

Conversion of the Organic Matter of Domanic Shale and Permian Bituminous Rocks in Hydrothermal Catalytic Processes

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ABSTRACT: Comparative studies of hydrothermal transformation of organic matter samples of bituminous rocks from Domanic and Permian deposits of the Tatarstan Republic (Russian Federation) have been carried out. The experiments have been taken at a temperature of 300 °C in a vapor-gas carbon dioxide environment, with a content of 30% water in the reactionary system and an initial pressure of carbon dioxide of 2 MPa. It is shown that the distinguishing features of the organic matter of the analyzed species according to thermal analysis data are most prominent in the loss of its mass at various temperature intervals. Also, changes take place in group and structural composition and hydrocarbon composition, which have an impact on the composition of the initial products of experiments. Hydrothermal effects on the Domanic rock sample result in the destruction of structural polymer fragments of kerogen. It results in an increase in the contents of asphaltenes and their modified structures in the form of carben-carboids, insoluble in solvents characteristic of asphaltenes, thus reducing the relative content of saturated hydrocarbons in the products of the experiment. Under similar hydrothermal conditions, changes in the physical composition of the Permian rock are less significant. For the investigation of activation processes of the transformation of organic matter of the Permian rock, an experiment was conducted using catalysts. As catalysts, a composition of oil-soluble iron(II), cobalt(II), and copper(II) carboxylates with an additive of propanol was used. The use of the catalyst has increased the output of light fractions and reduced the content of resins and asphaltenes as part of Permian rock.

1. INTRODUCTION

Industrial development of the deposits of nontraditional hydrocarbon raw material resources (such as heavy crude oils and black shale rocks) is connected with the investigation of numerous problems such as their recovery, transportation, and refining.^{1–9} One of the perspective trends in this sphere is the study of the possibility to transform Domanic and Permian rocks. To increase shale oil recovery from Domanic rock, we can use thermal treatment to initialize the kerogen cracking process. In the case of heavy Permian oils, thermal treatment is used in order to decrease their viscosity under reservoir conditions.^{6,7,10–12}

There are number of technologies for development of heavy hydrocarbon raw materials: hot water, steam, and solvent injection and in situ combustion. They have already found their solution and received industrial approbation and introduction into practice.^{4,8,10} The high content of high molecular compounds of complicated composition and structure causes some difficulties in the recovery of raw materials. That is why it is necessary to develop new technologies of heavy crude oil refining. The main goal of such developments is to convert high-molecular-mass components into light hydrocarbons by means of thermal reactions. Mutual molecular transformations in such a complicated hydrocarbon system as oil have various rates. The reaction rate usually increases under thermal treatment; it is not the only method of acceleration of chemical transformations. The more efficient method is injection of a catalyst; it is widely used at the moment in oil chemistry.^{13–15} Usually, catalysts in oil-production processes are water- and oil-soluble compounds of transition metals as well as heterogeneous catalysts.^{16–21}

In recent years, there has been growing interest in the methods of oil recovery by means of injections into the reservoir of mixed hydrocarbon solvents, inert gases, and CO₂, capable of creating a hypercritical medium under relatively low temperatures and pressures. The efficiency of CO₂ employment to increase shell oil recovery has been proved not only by laboratory experiments but also by oilfield testing results.^{22–24} However, the problem of development of heavy crude oil deposits is complicated because of differences in conditions of each oil field.^{4,8,9,11} Therefore, despite the fact that in Tatarstan there are more than 150 fields occurring both in terrigenous and carbonate deposits, which are potentially prepared for industrial development^{4,8} according to their characteristics, only the Ashalchinsky field of heavy crude oil is currently under experimental–industrial development.

Domanic deposits in the territory above are still at the stage of laboratory research exploration.^{25–27} This determines the development of the selection of technological solutions which will be adapted to the conditions of certain deposits. In this connection, scientific basics of new technologies for nontraditional hydrocarbon raw material recovery and processing are important. Establishing mechanisms of conversion of the fuels' high-molecular components in hydrothermal-catalytic processes in the presence of carbon dioxide seems to be an important and relevant task.

The purpose of this research is to evaluate the effect of hydrothermal catalytic processes on the conversion degree of

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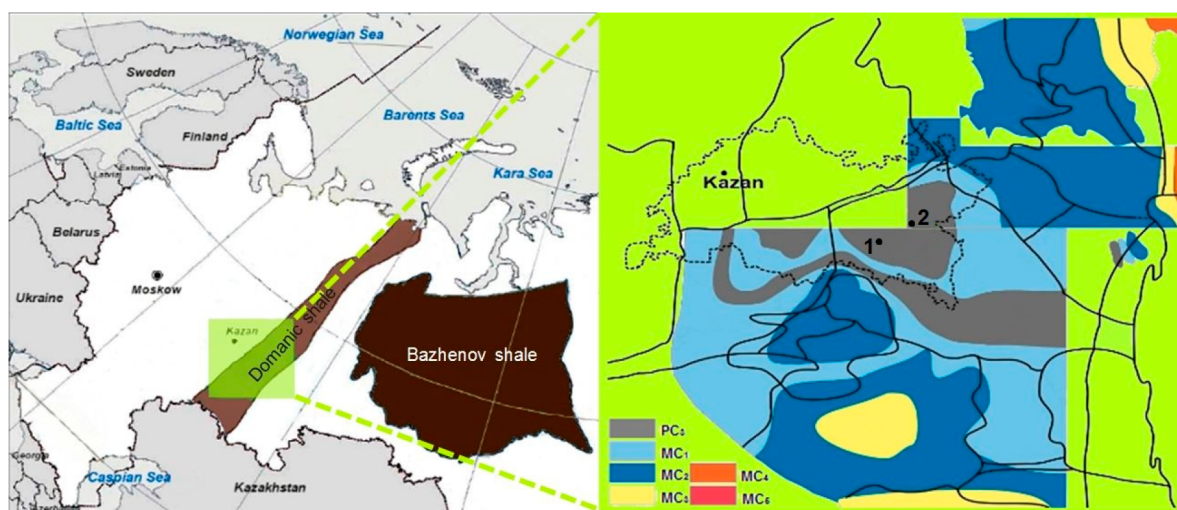


Figure 1. Location maps of the Volga-Ural Basin (modified after 23). One - Permian rock sample, 2 - Domanic rock sample. On the right map also present kerogen types and maturity in the Domanic shale.

