the Berezovskaya area sample.

In the group composition of the extracts is observed: the content of saturated hydrocarbons increases with a decrease in the content of aromatic hydrocarbons and resins. The content of asphaltenes also decreases. However, in the products of the experiments, along with asphaltenes, a newly formed solid phase is present in the form of carbonaceous substances such as carbenes and carboides insoluble in aromatic solvents. This distinctive feature of the composition of the products of hydrothermal treatment of Domanic rocks indicates the transformation of the polymer structure of kerogen to form not only the hydrocarbons that make up the liquid phase of oil but also the large structural asphaltene-like fragments.

Hydrothermal transformations of the organic matter of the Domanic rocks are also reflected in the spectral indices determined by the IR Fourier spectroscopy method, which characterize the structural-group composition of the investigated fluids [31]. The extracts from the rocks, which are, in fact, the liquid phase of the oil, after the experiments become more aromatic, as indicated by higher values of the

aromaticity index $C_1 = D_{1600}/D_{720}$ and a decrease values of the paraffinity index $C_4 = (D_{720} + D_{1380})/D_{1600}$ (Table 3). Based on the values of oxidation indices $C_4 = (D_{720} + D_{1380})/D_{1600}$ and $C_5 = D_{1030}/D_{1465}$, it can be assumed that the content of oxygen-containing and sulfoxide groups in the products is reduced.

The structure of asphaltenes becomes more carbonized (Table 3). Anomalously high values of the aromaticity index are characteristic for carbenes and carboides, especially from the rock sample of Zelenogorskaya area. This is clearly seen from the IR spectra of asphaltenes and carbene-carboides in Figure 4. The formation of carbenes and carboides indicates that hydrothermal destructive processes lead to changes in the structural and phase characteristics of asphaltenes and kerogen. Thus, in the paper [21], it was also shown in the case of debituminated samples of rocks from the house deposits of the Sarmanovskaya area of the Romashkino oil field that the increase in the content of asphaltenes and carbene-carboides in the products of hydrothermal experiments obtained in a hydrogen medium at 350°C is due to the destruction of insoluble kerogen. In the products of the experiments, saturated hydrocarbons, including n-alkanes, were also identified.

It should be noted that in all our experiments on the conversion of heavy oils and OM of Domanic and other sedimentary rocks, we observed an increase in the content of saturated hydrocarbons. But in the experimental products the degree of aromaticity, as determined by IR Fourier spectroscopy data, increased [32]. According to the IR Fourier spectroscopy, we estimate the structural-group composition of the averaged molecule. On the one hand, an increase in the values of the aromaticity index can be determined by the contribution to its value of highly condensed structures of the carbene-carboides type, which are formed during the thermal decomposition of kerogen [33]. In the experimental products, the degree of condensation of aromatic hydrocarbons, resins, and asphaltenes is also increasing [21, 32].

On the other hand, in the saturated fractions of the products of hydrothermal transformations of heavy oil, arylisoprenoids were identified by m/z 133 and 134, the content of which is increased with increasing temperature experiments. These are aromatic compounds containing a benzene ring and a long alkyl chain like isoprenoid alkanes [34]. The formation of hybrid naphthenic-aromatic hydrocarbons is also

TABLE 3: IR-analysis of Bitumoids before and after Experiments.

Object	Optical density at wavenumber (λ_{max}) (cm^{-1})						C_1	C_2	C_3	C_4	C_5	
	1740	1710	1600	1465	1380	1030						720
Berezovskaya area												
Semiluki-Mendym (Domanic) sediments, depth 1712.5–1718 m												
Bitumoids												
1	0.172	0.345	0.481	2	1.255	0.661	0.228	2.11	0.17	0.63	3.08	0.33
1*	0.076	0.204	0.593	2	1.194	0.244	0.168	3.53	0.10	0.60	2.30	0.12
Asphaltenes and carbene-carboides												
1	0.274	0.699	1.053	2	1.494	0.886	0.289	3.64	0.35	0.75	1.69	0.44
1*	0.084	0.338	1.297	2	1.456	0.490	0.281	4.61	0.17	0.73	1.34	0.24
1**	0.091	0.764	1.460	1.445	1.186	0.384	0.190	7.68	0.53	0.82	0.94	0.26
Zelenogorskaya area												
Dankov-Lebedyan (carbonate) deposits, depth 1379–1385.5 m												
Bitumoids												
2	0.156	0.317	0.457	2	1.311	0.425	0.313	1.46	0.16	0.66	3.55	0.21
2*	0.088	0.200	0.501	2	1.170	0.176	0.240	2.09	0.10	0.59	2.81	0.09
Asphaltenes and carbene-carboides												
2	0.133	0.414	1.023	2	1.479	0.627	0.262	3.90	0.21	0.74	1.70	0.32
2*	0.188	0.559	1.323	2	1.608	0.734	0.376	3.52	0.28	0.80	1.50	0.37
2**	0.175	0.422	1.570	2	1.700	1.388	0.087	17.95	0.21	0.85	1.14	0.70

