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Conversion of high-carbon Domanic Shale in sub- and supercritical water

Zukhra R. Nasyrova[a], Galina P. Kayukova[a,b], Yaroslav V. Onishchenko[a], Vladimir P. Morozov[a], Alexey V. Vakhin[a]

[a]*Institute of Geology and Oil & Gas Technologies, Kazan Federal University, Kazan, Russia*
[b]*A.E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Science Center, Russian Academy of Sciences, Kazan, Russia*

Correspondence should be addressed to Alexey Vakhin; vahin-a_v@mail.ru

ABSTRACT: This paper presents the results of the conversion of high-carbon Domanic rock from sediments of the Semulukskoe-Mendimskoe horizon of the Volga-Ural petroleum Basin in sub- and supercritical water at temperatures of 320, 374, 420°C in a neutral nitrogen environment for 1 hour. The initial sample is a siliceous-clay carbonate rock with an organic matter content of 10.6 wt %, the largest part of which is insoluble kerogen. The end products of all experiments are characterized by an increase in the content of saturated hydrocarbons with a noticeable decrease in the content of resins and asphaltenes. The highest yield of the extract (3.98 against 3.12 wt %) compared with the initial rock is observed in the experiment in subcritical water at 320°C as a result of the preferred degradation of resins and more complete extraction of asphaltenes from the rock. With an increase in temperature to supercritical water conditions at 374°C and pressure up to 24.6 MPa, kerogen destruction processes are observed due to the C-C, C-N, C-O bonds destructing with the formation of low-boiling saturated hydrocarbons and high-carbon components such as carbene-carboids in the products of the experiments. The highest yield of saturated hydrocarbons occurs at the experiment of Domanic rock in supercritical water at 420°C and 24.4 MPa. Under these conditions, in comparison with lower temperatures, the yield of the extract from the rock decreases due to intense gas formation. In the composition of the gases formed in the experiments, there are hydrocarbons: CH_4, C_2H_6, C_3H_8, i-C_4H_{10}, indicating the C-C bonds destructing. Dehydrogenation processes in supercritical water at 420°C are noted by the presence of H_2 in the reaction system. Structural and phase changes in the mineral composition of Domanic rock were discovered as a result of supercritical water exposure at 374, 420°C. In particular, the structure of mica was changed due to the isolation of a separate phase of montmorillonite from it.

1.   Introduction

Recently, the structure of world oil production has been characterized by an increase in the share of unconventional sources of hydrocarbon raw materials. According to the Energy Information Administration of the US Department of Energy (EIA), Russia has taken a leading position in the list of states with the largest reserves of shale oil - 75 billion barrels, or 22% of global reserves[1]. Shale strata in Russia are represented by weakly permeable and highly fractured strata of the Domanic deposits of the Volga-Ural and Timan-Pechora oil and gas provinces[2–6]. The deposits of the Semulukskoe (Domanic) horizon are a belt that stretches along the Urals from north to south from the Pechora Sea to the Caspian syneclise. These deposits are represented by bituminous clay, clay-carbonate, siliceous-clay-carbonate and siliceous rocks with a content of sapropel type dispersed organic matter (OM) from 5 to 20%[7].

Most of the OM in Domanic shale is represented by resinous-asphaltenic components and kerogen, which is a natural geopolymer with an irregular structure[8–13] and in many works [14–16] regarded as a source of petroleum hydrocarbon generation[17–19]. The geochemical processes of the conversion of OM at the stages of diagenesis, catagenesis and metagenesis are accompanied by a large number of chemical reactions with the breaking of aliphatic chains from kerogen, as well as hydrocarbon bonds in already formed hydrocarbons[20]. Partial destruction of the kerogen structure results in the

formation of hydrocarbons and heteroatomicic compounds of lower molecular weight[15,16].

Therefore, the huge reserves of kerogen and resinous-asphaltenic hydrocarbons in sedimentary Domanic rocks can be considered as an alternative source of hydrocarbon raw materials for the petrochemical industry.

In order to efficiently extract hydrocarbons from low-permeability high-carbon rocks, thermal methods are currently being used to influence these rocks. One of the new aspects in the application of thermal methods for the development of shale rocks is the use of supercritical water (SCW), because water under thermodynamic conditions above 374.3°C and a pressure of 22.1 MPa is able to exhibit the properties of a solvent, reagent, and hydrogen donor[21–23].

The conversion of shale in SCW is an environmentally harmless process and has several advantages over traditional thermal methods for the extraction of hydrocarbons from low permeability rocks[24,25]. The main advantages of SCW exposure are improved mass transfer, increased hydrocarbon conversion due to SCW's ability to dissolve gases and non-polar compounds, allowing more complete recovery of hydrocarbons from rocks[26].

In their study [27] on the effect of SCW on shale rock, Morimoto et al experimentally revealed a radical chain mechanism for the conversion of hydrocarbons. On the contrary, subcritical water conditions (sub-CW) led to the occurrence of an ionic mechanism for the conversion of shale hydrocarbons[28].