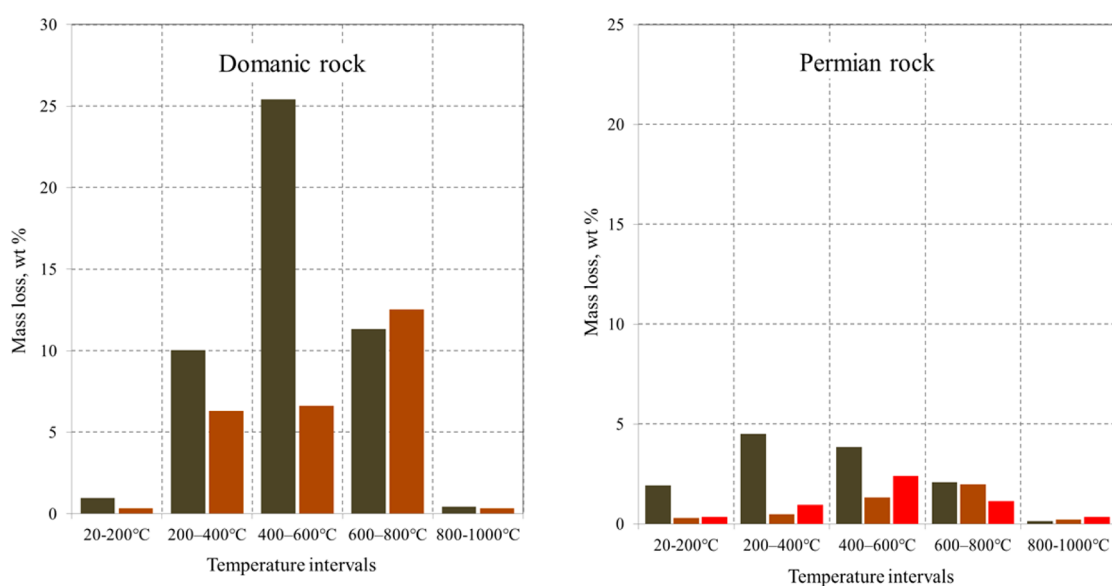


Figure 2. Diagram of the mass loss of the rock samples. Domanic rock before (brown) and after hydrothermal experiment (russet); Permian rock before (brown) and after hydrothermal (russet) and hydrothermal catalytic (red) experiments.

77 kerogen and high-molecular heteroatomic components of
78 various natures.

2. EXPERIMENTAL SECTION

79 The objects of the present research are the following:

80 • organic rich Domanic shale sample from the Berezovskaya area of
81 the Romashkinskoe oil field (Tatarstan) taken from a range of depths
82 of 1712.5–1718 m (Figure 1)

83 • bituminous rock from Permian sediments of the Ashalchinsky
84 field taken from a range of depths of 176.5–178 m (Figure 1)

85 • products of the hydrothermal and hydrothermal catalytic
86 conversions of the shale and bituminous rock samples' organic matter

87 Laboratory experiments on the conversions of the organic matter of
88 the Domanic and Permian rock samples were carried out in a Parr
89 Instruments (USA) laboratory autoclave of volume 1 L at a
90 temperature of 300 °C for 5 h in the steam-gas medium at the initial
91 CO₂ pressure in the system of 2 MPa. Water content in its mixture
92 with petroleum was 30 wt %. During the experiment, the pressure was
93 elevated up to 9.2 MPa. An additional hydrothermal-catalytic
94 experiment with the use of catalysts has been carried out with a

sample of Permian rock. A composition of oil-soluble iron(II), 95
cobalt(II), and copper(II) carboxylates obtained by means of an 96
exchange reaction between the sodium salt of tall oil and nonorganic 97
salts of corresponding metals^{28–30} was used as the catalyst. In this 98
work, the catalyst was injected into the disintegrated rock samples in a 99
solution of propanol in a total amount of 0.3 wt % of metals in the 100
calculation of the quantity (200 g) of oil-containing breeds. 101

To extract hydrocarbons from the rock samples, we used a method 102
of extraction with the addition of a solvent mixture, namely, 103
chloroform, benzene, and isopropanol taken in equal ratios. Both 104
initial rock samples and reaction products were analyzed with the use 105
of a complex of physicochemical methods. 106

Rock sample analysis revealed the presence of organic matter and 107
thermal effect availability. It was performed on a synchronous thermal 108
analysis instrument, STA 443F3 Jupiter (Netzsch, Germany) with the 109
Netzsch Proteus Thermal Analysis software. Measuring conditions 110
were as follows: oxidizing medium (air); heating rate, 10 °C/min; 111
temperature range, 20–1000 °C. TG-DTA curves were processed 112
using the Netzsch Proteus Thermal Analysis software computer 113
standard. 114

115 Analysis of the group composition of bitumen samples (SARA-
116 analysis) was carried out in accordance with the common technique.³¹
117 Asphaltenes were precipitated under the effect of a 40-fold amount of
118 an aliphatic solvent—hexane. Hexane is chosen to preserve the light
119 fractions of bitumoids. Maltenes were separated by means of liquid-
120 adsorption chromatography on aluminum oxide having been calcined
121 at 420 °C into saturated hydrocarbons via their elution with hexane as
122 an adsorbent, aromatic compounds via their elution with toluene, and
123 resins, which were extruded from the adsorbent with the help of a
124 solvent mixture, namely, benzene and isopropyl alcohol taken in equal
125 proportions.

126 The elemental compositions of bitumen and experimental products
127 (CHNS) were determined by means of weighed sample combustion
128 on a CHNS analyzer at a temperature of 1000 °C.

129 The structural-group compositions of the bitumen samples and
130 reaction products were investigated by an IR Fourier spectroscopy
131 method. IR spectra were taken on an IR-Fourier spectrometer Vector-
132 22 (Bruker) within the range of 4000–400 cm⁻¹ with a resolving
133 power of 4 cm⁻¹. For the comparative correlation of data, spectral
134 coefficients characterizing the structural-group composition of the
135 products investigated were used. Spectral factors are the ratios of the
136 optical densities of the absorption bands at 1710 (oxidation products),
137 1600 (arenes), 1380 and 720 cm⁻¹ (alkanes): $C_1 = D_{1600}/D_{720}$
138 (aromaticity index), $C_2 = D_{1710}/D_{1465}$ (state of oxidation), $C_3 =$
139 D_{1380}/D_{1465} (of branching degree), $C_4 = (D_{720}+D_{1380})/D_{1600}$ (of wax
140 content), and $C_5 = D_{1030}/D_{1465}$ (degree of sulfuring).³²

141 The investigation of the hydrocarbon composition of the rock
142 extracts was performed on a “Crystal 2000M” apparatus using the
143 capillary gas chromatography method in the mode of temperature
144 programming within the range of 100–300 °C. In the temperature
145 interval from 100 to 150 °C, the temperature increased at a rate of 10
146 °C/min and, within the 150–300 °C diapason, at a rate of 3 °C/min.
147 Hydrogen was used as the gas carrier. The evaporator temperature was
148 310 °C, and the detector temperature was 250 °C.