1 and 2 = initial rock sample; 1* and 2* = after extraction; 1** and 2** = carbene-carboides after experiments. *Spectral coefficients: $C_1 = D_{1600}/D_{720}$ (aromaticity index); $C_2 = D_{1710}/D_{1465}$ (state of oxidation); $C_3 = D_{1380}/D_{1465}$ (of branching degree); $C_4 = (D_{720} + D_{1380})/D_{1600}$ (of wax content); and $C_5 = D_{1030}/D_{1465}$ (degree of sulfuring).

possible, which in the SARA analysis fall into the saturated fraction, but not into the aromatic fraction.

Changes in the group and structure-group composition of extracts from rocks under the influence of hydrothermal processes confirm the most intensive course of processes of degradation of kerogen and high-molecular bituminous components with the formation of aliphatic hydrocarbons. Figure 5 shows the chromatograms obtained by gas chromatography [35] of saturated fractions from rock samples from Berezovskaya and Zelenogorskaya areas before and after their hydrothermal treatment.

The data of gas chromatography confirm earlier conclusions [21] that the destruction of high-molecular bituminous components and kerogen of the Domanic rocks by thermally unstable oxygen-containing and sulfur-containing bonds leads to the formation of low-molecular n-alkanes. This is particularly noticeable in the example of a rock sample from the Zelenogorskaya area (Figures 5(c) and 5(d)). Thus, in the initial rock sample, n-alkanes of composition C_{21} and higher are present in appreciable concentrations, in which the products of the experiment, their concentration decreases, due to a relative increase in the concentration of their lower molecular weight homologues. An increase in the content of n-alkanes of the composition C_{10} – C_{18} in the products of the experiment is also noticeable with respect to the content of pristane and phytane. According to the data of [36], along with the destruction processes, it is also possible to release light hydrocarbons under the influence of hydrothermal factors from the kerogen matrix in the structure of which they remain in the free state. The chromatograms of the products

of hydrothermal experiments are similar to the chromatograms of shale oil extracted from the Dankov-Lebedyan deposits of the Bavlinskaya area in the territory of Tatarstan [30]. This is reflected in the values of chromatographic indices (Table 4).

3.3. Transformations of Rocks in Pyrolytic Processes according to EPR Analysis. As it was said above, the EPR method was used to monitor the transformation of OM in pyrolytic conditions [23–25]. The essence of the phenomenon of electron paramagnetic resonance is the resonance absorption of electromagnetic radiation by unpaired electrons. One of the traditional objects of EPR spectroscopy research is free radicals—particles containing one or more unpaired electrons, the so-called paramagnetic centers. Paramagnetic centers are a fairly reliable diagnostic criterion for the reconstruction of sedimentation environments, as well as for the dismemberment and correlation of the sedimentary strata in the study area [37–39]. This information is necessary for understanding the nature of hydrocarbon fluids, as well as for creating scientific foundations and developing technologies for the industrial extraction of shale oil.

The EPR parameters of the analysis of initial rock samples and thermally activated at 350°C and 600°C in a hydrogen medium in a flow system are shown in Table 5 and in Figures 6–8. The EPR data confirm the differences in the lithological and mineral composition of the rock samples under investigation and the distinguishing features of the transformation of their OM in both hydrothermal and pyrolytic processes.