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The results of studies of the effect of SCW on shale rock are presented in investigation[29]. It was shown that with increasing temperature up to 400°C the yield of the extract increases. Moreover, the concentration of asphaltenes, saturated and aromatic hydrocarbons increases in the composition of the extract. With an increase in the residence time of oil-bearing rock in SCW, there is an increase in the concentration of low-boiling hydrocarbons, a decrease in the proportion of asphaltenes. Yanik et al. investigated conversion of Göynük oil shale in SCW pyrolysis, flash pyrolysis and SCW extraction experiments[30]. The highest yield of the extract, however, and the greater amount of asphaltenes in the experimental products corresponded to the extraction process in SCW. A comparison of the experimental data on the conversion of Chinese oil shale in SCW and supercritical toluene showed the following results: the polar components of the oil were better converted in SCW than in supercritical toluene[31].

The results on the conversion of asphalt into sub- and supercritical water at 340–400°C in argon and air environment are presented in[32]. The conversion of asphaltenes to SCW occurred to a lower extent in the oxidizing environment of air compared to a neutral argon environment. In this case, the oxidizing environment more favorably affected the course of desulfurization processes. SCW, as a source of hydrogen proton for newly formed radicals, contributed to an increase in the yield of maltene in both air and argon environment.

Conversion of petroleum asphaltenes in SCW at a temperature of 380°C and a pressure of 22.89 MPa for 3 hours was studied by Kozhevnikov[33]. The results showed the occurrence of processes of destruction of asphaltenes, dealkylation of substituents from aromatic fragments of molecules; aromatization with the formation of gaseous products about 4.3% and an insoluble residue (coke) about 48.6%.

This work is devoted to the study of the conversion of high-carbon Domanic rock into liquid hydrocarbons in sub- and supercritical water at temperatures of 320, 374 and 420°C.

2. Experimental section

2.1. Materials

The object of the study was Domanic rock taken from a depth of 1720 m, deposits of the Semulukskoe-Mendimskoe horizon of the Chishminskaya area of the Romashkinskoye field - one of the largest deposits in the territory of Tatarstan (Russia). By the amount of discovered oil reserves, the Romashkinskoye field is one of the ten largest fields in the world with reserves of more than 5 billion tons[20]. This field is located in the crest of the South Tatar Arch - one of the major structural elements of the Volga-Ural petroleum basin. Under the conditions of tectonic and volcanic activation in the Volga-Ural region, Domanic deposits with a high content of OM were accumulated[34]. The estimated oil generation potential of Domanic rocks is 700 million tons[20].

2.2. Autoclave experiments

The experiments on the conversion of high-carbon Domanic rock were carried out in a Parr Instruments reactor at temperatures of 320, 374 and 420°C in a neutral nitrogen environment with the addition of water to the reaction system in an amount of 50% by weight of the rock sample. The experimental apparatus is shown in Fig. 1.
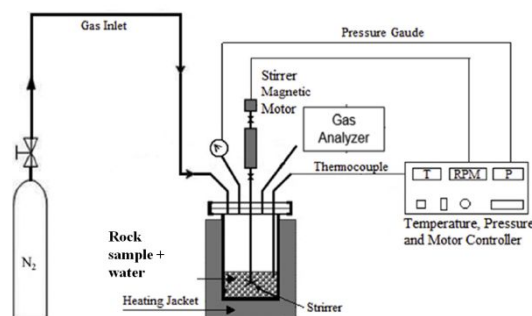

Figure 1. Experimental apparatus[35]

The initial nitrogen pressure in the system was 1 MPa. During the autoclave experiments, the pressure of the vapor-gas mixture increased to 17 MPa at 320°C, 24.6 MPa at 374°C; 24.4 at 420°C. The thermodynamic parameters of the experiments are shown in Fig. 2. The duration of the autoclave experiments was 1 hour.

2.3. Instrumental methods of analysis

The mineral composition of the rock was studied by X-ray diffraction analysis on a Shimadzu XRD7000S powder diffractometer.

The OM content in Domanic rock samples was determined by thermal analysis on a Netzsch STA 443 F3 Jupiter analyzer (Germany) in an oxidizing medium (air) with a heating rate of 10°C / min in a temperature range from 20 to 1000°C. TG - DTA curves were processed on a computer using standard Netzsch Proteus Thermal Analysis software.
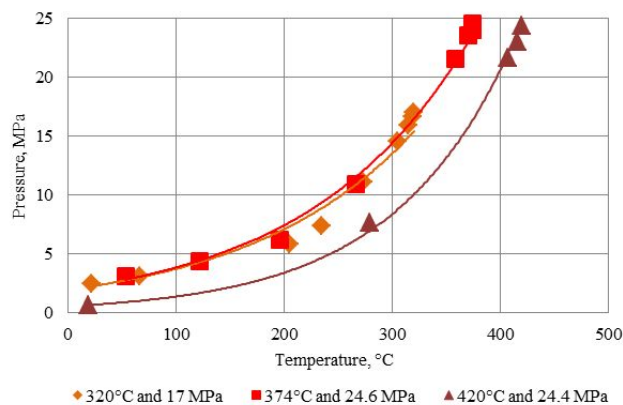