3. RESULTS AND DISCUSSION

149 According to the thermal analysis data,³³ the investigated rock
150 samples under study can be distinguished by mass loss at
151 various temperature intervals, from 20 to 1000 °C, and
152 consequently, they are not homogeneous in terms of their oil-
153 generating potential. The organic matter content in the
154 Domanic rock amounts is 35.48%, while the organic matter
155 content in the Permian rock is 8.36% (Figure 2). The organic
156 matter content was evaluated in terms of its significant mass
157 loss within the temperature interval of 200–600 °C. A
158 significant mass loss in the Domanic rock sample at
159 temperatures higher than 600 °C seems to be connected with
160 the carbonate rocks’ destruction. The mass loss at temperatures
161 from 20 to 200 °C is due to evaporating of the light
162 hydrocarbons and adsorbed water removal if the rocks contain
163 clay minerals.³⁴

164 After the Domanic rock hydrothermal processing and after
165 extraction of the reaction products from the rock above, the
166 organic matter content in this rock becomes about 3 times
167 smaller: from 35.48 up to 12.92%. It appears most brightly in
168 the case of mass loss within the temperature interval of 400–
169 600 °C, which is connected with nonsoluble kerogen thermal
170 destruction, i.e., that part of the organic matter which has not
171 finished maturation up to the status form of oil. The kerogen
172 from the Domanic rock sample is extremely unstable during
173 hydrothermal processes, which to a great extent leads to a
174 decrease in its content (as a result of its destruction) from
175 25.43 to 6.62%. According to some modern concepts, kerogen
176 is a natural geopolymer of the irregular structure and is
177 considered to be one of the possible sources of oil hydrocarbon
178 generation.^{35,36} The content of light hydrocarbons in the rock

also decreases significantly (from 10.17 to 6.30%) after the 179
experiment within the temperature interval of 200–400 °C, 180
presumably due to the easiness of their washing-out from the 181
rocks. 182

In accordance with the thermal analysis data, the total 183
organic matter content in the rock samples from Permian 184
sediments is 8.36%, which is 4 times less than in the Domanic 185
ones. In the process of the hydrothermal experiment, the 186
organic matter content decreases up to 0.35–0.40%, i.e., by a 187
factor of 7. The content of kerogen also goes down, which is 188
denoted by the fact that the mass decrease is from 3.85 to 189
1.33% in the temperature interval of 400–600 °C. Thus, it can 190
be concluded that after the experiment and extraction of 191
bitumen components from the rock, the latter still possesses a 192
rather high content of high-molecular components of kerogen 193
which does not undergo destruction within the above 194
temperature interval, but this value is considerably lower in 195
comparison with the Domanic rock. 196

According to the thermal analysis data, a different fractional 197
composition of the tested samples from various types of rocks is 198
also reflected in the values of fractional index F_{OM} . This index is 199
the ratio of the sample mass loss in the temperature interval of 200
200–400 °C to its losses at 400–600 °C.³⁵ The low value of 201
the index (0.39) given is typical of the initial Domanic rock 202
sample due to the low content of movable hydrocarbons in it 203
(0.25%). 204

On the other hand, for the initial Permian rock samples, the 205
value of F_{OM} is rather high, 1.17, due to the high content of 206
moveable hydrocarbons in it, which results from the fact that 207
the rock sample was taken from the highly productive reservoir. 208
In the experiment with the employment of the catalyst (Fe, Co, 209
and Cu carboxylates composition) and propanol addition, the 210
moveable hydrocarbon content in the rock samples somehow 211
increases to a bit bigger value, 3.4%, maybe due to the 212
adsorption of the catalyst and resulting coke-like products of 213
the rock. The catalyst usage leads to some increase in the 214
relatively light hydrocarbon content in the rock. However, light 215
movable hydrocarbons are easily extracted from the rock by 216
organic solvents after the latter undergoes the effect of 217
hydrothermal and hydrothermal-catalytic factors; that is why 218
their content in the previously extracted rock practically does 219
not increase. 220

The distinctive characteristics of the organic matter 221
composition of the tested rock samples in hydrothermal 222
experiments are presented in Figure 2 according to the thermal 223
analysis data 224

Group and Hydrocarbon Composition of Extracts 225
from the Rocks. As it follows from Figure 2, the amount of 226
Domanic bitumen extracted after the experiment increases from 227
0.25 to 3.85%, while that of the Permian bitumen extract even 228
decreases a little, which is probably connected with the light 229
fraction loss in the process of extracts being brought up to the 230
constant weight. 231

We can see a noticeable decrease (from 8.96 to 7.03%) in the 232
extract from the sample of the species exposed to hydro- 233
thermal-catalytic transformations. There is an increase of the 234
content of higher molecular organic matter in this specimen 235
after the experiment with thermal analysis data, compared to 236
the experiment without a catalyst. This gives reason to believe 237
that under these experimental conditions, along with the 238
processes of cracking, there are processes of compression. 239
These processes occur due to the hydrogen de-enrichment of 240
the molecules of resins and asphaltenes, leading to the 241

242 formation of coke-like products. They have been sorbing with
243 the breed and hence are not extracted from it by organic
244 solvents. By the way, the lighter oil could have been extracted
245 from the rocks. In ref 28, we show that, in the absence of a
246 hydrogen donor in a reactionary catalytic system, more coke-
247 like products occur, which concentrates in the rocks. While in
248 the presence of a hydrogen donor, in particular tetralyne, the
249 transfer of hydrogen from the naphthenic-aromatic component
250 in the presence of the transition metals effectively inhibits coke
251 formation.

252 In addition, at high temperatures, there is a dealkylation with
253 the break of C–C bonds, which increases the degree of
254 aromaticity of resins and asphaltenes. Asphaltenes with short
255 aliphatic chains undergo a reaction of the internal cyclization
256 with the formation of a bunch of structures, which are the
257 precursor of the coke.¹⁰

258 The main distinctive feature of the conversion of the organic
259 substance of the Permian rock sample in the presence of a
260 catalyst is the activation of destruction reactions by C–C, C–
261 N, C–O, and C–S bonds and the blocking of the polymer-
262 ization reactions. This is evidenced by the decline in the
263 catalytic experience of resins and asphaltenes content and by
264 the noticeable increase in the content of saturated hydro-
265 carbons compared with the products gained from the
266 uncatalytic experiment.

267 In addition, there is a high concentration of methane gas in
268 the products of hydrothermal experiments, as well as
269 hydrothermal-catalytic ones. This indicates the flow of
270 hydrogenolysis reactions of the C–C bonds. In particular,
271 these reactions result in both gaseous products and compounds
272 of greater molecular mass (coke) occurring as a result of
273 reactions between free radicals. This is confirmed by the
274 thermal analysis of the rock sample of this experiment.

275 Since the experiments were conducted in a carbon dioxide
276 environment, we cannot exclude the possibility of an oxidation
277 cracking process. In this case, we will have the formation of the
278 coke that will remain in the rock, because of the insufficient
279 content of the free hydrogen, required to hydrogenate the
280 generated active radicals in the processes of destruction of high-
281 molecular-weight components.

282 It should be said that, in the choice of propanol as an
283 activating additive, it was assumed that a solvent with high
284 polarity in conjunction with the metal carboxylates would
285 contribute to reducing the viscosity by interacting with the
286 polar groups of resins and asphaltenes, while destroying their
287 associative entities. It was also taken into account that propanol
288 refers to proton solvents, which are hydrogen donors.³⁵

289 According to the SARA analysis data (Table 1), hydro-
290 thermal and hydrothermal-catalytic influences on the bitume-
291 nous rocks' organic matter affect considerably the group
292 composition of the moveable hydrocarbons. The peculiarity of
293 the Domanic rock is the transformation of the kerogen polymer
294 structure accompanied by the formation of big asphaltene-like
295 fragments, which leads to an increase in asphaltene content in
296 the experimental products from 14.2 to 33.1% (marked as
297 fraction A) and in their modified products, namely, carben-
298 carboids (fraction B).¹⁰ As a result, the saturated hydrocarbon
299 content in the experimental products decreases from 18.58 to
300 12.38%. The resin and aromatic compound content also
301 decreases, but inconspicuously if compared with the initial
302 bitumen sample.