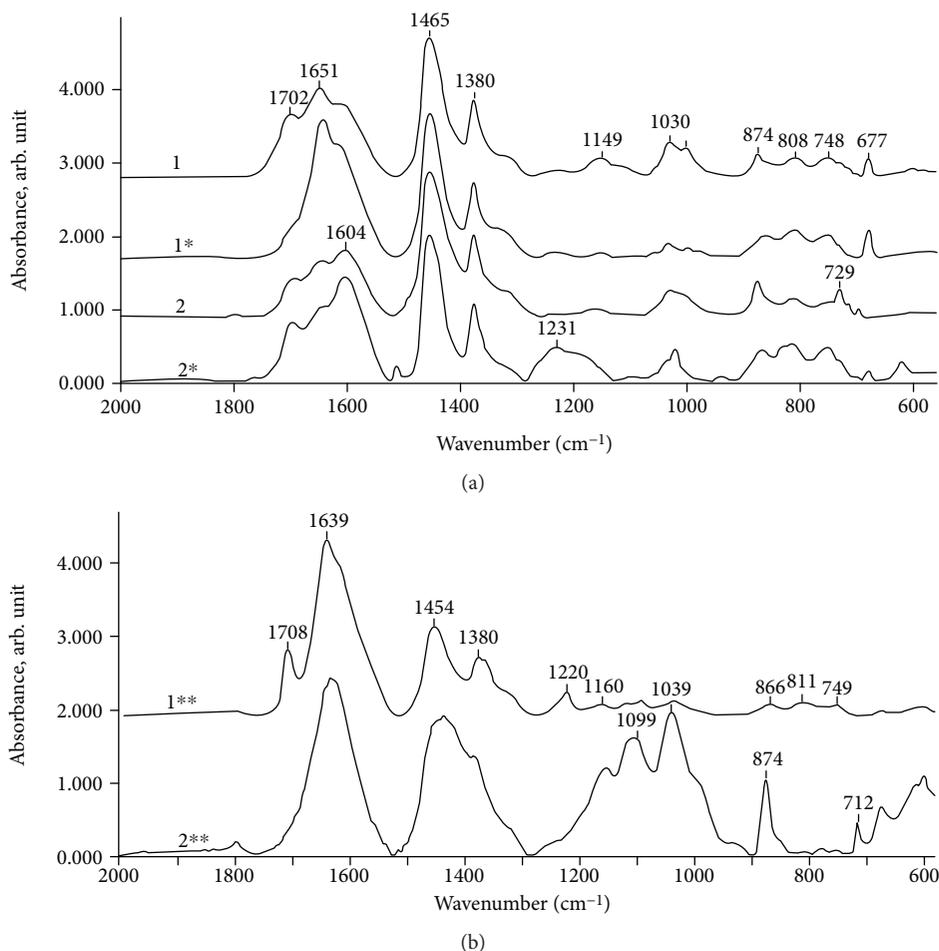


FIGURE 4: IR spectra of asphaltenes (a) and carbene-carboides (b) from the initial rock and products of experiments: 1,1*, 1** = Berezovskaya area; 2,2*, 2** = Zelenogorskaya area (for designations see Table 3).

A sample of the rock of Berezovskaya area is characterized by the presence of manganese, silicon, and carbonate minerals, which are fixed on the EPR spectra (Figures 6(a) and 6(c)). EPR spectra also contain an intense signal of stable free organic radicals (R^*) and a signal of vanadyl complexes (VO^{2+}), which are superimposed on the manganese spectrum (Figure 6(c)).

The sample from Zelenogorskaya area is distinguished by the presence of trivalent iron, manganese, and carbonate minerals (Figures 6(b) and 6(d)). The character of the EPR spectra of this sample indicates the absence of silicon, vanadyl ions, and an organic radical in it.

In carbonate minerals, the ion radicals SO_3^- and SO_2^- enter their structure and are indicative of the early diagenesis of carbonate silts with the participation of syngenetic organic matter [38]. The predominance of the SO_3^- radical over the SO_2^- radical ($SO_3^-/SO_2^- > 0.5$) indicates that the formation of carbonates occurred in the oxidative environment of sedimentation. The reverse picture, where the SO_2^- radical predominates over the SO_3^- radical, shows that the formation of the rock occurred in a reducing atmosphere of sedimentation. According to the measured EPR method, the SO_3^- and SO_2^- concentrations of the rock samples studied differ

according to the formation conditions: the sample of the rock from the Berezovskaya area reflects the oxidative situation of sedimentation, and the rock sample from the carbonate of the Dankov-Lebedyan deposits of the Zelenogorskaya area is more typical for the reducing situation.

To assess the petroleum potential of these rocks, pyrolysis was carried out at 350°C in a hydrogen medium in a flow system with the rocks treated with hydrochloric acid to dissolve the calcite in order to increase the clarity of the ESR signal. During the pyrolysis of the sample of the Berezovskaya area, the OM undergoes a thermal transformation, which leads to the formation of a new organic radical C_{350} , whose signatures differ markedly in amplitude and form from the signal of the original organic radical R^* (Figure 7). The shape of the signal C_{350} is similar to the signals characteristic for oil samples; therefore, the appearance of mobile hydrocarbons in the rock after its thermochemical treatment can be concluded. The results simulate the natural conditions of maturation of OM: an increase in temperature causes decomposition, or its destruction, including kerogen, whose polymer structure decomposes, forming less complex compounds. It was shown in [7] that this is due to the destruction and loss of aliphatic chains by kerogen and the redistribution of aromatic