Figure 2. Thermodynamic parameters of the experiments

Table 1. Mineral composition of Domanic rock before and after experiments in sub- and supercritical water

Object	Mineral compound, wt %						
	Quartz	Calcite	Microcline	Mica	Dolomite	Pyrite	Mixed layer
Initial rock	43	19	19	12	6	1	0
Experiment at 320°C, 17 MPa	46	19	20	9	4	1	2
Experiment at 374°C, 24.6 MPa	43	18	21	6	4	1	7
Experiment at 420°C, 24.4 MPa	41	18	20	9	4	1	7

The hydrocarbons of the initial Domanic rock and samples after autoclave experiments, were extracted in a Soxhlet apparatus using a mixture of organic solvents consisting of chloroform, toluene and isopropanol, taken in equal proportions. The extraction time was 72 hours. Domanic rock extracts before and after autoclave experiments were divided according to SARA analysis into four fractions: saturated hydrocarbons, aromatic hydrocarbons, resins and asphaltenes. Asphaltenes were precipitated from extracts with a 40-fold amount of an aliphatic solvent of n-hexane. The remaining maltenes were separated by liquid column chromatography using aluminum oxide (Al_2O_3), previously calcinated at 425°C. As a result, saturated hydrocarbons eluted with hexane, aromatic compounds eluted with toluene, and resins displaced from the adsorbent with a mixture of benzene and isopropyl alcohol in equal proportions.

The composition of the gases was studied by gas chromatography on a Khromatek-Crystal 5000.2 instrument using computer data processing with recording the signal of the detector for thermal conductivity. Gas separation was carried out on a capillary column 100 m long, 0.25 mm in diameter. Chromatography was carried out in the following temperature conditions: 90°C for 4 minutes, and then heating 10°C/min to 250°C. The temperature of the evaporator is 250°C. The carrier gas is helium, the flow rate is 15 ml/min.

The structural group composition of the extracts was determined by IR Fourier spectroscopy on a Vector 22 (Bruker) IR spectrometer in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.
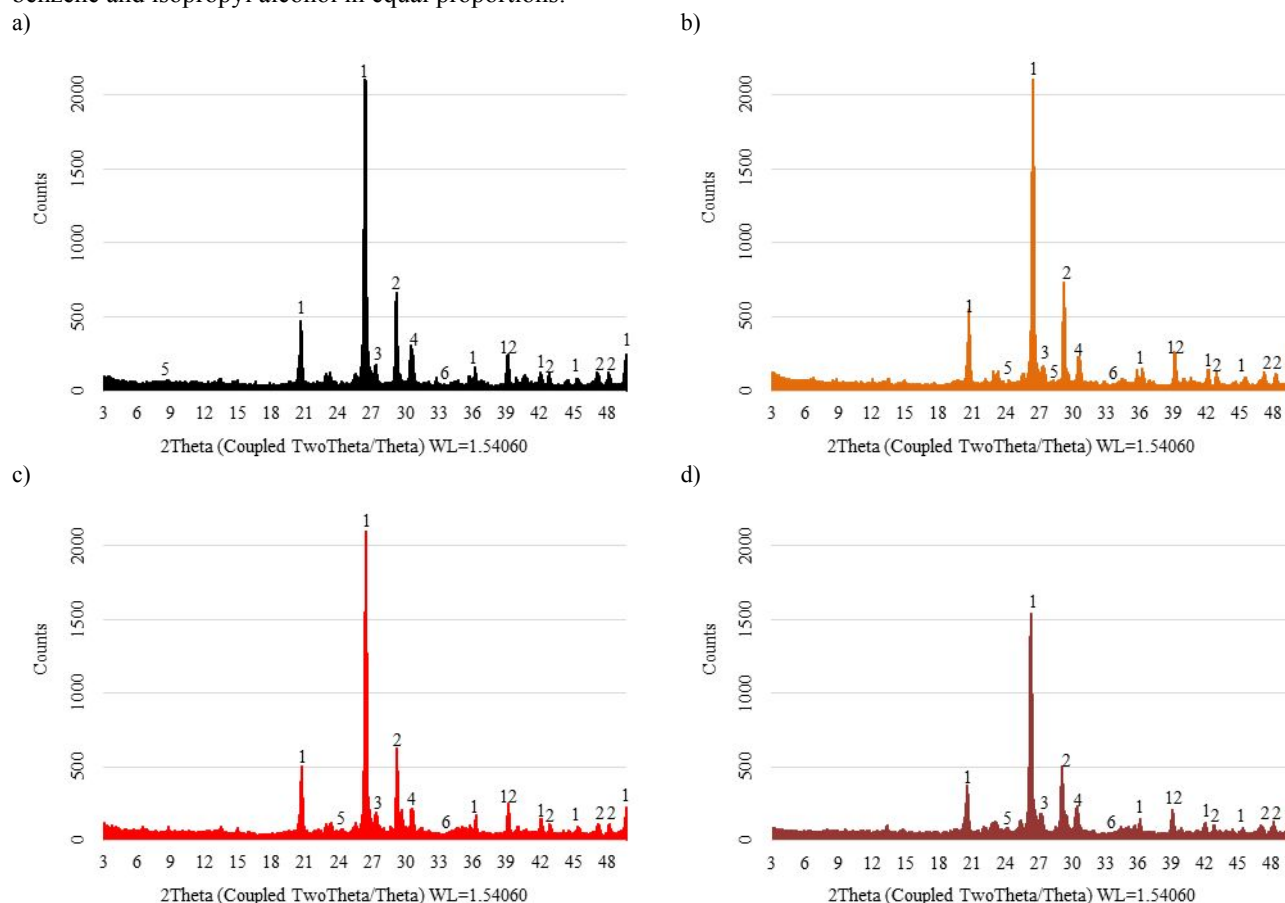