303 The effect of hydrothermal processes on the Permian rock
304 sample does not cause significant changes in the group

Table 1. SARA Analysis of the Bitumoids before and after Experiments

object	amount, wt %	group composition, wt % ^a				carben-carboids
		S	A	R	Asp	
Domanic rock (depth 1712.5–1718 m)						
initial sample	0.25	18.58	38.94	28.32	14.16	
after thermal treatment	3.85	12.38	23.10	25.29	33.09	6.14
Permian rock (depth 176.5–178 m)						
initial sample	8.96	37.86	39.95	15.98	6.21	
after thermal treatment	8.62	37.57	34.49	21.77	6.17	traces
after thermal-catalytic						
treatment by Fe/Co/Cu carboxylate	7.03	47.43	31.63	14.96	5.98	traces

^aS, saturated hydrocarbons; A, aromatic hydrocarbons; R, resins; Asp, asphaltenes.

305 composition of the experimental products (Table 1). In
306 comparison with the initial rock, the resin content in the
307 hydrothermal reaction products even increases from 15.98% to
308 21.77%, whereas in the catalytic experiment with the employ-
309 ment of the Fe-, Co-, and Cu-carboxylate catalyst composition,
310 their content decreases to 14.96% as well as that of asphaltenes
311 from 6.21 to 5.98% along with the substantial growth of
312 saturated hydrocarbon content from 37.8 to 47.4%. The
313 aromatic compound and resin content similar to that in the
314 Domanic rock hydrothermal experiment products decreases
315 dramatically (Table 1).

316 The distinctive features of the group composition of the
317 bitumen extracts under study before and after the hydrothermal
318 and hydrothermal-catalytic treatment of the rock are given in
319 Table 1.

320 According to the gas chromatographic analysis data (Figure
321 3), the initial Domanic bitumen extract can be classified as oil
322 of the A type, in which the sum of *n*-alkanes (*n*C₁₇ and *n*C₁₈)
323 composition dominates over the alkanes of isoprene-like
324 structure, namely, pristane (iC₁₉) and phytane (iC₂₀),³⁷ the
325 result of which gives the index value as follows:

$$k_i = (\text{Pr} + \text{Ph}) / (nC_{14} + nC_{18}) < 1 (0.90)$$

326 Among *n*-alkanes, lower molecular weight homologues
327 (*n*C₁₂–*n*C₂₁) prevail over their high molecular weight counter-
328 parts (*n*C₂₂–*n*C₃₁) so the value of the *n*-(C₁₂–C₂₁)/*n*-(C₂₂–
329 C₃₁) ratio is bigger than 1 and equals 4.43. The hydrothermal
330 effect on the Domanic rock sample (Table 1) leads to a 4-fold
331 decrease in the given ratio value to 1.06 because of the increase
332 in high-molecular alkane relative content in the experimental
333 products' composition. The value of index *k_i* remains without
334 particular changes and accounts for 0.92. Everything above
335 speaks about the fact that, at a temperature of 300 °C, high
336 molecular weight *n*-alkanes and other high molecular weight
337 hydrocarbons generated from the kerogen matrix but not the
338 C–C bond rupture with alkyl substituent breakoff takes place
339 as it happens with the higher temperatures.²⁵ The Pr/Ph index
340 value rises from 0.82 to 0.92 but still remains less than 1, which
341 is characteristic for the heavy crude of the Volga–Ural basin.

342 The initial Permian bitumen according to the value of index
343 *k_i* (0.25), as well as the initial Domanic one, can be attributed to
344 A-type oils. However, it has a much higher content of *n*-alkanes
345 (Figure 4), just as it takes place in high-paraffin oils or paraffin

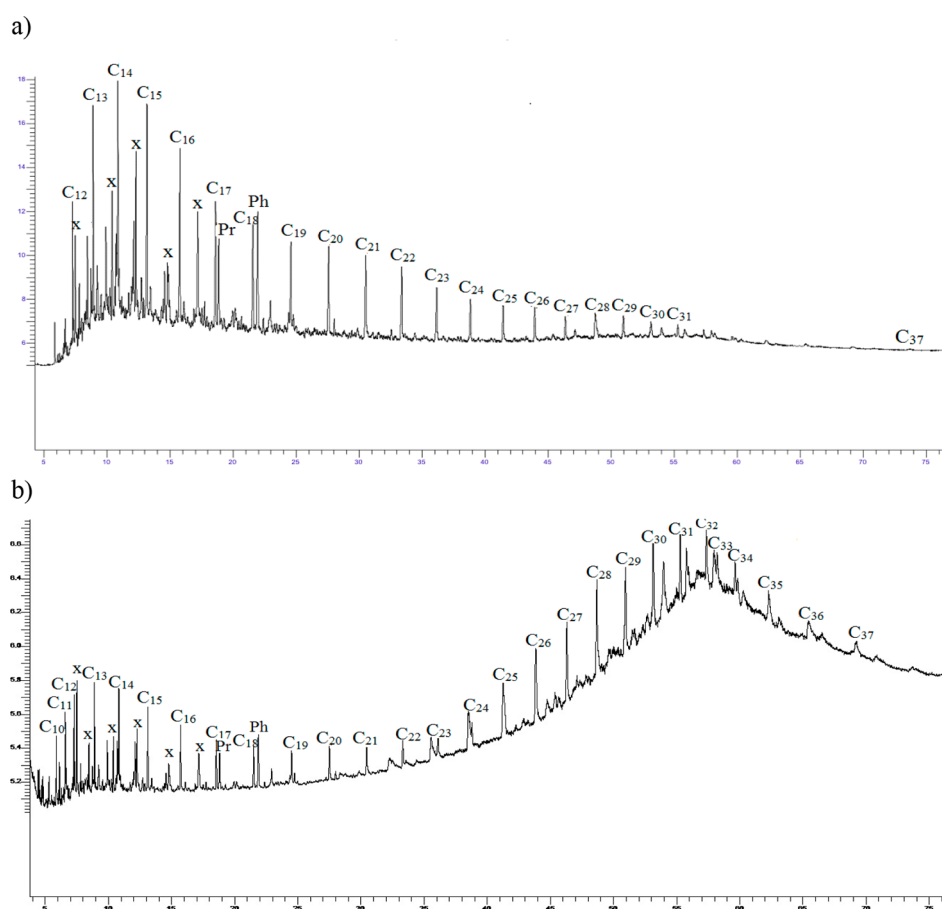


Figure 3. Gas chromatography of Domanic bitumen extract: initial (a), after thermal treatment (b). C_{10} – C_{37} , n -alkanes; x, isoprenoid alkanes iC_{13} – iC_{18} ; Pr, pristane (iC_{19}); Ph, phytan (iC_{20}).

346 sediments occurring in oil reservoirs. High molecular n -alkanes
347 prevail over their lower molecular weight homologues; the
348 value of ratio n -(C_{12} – C_{21})/ n -(C_{22} – C_{31}) is 0.91.