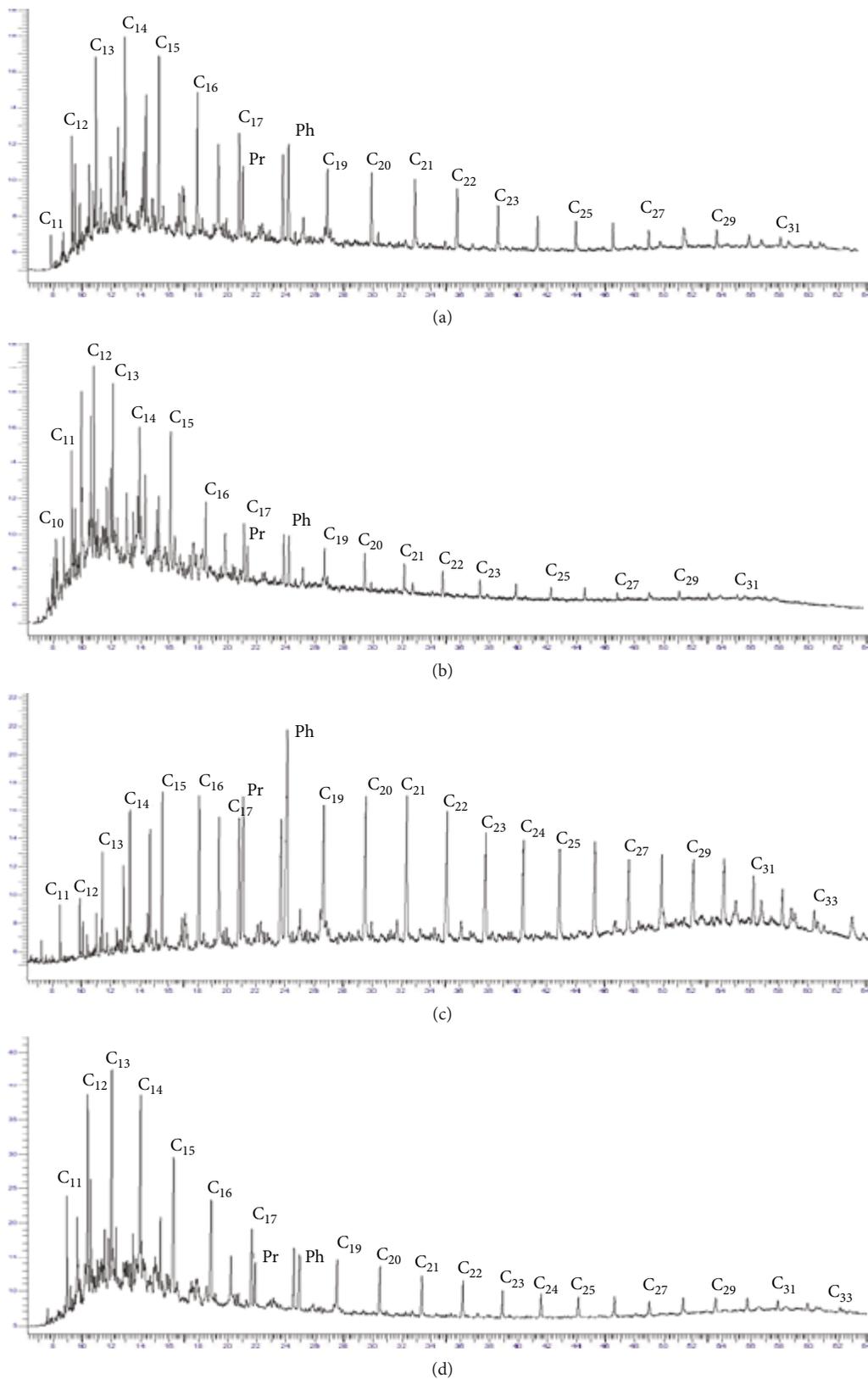


FIGURE 5: Chromatograms of saturated fractions of extracts from Domanic rocks: Berezovskaya area before (a) and after (b) experiments; Zelenogorskaya area before (c) and after (d) experiments. Pr = pristane (i-C₁₉); Ph = phytane (i-C₂₀).

TABLE 4: Values of biomarker parameters normal alkanes and isoprenoids before and after hydrothermal experiments.