Figure 3. Diffraction patterns: a) Initial Domanic rock, b) Rock after the experiment at 320°C, 17 MPa, c) Rock after the experiment at 374°C, 24.6 MPa, d) Rock after the experiment at 420°C, 24.4 MPa:
1-quartz, 2-calcite, 3-microcline, 4-dolomite, 5-mica, 6-pyrite

Table 2. The results of a thermal analysis of the initial Domanic rock, after experiments in sub- and supercritical water and extraction

| Sample no.	Loss rock mass (wt %) in ranges of temperature from 40°C to 1000°C					$\sum$OM (200–600°C)	*F
	40-200	200-400	400-600	600-800	800-1000		
Initial rock	0.97	3.68	6.93	12.46	0.82	10.61	0.53
The same rock after extraction	0.14	1.47	5.16	12.04	0.37	6.63	0.28
Experiment at 320°C, 17 MPa	2.91	5.93	6.59	8.85	1.05	10.52	0.90
The same rock after extraction	0.89	2.81	5.26	9.85	0.94	8.07	0.53
Experiment at 374°C, 24.6 MPa	1.37	3.27	6.44	8.34	0.92	9.22	0.52
The same rock after extraction	0,92	1,45	5,02	8,20	0,93	6.47	0.29
Experiment at 420°C, 24.4 MPa	1.43	1.33	6.38	7.25	0.77	7.71	0.21
The same rock after extraction	0.79	0.61	5.75	10.84	0.65	6.36	0.11

*F= Δm_1(200–400)/Δm_2(400–600).

3. Results and discussion

According to X-ray diffraction analysis, a sample of the initial rock from Domanic deposits of the Semulukskoe-Mendimskoe horizon of the Chishminskaya area contains 43% quartz, 19% calcite, 19% microcline, 12% mica and 6% dolomite (Table 1, Fig. 3). The content of mica is reduced from 12% to 6% due to the influence of SCW at 374°C on the Domanic rock. In this case, 7% of the mixed layer of mineral mica-montmorilonite appears in the rock. This indicates phase conversion of mica, the averaged chemical composition according to published data is:

$K_{0.58} Na_{0.03}(Al_{1,71}Fe^{3+}_{0.012} Fe^{2+}_{0.005}Mg_{0.15})$ x $[Si_{3.46} Al_{0.54} O_{10}](OH)_2$[36].
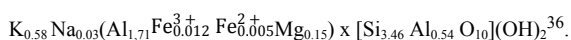
Mica passes into a mixed layer of mica-montmorillonite, with the release of montmorillonite as a separate phase. The average chemical formula of mica-montmorillonite is presented below:

$K_{0.35} Na_{0.04} Ca_{0.11} Mg_{0.25} Al_{1.79} Fe_{0.17}$ x $[Si_{3.07} Al_{0.93} O_{10}]$ $(OH)_2 \cdot nH_2O$ [36].
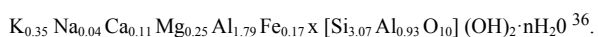
The conversion of mica to a mixed layer of mica-montmorillonite is an intermediate form in the conversion of mica to kaolinite[36]. The presence of clayed rock-forming minerals with catalytic properties in the hydrothermal system of water in the sub- and supercritical conditions can have a significant effect on the conversion of the OM of these rocks[37,38].

The degradation processes of OM and inorganic components of Domanic rock can increase mass loss under thermal analysis[39]. According to the TGA analysis, presented in table 2., mass losses in the temperature range of 200–600°C characterize the content of OM in the rock[40–42]. For the initial rock sample of the Chishminskaya area of the Romashkinskoye field, the OM content is 10.61%. After extraction of the initial rock, the OM content decreases to 6.63%, which indicates the presence of a sufficiently high content of free hydrocarbons in the rock (3.27%). Judging by the mass loss of the rock after the experiments and the following extraction of free hydrocarbons, it can be assumed that after exposure to the rock at a temperature of 320°C, the recovery of free hydrocarbons from the rock is mainly carried out, since the mass loss of the rock is close to the initial rock (3.45%).

Influence of supercritical water at 374, 420°C on Domanic rocks leads to intense OM destruction processes, which also affect the kerogen structure, which is characterized by reduced mass loss values in the range of 200-600°C in the samples after extraction.