349 Alkanes $> nC_{22}$ concentration remains relatively high in the
350 saturated fraction of the hydrothermal experimental product
351 (Table 1). The value of the above-mentioned ratio decreases
352 only to 0.83. In parallel with that, the relative content of
353 isoprene-like alkanes (iC_{13} – iC_{18}) increases in comparison with
354 the initial bitumen extract, which leads to a considerable
355 increase in the value of index $B = \Sigma iC_{13-18}/(iC_{19} + iC_{20})$ from
356 2.35 to 5.14. Everything above indicates the partial destruction
357 of high molecular weight components accompanied by the
358 break-off of the alkyl substituents of the isoprene-like structure.

359 The formation of gas with a high methane concentration was
360 registered in the hydrothermal experimental products, which
361 points to the occurrence of the reaction of C–C bond
362 hydrogenolysis. In particular, these reactions result in both
363 gaseous products and compounds of greater molecular mass
364 (coke) occurring as a result of reactions between free radicals.

365 In the saturated fraction of the hydrothermal-catalytic
366 experiment product, the value of index $B = \Sigma iC_{13-18}/(iC_{19} +$
367 $iC_{20})$ is much lower in comparison with that in the
368 hydrothermal experiment and a bit higher in the initial extract
369 (2.43 versus 2.35). The value of index k_i is also a little higher
370 than for the hydrothermal experiment product (0.29 versus
371 0.25). At the same time, it is important to note that in the
372 hydrothermal-catalytic products, compared to the initial extract
373 and the hydrothermal experience, the ratio n -(C_{12} – C_{21})/ n -
374 (C_{22} – C_{31}) decreases from 0.91 to 0.83 and to 0.54. That

indicates either the additional extraction of supermolecular 375
alkanes from the Permian rock or the loss of light fractions in 376
the research process. 377

It can be assumed that the employed catalysts catalyze the 378
hydrocarbon fractions' formation as a result of the destruction 379
of the bitumen components (asphaltenes and resins);^{16,17} they 380
indicate the increase in content of the saturated fractions in the 381
hydrothermal-catalytic test product. At the same time, it is 382
important to mark that in the hydrothermal-catalytic experi- 383
ment product in comparison with the initial extract and 384
hydrothermal experiment products, the value of ratio n -(C_{12} – 385
 C_{21})/ n -(C_{22} – C_{31}) decreases from 0.91 to 0.83 and 0.54, 386
respectively, which points to the additional extraction of high- 387
molecular n -alkanes from the Permian rock. According to the 388
literary date,^{22–24} the usage of carbon dioxide improves 389
hydrocarbon extraction. It can be assumed that the above- 390
mentioned is connected with the CO_2 solvent action. In the 391
steam and carbon dioxide medium, more extensive extraction of 392
high-molecular hydrocarbons including solid n -alkanes, which 393
are not washed out from the rock completely in different 394
reaction media, takes place. Moreover, we can suppose that the 395
selected conditions of the laboratory experiments' performance 396
are close to supercritical because the temperature and pressure 397
are critical parameters for the CO_2 amount to reach an order of 398
magnitude of 31.1 °C and 7.4 MPa, respectively.²² 399

Structural-Group Composition. We performed the IR 400
spectroscopy analysis of Domanic rock after hydrothermal 401
treatment (Figure 5a). The IR spectrum of the test products 402
shows that the intensity of the absorption spectrum bands in 403

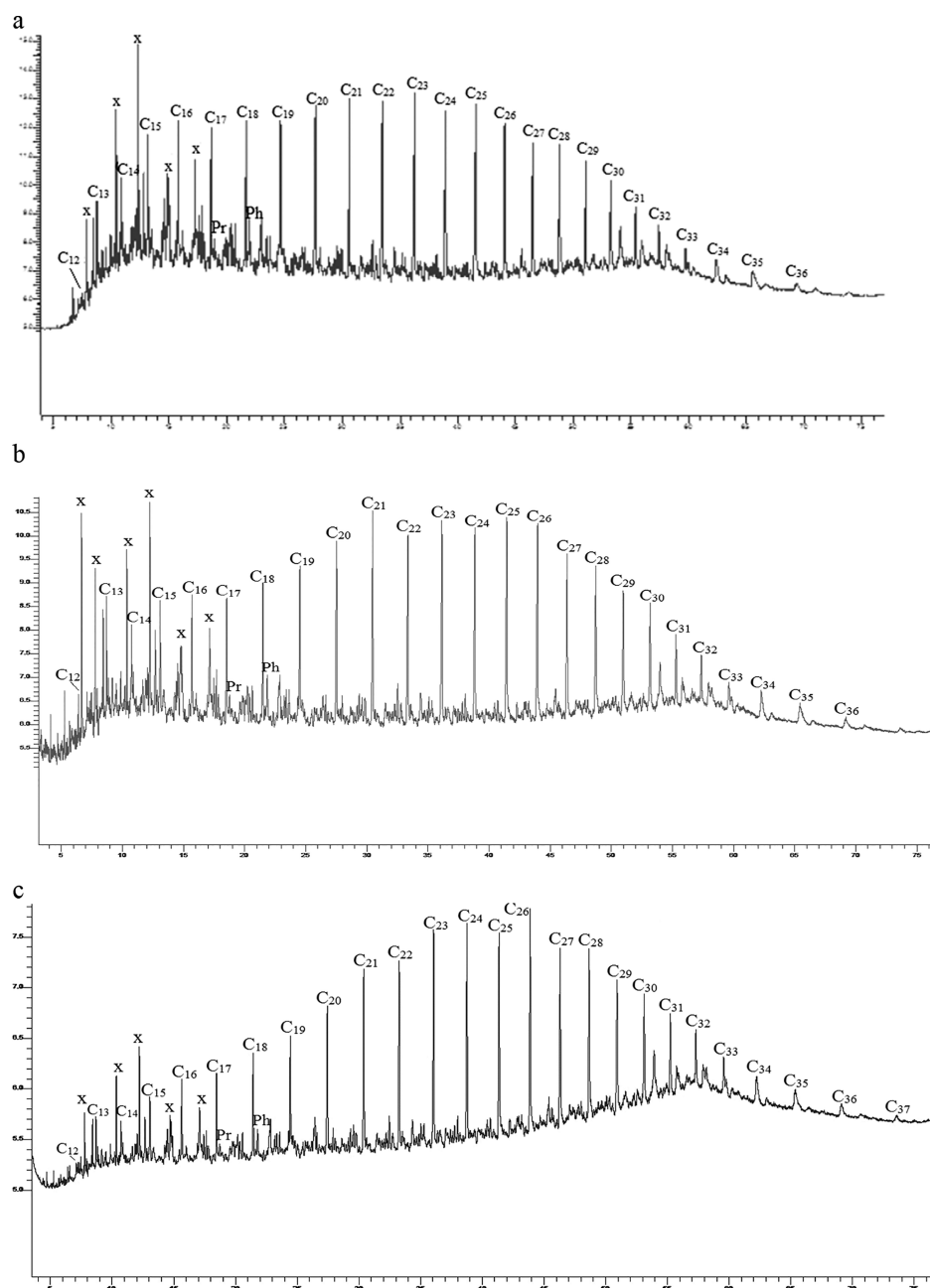


Figure 4. Gas chromatography of Permian bitumen extract: initial (a), after thermal treatment (b), and after thermal treatment with catalyst (c). C_{10} – C_{37} , *n*-alkanes; x, isoprenoid alkanes iC_{13} – iC_{18} ; Pr, pristane (iC_{19}); Ph, phytan (iC_{20}).