Parameters	Object			
	Berezovskaya area		Zelenogorskaya area	
	Before experiments	After experiments	Before experiments	After experiments
Pr/Ph	0.75	0.74	0.71	0.75
Pr/C ₁₇	0.70	0.67	1.15	0.69
Ph/C ₁₈	1.12	1.00	1.69	1.12
C ₂₇ /C ₁₇	0.19	0.17	0.57	0.19
$\Sigma(C_{27}-C_{31})/\Sigma(C_{15}-C_{19})$	0.15	0.11	0.48	0.15
odd/even = $2n-C_{29}/C_{28} + C_{30}$	0.97	1.13	0.98	0.97
(Pr + Ph)/(n-C ₁₇ + n-C ₁₈)	0.89	0.82	1.43	0.89
n-(C ₁₂ -C ₂₁)/n-(C ₂₂ -C ₃₀)	2.75	3.89	0.92	6.60

TABLE 5: EPR-analysis of samples of Domanic rocks before and after pyrolytic experiments.

Object	The content of paramagnetic centers (u.e.)						
	Free hydrocarbon radicals			Inorganic ions			Mn ²⁺
	23°C	350°C	600 °C	SO ₂ ⁻	SO ₃ ⁻	VO ²⁺	
Berezovskaya area							
Semiluki-Mendym (Domanic) sediments, depth 1712.5–1718 m							
Initial sample	613.2	5860.9	437.3	322.2	472.4	720.9	2375.2
The sample after extraction	512.9	5676.5	356.3	—	—	402.8	2137.5
The sample after hydrothermal treatment in autoclave T 350°C	1057.2	2690.7	412.6	295.2	916.0	979.6	2708.6
Zelenogorskaya area							
Dankov-Lebedyan (carbonate) deposits, depth 1379–1385.5 m							
Initial sample	0	17.3	287.6	94.6	50.27	141.7	2082.2
The sample after extraction	70.2	135.7	250.7	66.37	28.0	0	2112.7
The sample after hydrothermal treatment in autoclave T 350°C	0	0	520.8	145.57	77.85	441.7	844.8

structural fragments in its matrix. Due to this, as the depth of occurrence increases in the organic matter of the sedimentary rocks, the bitumen content increases, and in the latter the quantity of mobile petroleum hydrocarbons increases.

Pyrolysis at 600°C is accompanied by an intensive separation of ferric iron from the structure of siliceous minerals. A new radical C₆₀₀ is also formed. The overlapping of lines with different EPR parameters can be seen from the type of spectrum in the C₆₀₀ region (Figures 7(a) and 7(c)). The resulting radical differs from C₃₅₀. Most likely, this is due to the exhaustion of the generation potential of kerogen and the destruction of newly formed compounds. In nature, the process of formation of hydrocarbons from kerogen occurs at temperatures of 150–200°C. A further increase in temperature leads to the destruction of the formed liquid and solid hydrocarbons.

Comparison of the EPR spectra of the initial sample and the sample after the hydrothermal experiment showed that they are practically identical (Table 5). The radical C₃₅₀, formed after pyrolysis, is not registered. In this case, after pyrolysis at 350°C carbon dioxide environment, the concentration of the organic radical increases. Perhaps this is due to the insufficient temperature of the sample heating or the time of exposure. Changes in the content of the vanadyl

group (VO²⁺), in the initial and debiturized sample of rocks of Berezovskaya area, suggest that this group is in the structure of kerogen [25]. In this case, the thermal effect on kerogen (a sample after an autoclave experiment) reduces its content, which may indicate the destruction of vanadylporphyrin complexes, as a result of which vanadium leaves the structure of the kerogen in the composition of the liquid phase.

An interesting fact is that the formation of a free radical in a carbonate rock sample from the Dankov-Lebedyan deposits of the Zelenogorskaya area after pyrolysis at a temperature of 350°C, unlike the Berezovskaya area, is not fixed (Figure 7(b)). At the same time, after exposure to a given sample of rock at a temperature of 600°C, the intensity of the signal in the region of manifestation of free radicals, on the contrary, increased significantly (Figure 7(d)).

A comparative analysis showed that the intensity of free radical signals in the EPR spectrum of the original rock from the Zelenogorskaya area is almost zero. After the hydrothermal experiment with this rock, it is about 70 rel. units, and after pyrolysis at 600°C, it increases to 130 and above. The shape of the signal (Figure 7(d)) gives reason to believe that an organic radical forms. Thus, depending on the different content and type of OM in rocks and their lithological