According to the DSC curves (Fig. 4), under the conditions of these experiments, the area of thermal effects significantly increases. The destruction of the organic part of the rock is accompanied by heat and, as a consequence, the appearance of exothermic effects on the DSC curve with increasing temperatures to 550°C. On the DSC curves of the initial rock, before and after experiments at 320°C, two exothermic effects are observed. The first indicates the release of free hydrocarbons, and the second peak indicates the destruction of the high-molecular weight part of OM. With an increase in the experimental temperature, an increase in the exothermic effect in the higher temperature area of the curve is noticeable, which indicates not only the destruction of high-molecular weight components and kerogen, but also the formation of carbonaceous substances.

The destruction of the carbonate part of Domanic rock is evaluated by the endothermic peak in the temperature range from 650 to 750°C [43].
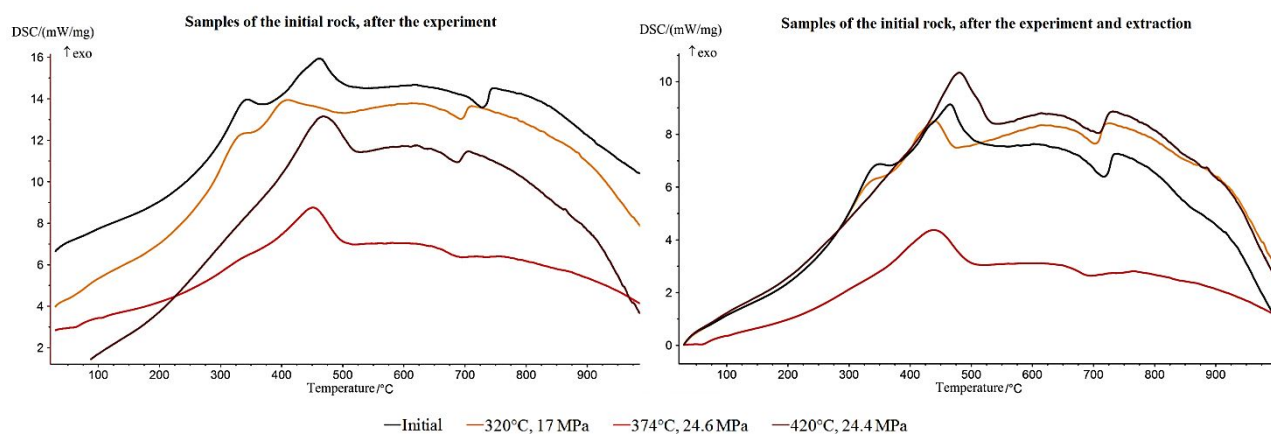
Figure 4. Thermograms of samples of the initial Domanic rock, after experiments in sub- and supercritical water and extraction

The processes of kerogen degradation are reflected in the group composition of the extracts (Table 3). The extract from the initial rock sample is characterized by a high content of asphaltenes (29.0 wt %), resins (37.0 wt %) and low concentration of saturated (14.8 wt %), aromatic (19.17 wt %) hydrocarbons. The presence of subcritical water at 320°C allows more complete recovery of free hydrocarbons from the rock, including asphaltenes components, the content of which in the sample increases to 32.91 against 29.02 wt %. The impact on Domanic rock in the presence of SCW at a temperature of 374°C leads to an increase in the products of the experiment of a content of saturated hydrocarbons by more than two times (33.91 against 14.8 wt %) with a decrease in the content of resins and asphaltenes.

As the temperature increases to 420°C according to thermal analysis (Table 2), the OM content in the rock, compared with the initial one, decreases from 10.61 to 7.71%, i.e., by 2.90%. After the extraction of the rock, the decrease in organic matter was insignificant (1.35%) as in the experiments at lower temperatures, which is apparently due to a more intense destruction of OM, which proceeds with significant gas formation. During the experiment in SCW at 420°C and 24.4 MPa, the greatest destruction of asphaltenes occurs from 29.0 to 7.3 wt % with an increase in the content of saturated hydrocarbons to 36.2 wt % and aromatic hydrocarbons to 32.6 wt %. The presence of insoluble high-carbon substances such as carbene-carboids in the products of experiments at 374°C and 420°C indicates the processes of destruction of asphaltenes and high-molecular weight fragments contained in kerogen by destructing its heteroatomic bonds with the formation of saturated, aromatic hydrocarbons and carbonaceous products.

The formation of a high amount of solid high-carbon phase (14.45%) in SCW at 374°C in the reaction mixture indicates the initial stage of formation of carbonaceous substances. With an increase in SCW temperature to 420°C, carbonaceous substances are apparently adsorbed on the surface of the mineral part of the rock. They are not extracted with solvents, which is characterized by a low yield of extract (0.91%) and a low content of carbonaceous substances (2.03%). The highest yield of the extract (3.98%) from Domanic rock was detected after exposure to subcritical water at 320°C.