404 the 1600 cm^{-1} zone as well as in the 952 and 817 cm^{-1} zones,
 405 connected with $C=C$ aromatic structure bond oscillations,
 406 increases in comparison with the initial bitumen extract given.
 407 This is reflected in the rise of aromaticity spectral index $C_1 =$
 408 D_{1600}/D_{720} from 2.33 to 7.33 (Table 2). The reduction of the
 409 absorption spectrum band intensity at 1030 cm^{-1} in
 410 comparison with that of the initial bitumen extract demon-
 411 strates the decrease in the content of sulfur oxide groups in the
 412 test products. It leads to a decrease in the sulfuring index value
 413 $C_5 = D_{1030}/D_{1465}$. We can also mark the occurrence of quite
 414 intensive spectrum bands in the area of oxygen-containing
 415 groups of oscillations, namely, 1105 – 1161 cm^{-1} .
 416 In the IR spectra of the Permian bitumen extracts, along with
 417 the intensive bands in the area of the paraffin structures' methyl
 418 ($-CH_3$) group oscillations 1337 and 1465 cm^{-1} , the intensive

oscillations of the aromatic ring $C=C$ bond spectrum bands in 419
 the 1600 cm^{-1} area can also be observed. In the catalytic 420
 experiment, when the composition of Fe-, Co-, and Cu- 421
 resins was used, there was a considerable increase in the 422
 number of oxygen-containing carbonyl (CO) groups in the area 423
 of 1700 – 1740 cm^{-1} . This leads to an increase in the state-of- 424
 oxidation index C_2 equal to D_{1710}/D_{1465} , which, in its turn, 425
 points to the more intensive oxidizing cracking processes in the 426
 steam and carbon dioxide medium and in the presence of the 427
 catalysts. 428

We have studied the structural-group composition of the 429
 asphaltenes from bitumen extracts before and after experiments 430
 (Table 3, Figure 5b) apart from the extracts. As shown above 431 13
 (Table 1), the Domanic kerogen under the influence of 432
 hydrothermal factors in a carbon oxide medium generates two 433

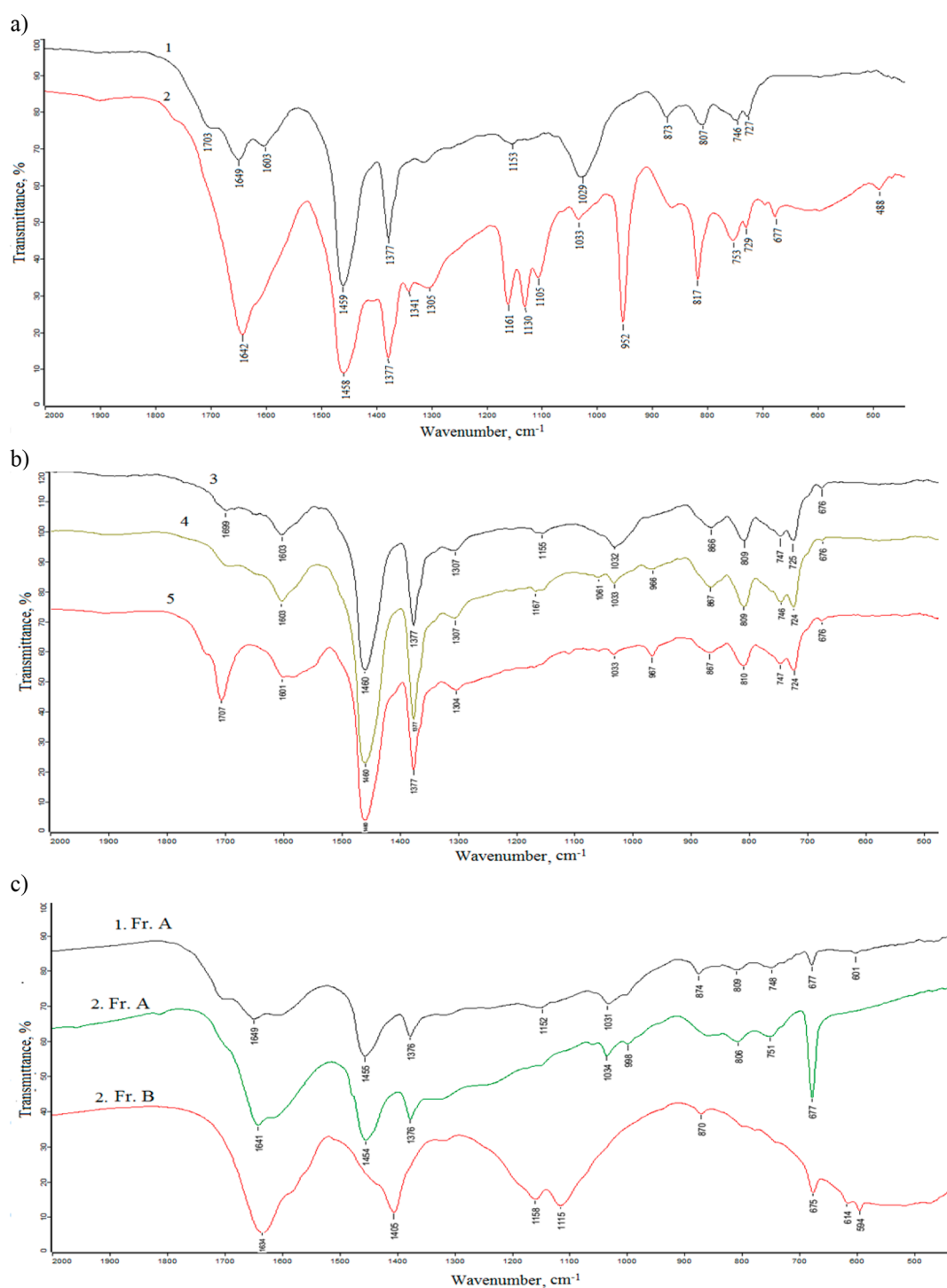


Figure 5. IR spectra of Bitumoids and Asphaltenes. (a) Domanic rock: bitumoid before (1) and after thermal treatment (2). (b) Permian rock: bitumoid before (3) and after thermal treatment (4) and after thermal treatment with catalyst (5). (c) Asphaltenes of domanic rock: fraction A of asphaltenes before (1.Fr.A) and after thermal treatment (2.Fr.A) and fraction B of the asphaltenes (2.Fr.B).

434 types of asphaltenes with different solubilities in organic
 435 solvents: common asphaltenes (fraction A) and products of
 436 their modification: carbon-carboids (fraction B). This correlates
 437 with the results of hydrothermal transformations of the
 438 Domanic kerogen from the Sarmanovskaya area of Romash-
 439 kinskoe field. It is shown in ref 11 that the hydrothermal effect
 440 on the previously extracted rock in the reduction medium
 441 results in the destruction of the matrix kerogen accompanied by
 442 the formation of two types of asphaltene-like substances which

443 have different degrees of aromaticity, heteroatom and micro-
 444 element content, paramagnetic center concentration, and
 445 solubility in organic solvents, i.e., the factors influencing the
 446 formation of the oil disperse phase of the oil extracted from the
 447 rocks.