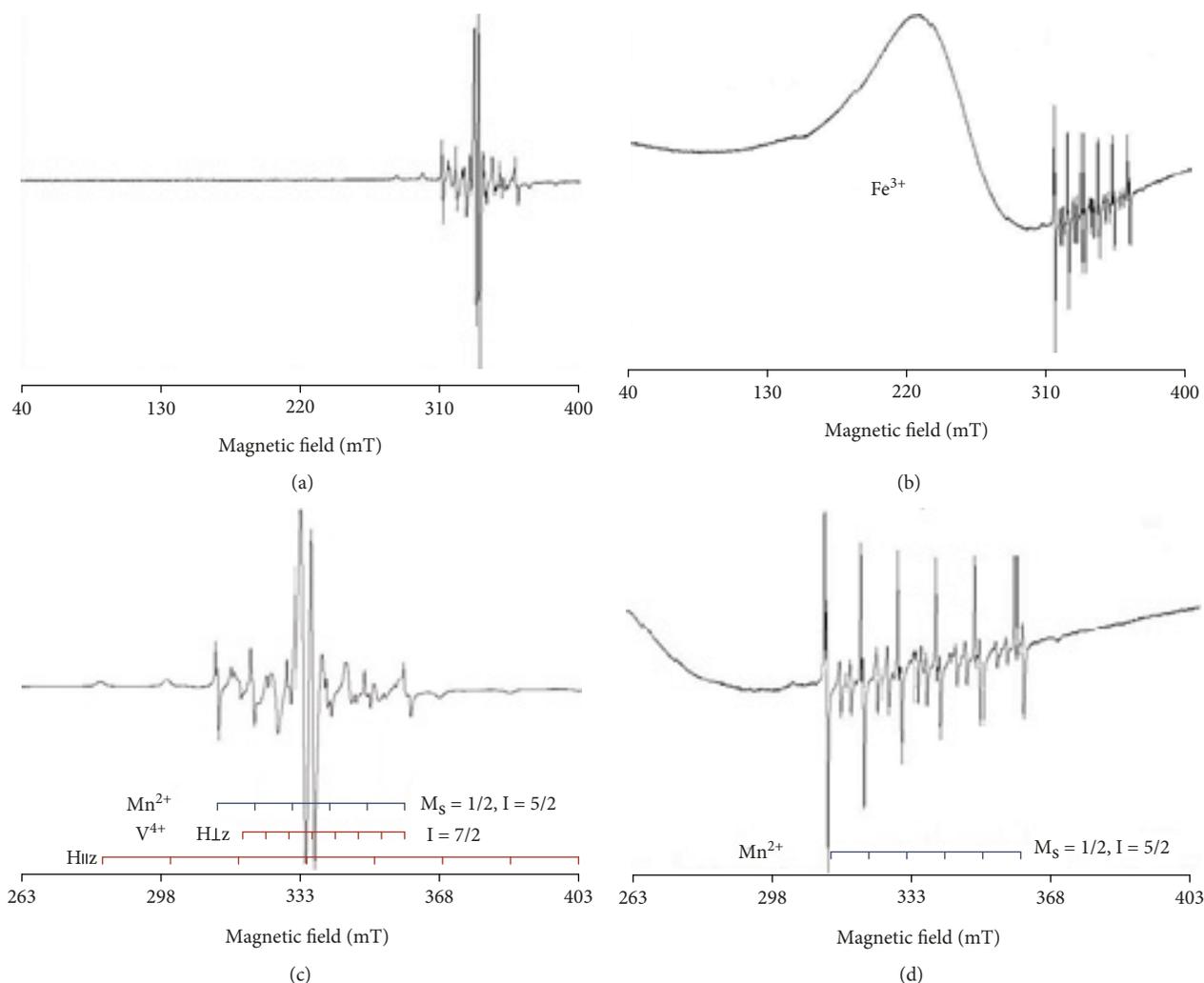


FIGURE 6: ESR spectra of the initial Berezovskaya (a, c) and Zelenogorskaya (b, d) rocks.

composition, the realization of the oil-generation potential of these rocks occurs at different temperatures. This follows from the diagrams shown in Figure 8.

In both rock samples, after pyrolysis at 600°C, an intense trivalent iron signal is fixed. It should be noted that the decrease of vanadium under thermal action is accompanied by a change in its valence. The catalytic activity of vanadium is well known, especially when pyrite is destroyed with the formation of iron oxide, with the release of heat and SO_3^- and SO_2^- radicals. The carbonate component of SO_2^- during the pyrolysis of the sample of the Berezovskaya area is reduced both in the original rock and after extraction of the OM and hydrothermal exposure, which increases the pore space. A different picture is observed in the rock of the Zelenogorskaya area, where the recrystallization and sealing of the pores by the newly formed calcite occur.