The IR absorption spectra of asphaltenes and carbonaceous substances (carbene-carboids) were compared by optical density at the maximum of the corresponding absorption bands: alkane formations at 720 cm^{-1} (methylene of the CH group> 4), 1380 cm^{-1} and 1465 cm^{-1} (CH$_3$ methyl and CH$_2$ methylene group); aromatic compounds at 1600 cm^{-1} (bonds C = C); oxygen compounds in the carbonyl groups of acids at 1710 cm^{-1}, in the ester carboxyl groups at 1740 cm^{-1} and in sulfoxide groups 1030 cm^{-1} [40].

The spectra of asphaltenes after the experiment at 320°C (Fig. 3) differs slightly from the spectra of the initial asphaltenes, but differs significantly from the spectra of asphaltenes after 374°C with a higher intensity of absorption bands characteristic of aromatic structures (1600 and 900-730 cm^{-1}). The absorption spectra of carbonyl structures (1710 cm^{-1}) are absent in these spectra; the intensity of sulfoxide absorption bands (1030 cm^{-1}) decreases. An increase in the intensity of absorption bands is observed at 1450-1455, 1380 cm^{-1}, which indicates an increase in the content of aliphatic structures of asphaltenes.

Table 3. The group composition of the extracts of the initial Domanic rock, after experiments in sub- and supercritical water

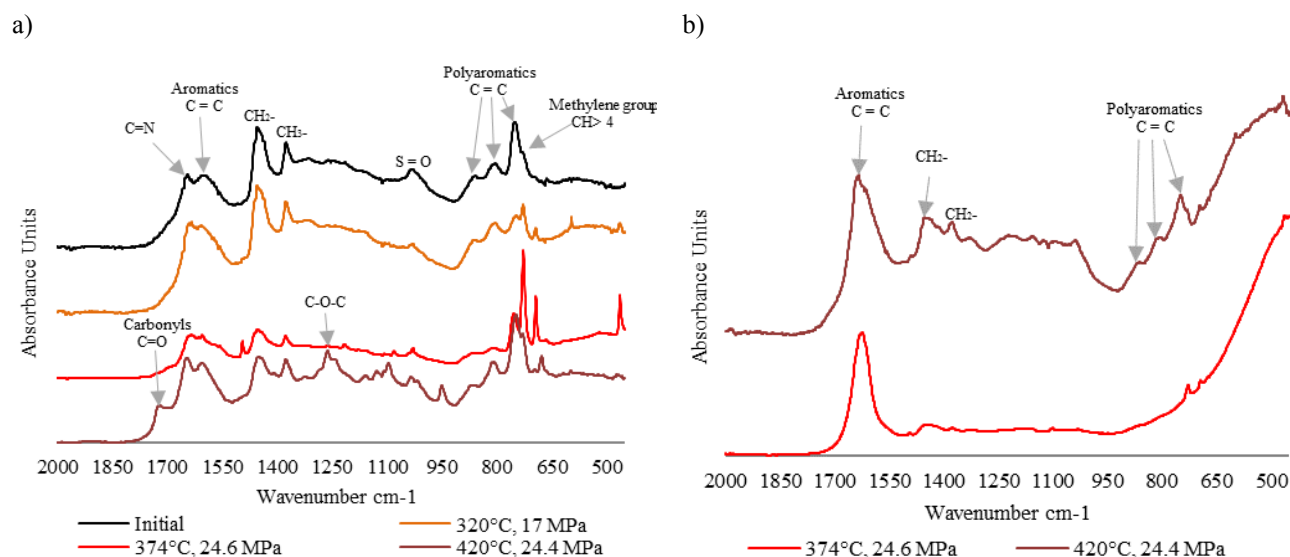| Sample no.	Extract yield (wt %)	Group composition (wt %)				
		Saturates	Aromatics	Resins	Asphaltenes	Carben-carboids
Initial Domanic rock	3.12	14.8	19.2	37.0	29.0	-
Experiment at 320°C, 17 MPa	3.98	16.9	22.7	27.5	32.9	-
Experiment at 374°C, 24.6 MPa	3.08	33.9	14.3	13.5	23.8	14.5
Experiment at 420°C, 24.4 MPa	0.91	36.2	32.6	21.9	7.3	2.0

a)

b)

Figure 5. IR spectra: a) asphaltenes, b) carbenes-carboids of the initial extract and extracts after the conversion of Domanic rock under sub- and supercritical water conditions at 320, 374 and 420°C

The IR spectra of asphaltenes from the experiment products at 420°C is characterized by a sharp increase in the intensity of the absorption band at 1250 cm^{-1}, 1100 cm^{-1}, which indicates the presence of oxygen-containing groups in ethers and alcohols. Changes in the intensity of absorption bands in the area of manifestation of the aromatic triplet of 900–730 cm^{-1} are noticeable. The intensity of aromatic groups in the area of 900–730 cm^{-1} is associated with the vibration of 4 hydrogen atoms adjacent to the aromatic ring. In this area the intensity of the absorption bands decreases markedly in comparison with the spectra of the initial asphaltenes and after the experiment at 320°C. The greatest decrease in intensity of the aromatic triplet in the area of 900–

730 cm^{-1} is observed in the spectra of asphaltenes after the conversion of Domanic rock in SCW at 374°C. At the same time, the intensity of the absorption bands at 1710, 1030, 500–400 cm^{-1} increases, indicating an increase in their structure of the content of oxygen groups.