On the IR spectra of the Domanic asphaltenes from kerogen
 448 transformation products (Figure 5b, fraction A and B) in
 449 contrast to the initial bitumen extract asphaltenes, the intensity
 450 of the absorption spectrum bands in the area of aromatic
 451

Table 2. IR Analysis of Bitumoids before and after Experiments

object	optical density at wavenumber (λ_{\max}), cm^{-1}							spectral coefficients				
	1740	1710	1600	1465	1380	1030	720	C_1	C_2	C_3	C_4	C_5
Domanic rock												
initial sample	0.17	0.35	0.49	2	1.27	0.67	0.21	2.33	0.18	0.64	3.02	0.34
after thermal treatment	0	0.03	0.22	2	1.07	0.05	0.03	7.33	0.01	0.53	4.98	0.02
Permian rock												
initial sample	0.08	0.18	0.36	2	1.20	0.43	0.34	1.06	0.09	0.60	4.28	0.22
after thermal treatment	0.04	0.09	0.25	2	1.09	0.17	0.25	1.00	0.05	0.55	5.36	0.09
after thermal-catalytic treatment by Fe/Co/Cu carboxylate	0.18	0.48	0.35	2	1.14	0.22	0.28	1.25	0.24	0.57	4.06	0.11

Table 3. IR Analysis of the Asphaltenes before and after Experiments

object	optical density at wavenumber (λ_{\max}), cm^{-1}							spectral coefficients				
	1740	1710	1600	1465	1380	1030	720	C_1	C_2	C_3	C_4	C_5
asphaltenes of Domanic rock												
initial sample	0.27	0.69	1.04	2	1.49	0.87	0.29	3.61	0.35	0.75	1.71	0.44
after thermal treatment fraction A	0.05	0.27	1.35	2	1.52	0.60	0.29	4.67	0.14	0.76	1.34	0.30
after thermal treatment fraction B	0.08	0.23	1.14	0.59	0.68	0.38	0.17	6.81	0.39	1.14	0.74	0.64
asphaltenes of Permian rock												
initial sample	0.03	0.09	0.94	2	1.55	0.73	0.48	1.96	0.05	0.78	2.16	0.37
after thermal treatment	0.49	0.53	1.00	2	1.49	0.69	0.31	3.21	0.26	0.75	1.80	0.35
after thermal-catalytic treatment by Fe/Co/Cu carboxylate	0.11	0.40	1.04	2	1.51	0.69	0.45	2.33	0.20	0.76	1.88	0.35

structures' valent oscillations ($1600\text{--}1642\text{ cm}^{-1}$) increases, whereas the intensity of the aliphatic structures' absorption spectrum band (1454 cm^{-1}) decreases, which is reflected in the rise in the aromaticity index values $C_1 = D_{1600}/D_{720}$ and confirms the increase in the aromaticity of the Domanic rock organic matter transformation products in a steam and carbon dioxide medium (Table 3).

In the IR spectra of the test product asphaltenes (fraction A) as well as in those of the initial asphaltenes, there is an intensive absorption spectrum band in the 1450 cm^{-1} area corresponding to the valent oscillations of methyl ($-\text{CH}_3$) groups, the band above being practically absent in the insoluble products of the carben-carboids fraction (fraction B). At the same time, an intensive absorption band appears in the spectrum at 1405 cm^{-1} pointing to a certain type of substitution at the double $\text{C}=\text{C}$ bonds.³⁸ It is also important to note that the occurrence of two intensive peaks in the zone of valent oscillations $1170\text{--}1110\text{ cm}^{-1}$ demonstrates an increase in the content of hydroxyl and ether groups in their structure. The relative intensity of carbonyl group absorption bands in spectra at 1700 cm^{-1} , as well as sulfur oxide groups at 1030 cm^{-1} , in comparison with asphaltenes practically does not increase. However, the decrease in the aliphatic structures' absorption intensity in the 1454 cm^{-1} area finds its reflection in much higher values of oxidation ($C_2 = D_{1710}/D_{1465}$) and sulfuring indexes ($C_5 = D_{1030}/D_{1465}$) as well as in the degree of branching $C_3 = D_{1380}/D_{1465}$ (Table 3). From the IR spectra and spectral index values (Table 4), the more aromatic structures were those of carben-carboids (fraction B). They were characterized by much higher values of the indexes of oxidation (C_2), degree of branching (C_3), and sulfuring (C_5), if compared with common asphaltenes (fraction A). At the same time, the value of the wax content index (C_4) is the lowest in comparison with the asphaltenes from the initial bitumen extract and test products (0.74 versus 1.71 and 1.34, respectively), and on the contrary, the value of the branching degree index is the highest (1.14 versus 0.75 and 0.76). The above-mentioned indicates that carben-carboids can be

Table 4. Elemental Composition of Bitumoids and Asphaltenes of Bitumoids before and after Experiments

object	element composition, wt %					
	H	C	N	S	O	H/C
bitumoids of Domanic rock						
initial sample	5.57	73.25	1.44	2.79	16.95	0.91
after thermal treatment	3.86	75.42	1.66	2.85	16.21	0.61
asphaltenes of Domanic rock						
initial sample	8.41	73.56	0.51	2.84	14.68	1.37
after thermal treatment fraction A	3.53	75.68	3.45	8.83	8.51	0.56
after thermal treatment fraction B	2.81	78.06	1.97	3.91	13.25	0.43
bitumoids of Permian rock						
initial sample	3.15	74.38	0.78	1.79	19.90	0.51
after thermal treatment	4.33	71.30	0.60	0.56	23.21	0.73
after thermal-catalytic treatment by Fe/Co/Cu carboxylate	5.02	69.14	0.61	0.35	24.88	0.87
asphaltenes of Permian rock						
initial sample	4.23	78.90	2.95	9.69	4.23	0.64
after thermal treatment	11.95	75.63	1.37	3.08	7.97	1.89
after thermal-catalytic treatment by Fe/Co/Cu carboxylate	5.78	75.7	2.81	8.98	6.73	0.92

characterized by the absence of long alkyl chains, which determines their insolubility in aromatic solvents.

The comparison of the asphaltenes from the two types of bitumen extracts leads to the fact that the aromaticity of the Domanic asphaltenes is much higher than that of the asphaltenes from the Permian rock sample (3.61 versus 1.96). As a result, the hydrothermal and hydrothermal-catalytic effects on the Permian rock sample produce a rise in the content of oxygen-containing groups in asphaltenes, which corresponds to the increase in the state-of-oxidation index values (Table 3).

499 The decrease in the wax content index (C_4) for the asphaltenes
500 of both tests is not as sharp as that observed in the case of the
501 Domanic carben-carboid fraction. Everything above testifies to
502 the occurrence of the oxidation cracking processes in the
503 carbon dioxide medium and in the presence of catalysts, which
504 reflects the structural peculiarities of asphaltenes.