4. Conclusions

The results of conducted investigations on rock samples from Domanic deposits of Berezovskaya area and Dankov-

Lebedyan carbonate deposits of Zelenogorskaya area of Romashkino oil field revealed the specific difference in the composition of organic matter and kerogen. Moreover, the change in composition of hydrocarbon fluids extracted under hydrothermal processes was observed. It is affirmed that the yield of extracts from the rocks increases under the hydrothermal influences at 350°C in the presence of carbon dioxide. In the composition of extracts after the treatment, the share of saturate hydrocarbons increased, while the content of aromatics and resins declined. The content of asphaltenes in the products of experiment also decreased. However, the destruction of kerogen resulted to the formation of new highly carbonic insoluble compounds like carbene and carboides, which were absent in initial extracts. The destruction processes increased the n-alkane content ($\text{C}_{11}\text{-C}_{17}$) in the products of experiments in contrast with their high molecular homologues ($\geq \text{C}_{20}$). The pyrolysis of organic matter of investigated rock samples at temperatures of 350 and 600°C in a hydrogen medium was followed by formation of new free radicals C_{350} and C_{600} , which had an organic origin. This shows that investigated rock samples from Domanic

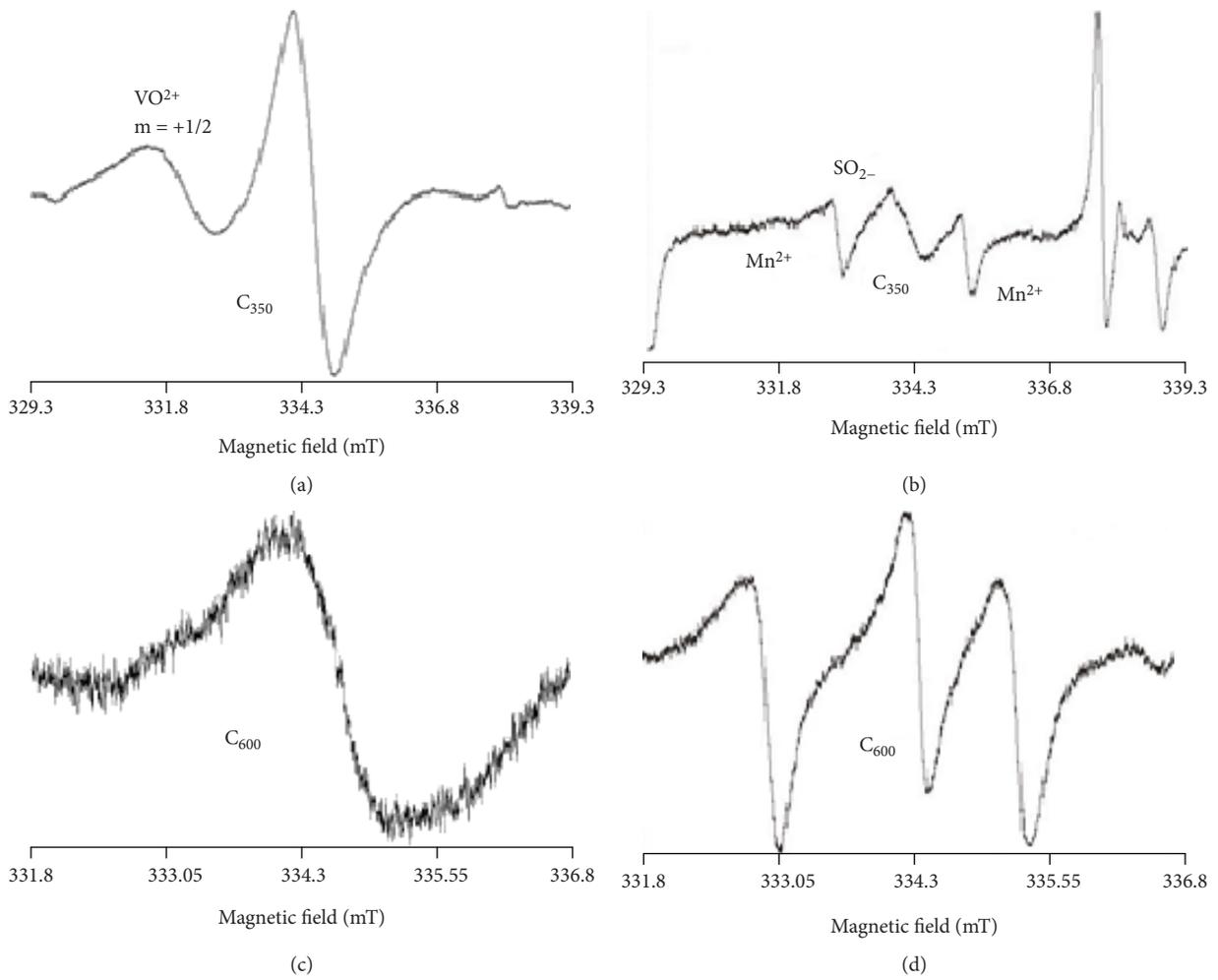


FIGURE 7: EPR spectra of rock samples of Berezovskaya (a, c) and Zelenogorskaya (b, d) areas after pyrolytic heating at different temperatures.