The spectra of carbene-carboids (Fig. 5 b), which were obtained after experiments at 374 and 420°C, did not contain an absorption band of carbonyl groups (1710 cm^1) and ester groups (1740 cm^{-1}). Increasing temperature of SCW to 420°C leads to increasing in absorption bands 720–900, 1640 cm^{-1} (degree of aromatization); 1435, 1380 cm^{-1} (degree of saturated hydrocarbons), 1030 cm^{-1} (degree of sulphurization).

Table 4. Structural-group composition of asphaltenes, carbenes-carboides of the initial Domanic rock extract, after experiments in sub- and supercritical water

| Sample no.	Absorbance A at maxima of absorption bands at ν, cm^{-1}							* Spectral coefficient				
	1740	1710	1600	1465	1380	1030	720	C_1	C_2	C_3	C_4	C_5
Asphaltenes from rock extracts												
Initial	0.07	0.16	0.58	0.74	0.77	0.63	0.67	0.86	0.21	1.04	2.48	0.86
Experiment at 320°C, 17 MPa	0.06	0.14	0.68	0.79	0.82	0.55	0.70	0.98	0.18	1.03	2.22	0.70
Experiment at 374°C, 24.6 MPa	0.03	0.06	0.32	0.33	0.31	0.24	0.45	0.71	0.19	0.96	2.38	0.74
Experiment at 420°C, 24.4 MPa	0.13	0.28	0.62	0.55	0.63	0.51	0.67	0.92	0.51	1.14	2.09	0.92
Carbene-carboids												
Initial	-	-	-	-	-	-	-	-	-	-	-	-
Experiment at 320°C, 17 MPa	-	-	-	-	-	-	-	-	-	-	-	-
Experiment at 374°C, 24.6 MPa	0.02	0.03	0.30	0.12	0.12	0.11	0.26	1.15	0.30	1.01	1.26	0.98
Experiment at 420°C, 24.4 MPa	0.04	0.11	0.53	0.41	0.47	0.38	0.47	1.14	0.26	1.14	1.77	0.92
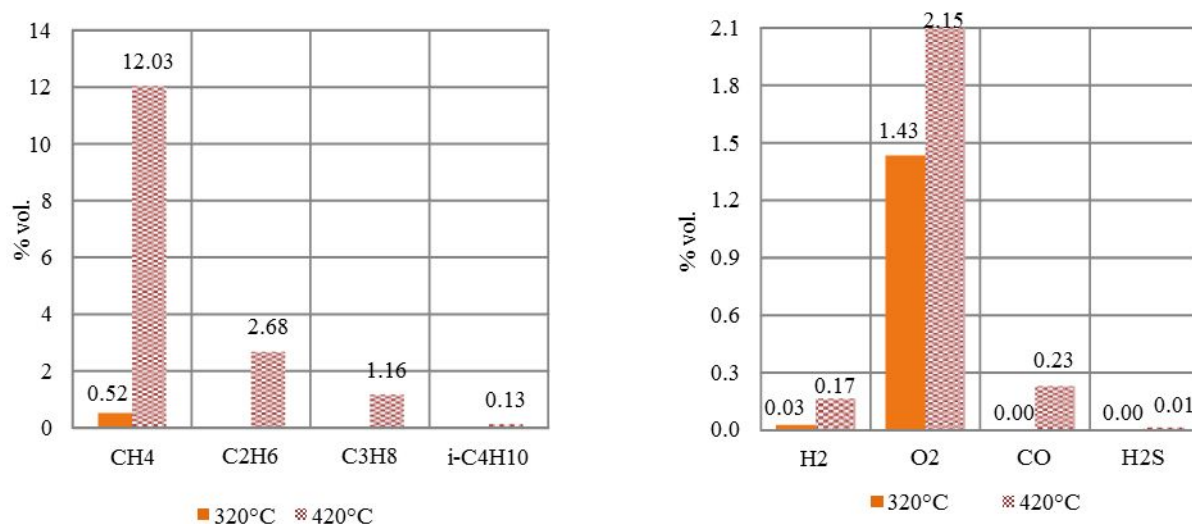
Figure 6. The composition of the gases generated as a result of hydrothermal impact on the Domanic rock of the Chishminskaya area at a temperature of 320°C and 420°C

The observed changes in the structure of asphaltenes and carbene-carboids of the products of the Domanic rock conversion in sub- and supercritical water are reflected in the spectral coefficients presented in Table 4. To assess changes in the structural-group composition of asphaltenes and carbene-carboids, we used spectral coefficients defined as ratio absorption values at the maximum of the corresponding absorption bands: $C_1 = A_{1600}/A_{720}$ (aromaticity), $C_2 = A_{1710}/A_{1465}$ (oxidation state), $C_3 = A_{1380}/A_{1465}$ (branching), $C_4 = (A_{720} + A_{1380})/A1_{600}$ (saturated) and $C_5 = A_{1030}/A_{1465}$ (sulfurization degree)[40].