505 Changes in elemental composition of the extracts from two
506 types of rocks after hydrothermal experiments have different
507 characters (Table 4). In the Domanic bitumen extract after the
508 hydrothermal treatment, a hydrogen content decrease and
509 carbon content increase take place, and as a consequence of
510 that, the ratio value H/C goes down from 0.91 to 0.61. The
511 above-mentioned can be explained in terms of hydrogen
512 disproportionation and a rise in the aromaticity degree of the
513 test products forming as a result of kerogen destruction in the
514 hydrothermal process. Similar changes also occur in the
515 processes of natural catagenesis of the organic matter from
516 Domanic source rocks.³⁶ Sufficiently high nitrogen content
517 (1.44 and 1.66) in the Domanic bitumen extracts can give
518 evidence of its immaturity.

519 In the Permian bitumen extracts, the H/C ratio grows from
520 0.51 to 0.73 as a result of the hydrothermal treatment, while in
521 the case of the hydrothermal-catalytic test, such a value
522 increases up to 0.87, which results from the partial decarbon-
523 ization and hydrogen content increase within the reaction
524 system. At the same time, the sulfur content also decreases,
525 which indicates the hydrothermal destruction of sulfur-
526 containing bonds in the steam and carbon dioxide medium
527 with the subsequent formation of hydrogen sulfide and
528 mercaptans, whose effect grows stronger in the presence of
529 catalysts.

530 Asphaltene elemental analysis showed that after the hydro-
531 thermal test with the Domanic rock sample, a considerable
532 increase in sulfur content took place in such asphaltenes'
533 composition, the main part of the sulfur above being localized
534 in carben-carboids: 9.91%. This fraction displays a significant
535 decrease in hydrogen content (from 8.41 to 2.81) and an
536 increase in carbon content, which finds its reflection in the
537 decrease in the value of H/C ratio from 1.37 to 0.43. Nitrogen
538 content also grows with reference to its content in the initial
539 asphaltenes, nitrogen being largely present in Fraction A:
540 3.45%.

541 Asphaltenes from the Permian rock sample are also
542 characterized by high sulfur content. At the same time, after
543 the test, the sulfur content goes down. The lowest sulfur
544 content is in the asphaltenes extracted from the hydrothermal-
545 catalytic test product, where Fe-, Co-, and Cu-resinates are
546 used. It should be also noted that there is an increase of
547 hydrogen content in asphaltenes with a considerably high value
548 of the H/C index.

549 The results of the microelement composition investigation
550 using the RFA method have shown that the Domanic bitumen
551 extract demonstrates increased vanadium and nickel content
552 after the hydrothermal experiment, namely, from 2.52 to 3.86
553 and from 0.68 to 0.97, respectively. In the initial extract
554 asphaltenes, vanadium content amounts to 0.55 and 0.13%. The
555 content of vanadium and nickel increases in the asphaltene
556 fractions of the test products as well. The main part of
557 vanadium (99.10%) and nickel (91.74%) concentrates in the A-
558 fraction asphaltenes, which speaks about the fact that these are
559 kerogen fragments enriched with microelements. In carben-
560 carboids (fraction B), vanadium content is only 0.37%, whereas
561 the presence of nickel has not been revealed.

In the extracts from the Permian rock samples, the content of
V and Ni after hydrothermal and hydrothermal-catalytic tests,
on the contrary, decreases, namely, for V, from 1.75 to 1.31 and
0.75%, while for Ni it decreases from 0.38 to 0.32 and 0.25%,
respectively. Microelement content in the test product
asphaltenes, in contrast to the Domanic rock ones, also
decreases: V content, from 5.58 to 4.81 and 4.22%; Ni, from
1.02 to 0.98 and 0.70%, respectively, which is most likely to be
connected with the destruction of porphyrin complexes¹³
present in the asphaltene composition. The catalyst application
allows us to cut down to a greater extent the microelement
content in the hydrothermal-catalytic test products in
comparison with the products obtained as a result of the
catalyst-free test.

CONCLUSION

A comparative study of the content and composition of the
organic matter from Domanic and Permian deposits has been
carried out with the use of the complex of physicochemical
methods. The analysis showed that the Domanic organic matter
content is for 4 times higher than that in the Permian rock
samples. However, the amount of Permian bitumen extract is
considerably higher (8.96%) than that of the Domanic rock
sample (0.25%). It has been established that the main part of
the Domanic organic matter falls on insoluble kerogen, which,
due to its complicated structuration, is unstable under thermal
effects. This, in turn, leads to significant losses in its weight in
thermal pyrolysis.

A comparative study of the content and composition of the
organic matter of Domanic and Permian sediments has been
carried out with the application of a complex of physicochem-
ical methods. The analysis showed that, in the Domanic rock,
the organic substance content was 4 times as much as in the
Permian rock. However, the extract from the Permian rock is
significantly higher (8.96%) than that of the Domanic rock
(0.25%). It is established that the major part of organic matter
of the Domanic rock is insoluble kerogen. It is unstable for
thermal pressure, because of its complex structure. It also
manifests in significant losses of its mass under thermal
pyrolysis.

Disparities were identified in the composition of extracts
from Domanic and Permian sediments after hydrothermal
treatment at a temperature of 300 °C and 7 MPa pressure in
the carbon-dioxide environment. It is shown that the
hydrothermal impact on the Domanic rock results in an
increase in the output of the extract by 15 times. The group
composition of the extract compared to the initial rock is
characterized by increasing the content of the asphaltenes with
the products of their modifications of the type carben-carboids.
This results in a relative decrease in the saturated hydrocarbon
content. In the process of carbonization, the products of the
experiments are reflected in the lower value of the H/C. During
hydrothermal effects on the Permian rock sample, changes in
the composition of extracts from the rocks are not as significant
as in the case of Domanic rock. However, in the presence of the
composition of oil-soluble iron(II), cobalt(II), and copper(II)
carboxylates with an additive of propanol, the components of
the experience are redistributed to increase the content of the
saturated fractions due to the reduction of resins and
asphaltenes. For the Permian test products, the value of the
H/C index in contrast to that of the Domanic ones rises; the
products above are also characterized by much lower values of
the aromaticity spectral index, which confirms their more

624 saturated character. The decrease in the values of the sulfuring
625 index points to the C–S bonds' destruction as a result of
626 hydrothermal treatment. The main distinctive feature of the
627 conversion of the organic substance of Permian rock in the
628 presence of a catalyst is the activation of destruction reactions
629 by C–C, C–N, C–O, and C–S bonds and the blocking of the
630 polymerization reactions. This is evidenced by the decline in
631 the catalytic experience of resin and asphaltene content and by
632 the noticeable increase in the content of saturated hydro-
633 carbons compared with the products gained from the
634 uncatalytic experiment.

635 The peculiarities of the composition and structure of the
636 Domanic and Permian rock asphaltenes before and after
637 thermal treatment have been revealed, too. The asphaltenes
638 from the tests products of both rocks are characterized by a
639 more carbonized structure. The value of the aromaticity index
640 of the Domanic rock asphaltenes is 3 times bigger than that of
641 the Permian rock ones. At the same time, the most aromatic
642 products are those of the Domanic rock destruction, present in
643 the carboid fraction composition. After hydrothermal treat-
644 ment, the value of the H/C ratio in the element composition of
645 the Domanic rock asphaltenes decreases, whereas in the
646 Permian rock asphaltenes, on the contrary, such a value
647 increases, which also repeats the analogous character of their
648 extracts' composition changes. In the Domanic rock asphal-
649 tenes, the content of V and Ni is higher than in the asphaltenes
650 from Permian deposits.

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