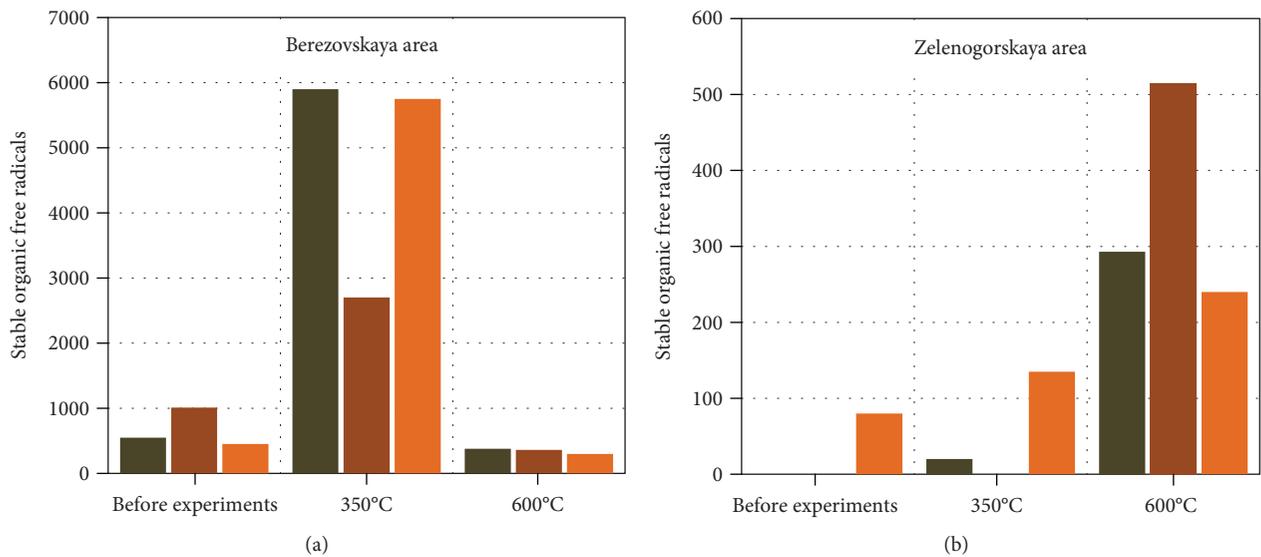


FIGURE 8: Diagrams of free radicals after pyrolysis at 350 and 600°C in Berezovskaya area and Zelenogorskaya area rock samples. 1 = initial rock (dark brown), 2 = rock after extraction (brown), and 3 = rock after hydrothermal treatment (light brown).

formations of Romashkino oil field in natural conditions did not realize their oil-generating potential at all. Moreover, depending on the content, type of OM and lithology of rocks, the realization of their potential occurred at different temperatures. The revealed OM transformation behaviors of Domanic rocks must be considered while designing hydrothermal and pyrolytic recovery technologies.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

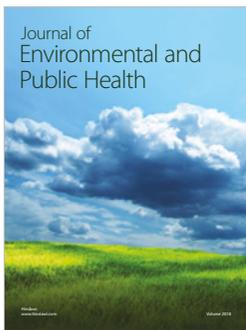
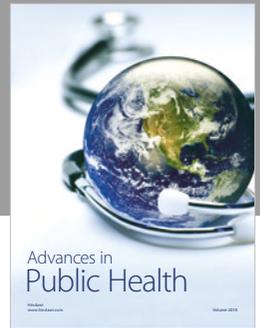
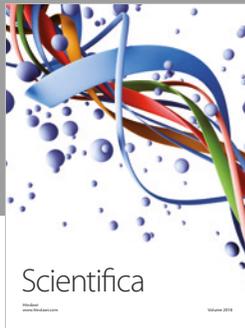
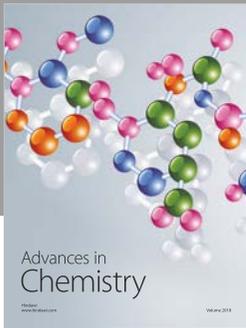
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