Asphaltenes of the initial sample contain a low amount of aliphatic and a high number of aromatic structures, as evidenced by the low value (2.48) of the saturated index C_4 and the high value (0.86) of the aromaticity coefficient C_1. The thermal effect on the Domanic rock in sub- and supercritical water at 320 and 420°C affects the course of intense aromatization processes, which affects the growth of the aromaticity coefficient C_1 to 0.98 and 0.92, respectively. The course of aromatization processes occurs due to the insufficient concentration of atomic hydrogen in the system, which is necessary for the hydrogenation of the formed reactive radicals. In SCW at 420°C there is an increase in the values of oxidation coefficient C_2 from 0.21 to 0.51 and sulfurization coefficient C_5 from 0.86 to 0.92.

The development of destructive processes during experiments with Domanic rock in sub- and supercritical water is indicated by the formation of noticeable concentrations of hydrocarbon gases: CH_4, C_2H_6, C_3H_8, i-C_4H_{10} and inorganic gases: H_2, O_2, N_2, CO, CO_2 (Fig. 6.) In small amounts, the formation of H_2S was observed in an amount of 0.015 vol. %. This indicates the destruction of hydrocarbons by sulfur-containing bonds. The increased amount of n-alkanes C_1 - C_4 corresponds to the energy of destruction of aliphatic C-C bonds as a result of the radical chain mechanism[44]. The smallest gas formation is observed during the conversion of Domanic rock in subcritical water at a temperature of 320°C and a pressure of 17 MPa.

With increasing temperature, the yield of hydrocarbon and inorganic gases increases. This confirms the occurrence of intensive processes of destruction of resins and asphaltenes with the formation of saturated and aromatic hydrocarbons, as well as decomposition of kerogen. Intense destruction of C-O heteroatomic bonds occurs under SCW conditions, as evidenced by an increased yield of O_2. Formation of H_2 in an amount of 0.16 vol. % during the conversion of Domanic rock in SCW is an interesting fact, because it indicates the occurrence of dehydrogenation processes.

4. Conclusions

The experiments on the conversion of high-carbon Domanic rock of the Semulukskoe-Mendimskoe horizon of the Republic of Tatarstan in sub- and supercritical water at temperatures of 320, 374, 420°C in a neutral nitrogen environment for 1 hour showed the following results.

The highest yield of the extract compared with the initial rock was observed in the experiment with subcritical water at 320°C (3.98 against 3.12%). This occurs as a result of degradation of resins from 37.0 to 27.5 wt % and more complete extraction of asphaltenes from the rock, the content of which increased from 29.0 to 32.9 wt %.

SCW at 374, 420°C affects the destruction of high-molecular hydrocarbons and Domanic rock kerogen due to the C-C, C-N, C-O bonds destructing with the formation of new saturated hydrocarbons from 14.8 to 33.9 wt % and carbenes-carboids in the amount of 14.5 wt %. These high-carbon substances are characterized by a high degree of aromaticity. They formed from asphaltenes and kerogen fragments as a result of the breaking of heteroatomic bonds with the separation of substituents. The results of IR spectroscopy indicate the occurrence of oxidative cracking of hydrocarbons in SCW: asphaltenes become more oxidized and carbene-carboids become more aromatic. The highest content of carbene-carboids is observed in the composition of the products of experiments at 374°C, which, apparently, is associated with the intensive decomposition of kerogen Domanic rock.

With an increase in the experimental temperature to 420°C, the formation of high-carbon substances is accompanied by oxidative destruction processes, which leads to a decrease in their content of liquid hydrocarbons from 3.12 to 0.91%. The decrease in the yield of the extract is also a consequence of intense gas formation and the loss of part of the low-boiling fractions during the experiment at 420°C. The end products of all experiments are characterized by an increase in the content of saturated hydrocarbons with a decrease in the content of resins and asphaltenes. The greatest destruction of asphaltenes occurs with initial rock from 29.0 against 7.3% with the formation of saturated hydrocarbons 36.2 against 14.8% in the experiment with SCW at 420°C and 24.4 MPa.

The destruction of C-C bonds of high-molecular resins, asphaltenes and kerogen of Domanic rock in SCW at 420°C is reflected in the formation of hydrocarbon gases: CH_4, C_2H_6, C_3H_8, i-C_4H_{10}. The processes of C-H, C-S, C-O, C-N bonds destructing are noted by the presence of H_2, H_2S, O_2, N_2 in the reaction mixture of this experiment.

Structural and phase conversion are discovered in SCW at 374, 420°C with the rock-forming mineral - mica into a mixed layer of mica-montmorillonite. This is an intermediate form in the conversion of mica to kaolinite, which can significantly affect the conversion of OM of Domanic rock due to the catalytic properties.

The results of the presented study may be useful in developing technologies for the development of Domanic shale.

Conflicts of Interest

The authors declare no competing financial interest.

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