

# Changes in Structural Group Composition of Asphaltenes and Carbene-Carboids of the Domanic Shale in Sub- and Supercritical Water: FT-IR Spectroscopy Data

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## Abstract

This paper presents the results of a change in the structural-group composition of asphaltenes and carbonaceous substances such as carbene-carboids in the products of the conversion of high-carbon Domanic rock from the sediments of the Semulukskoe-Mendimskoe horizon of the Volga-Ural petroleum basin, after exposure at temperatures of 320, 374 and 420 °C in sub- and supercritical water. IR Fourier spectroscopy showed that increasing the temperature to supercritical water conditions (374 and 420 °C) leads to chemical transformation of high molecular weight components and Domanic kerogen, accompanied by the formation of carbene-carboids – polymerization and condensation products that differ from asphaltenes in a higher degree of aromaticity. The highest content of carbene-carboids is observed in the composition of the products obtained from experiments at 374 °C, apparently associated with intensive decomposition of kerogen of Domanic rock. Increasing the temperature to 420 °C leads to the formation of coke-like products as a result of oxidative degradation processes, which leads to a decrease in their content in liquid hydrocarbons.

*Keywords: organic matter, Domanic rock, supercritical water, IR-analysis, asphaltenes, Volga-Ural basin*

## Introduction

Asphaltenes are important components of various fossil fuels, including heavy oils, coal, and oil shale. In Russia, the Bazhenov Formation in West Siberia and the Domanic formations of the Volga-Ural petroleum province are the analogues of shale rocks [1], [2], [3]. The horizons of Mendimskoe, Domanic (Semilukskoe) and Sargaevskoe from the Volga-Ural petroleum basin corresponds to the Domanic shale [4]. The Domanic shale rock is dark siliceous clayey bitumen limestone, with a content of organic matter (OM) up to 20% [5], [6]. A significant part of OM is insoluble kerogen.

The organic matter of shale rocks transforms under the hydrothermal influence and generates mobile hydrocarbons. A highly informative method to study the structural group composition of high molecular weight components of oil and OM rocks is IR Fourier Spectroscopy. This method allows evaluation of the conversion of various hydrocarbon and functional groups in both natural and man-made processes [7], [8].

This paper is an IR Fourier Spectroscopy study of chemical conversions of asphaltenes and coaly matters as a result of Domanic shale transformations in sub-and supercritical conditions (the temperature of which was 320, 374 and 420 °C).

## Methodology

This study focuses on the Domanic shale rock from the Chishminskoe area of Semilukskoe-Mendimskoe horizon of the Volga-Ural petroleum province. The samples were extracted from the TVD of 1720 m. The Chishminskaya area is located in one of the largest oil fields of Tatarstan Republic – Romashkino.

Laboratory simulation was carried out in an autoclave reactor at temperatures of 320°C, 374°C, 420°C for 1 hours. Heat treatment was performed in an inert atmosphere (nitrogen) in the autoclave reactor with 300 ml capacity by Parr Instruments. The ratio of water-rock sample was 1:1. During the simulation, the pressure of vapor-gas mixture increased up to 17 MPa at 320°C, up to 24.6 MPa at 374°C and up to 24.4 MPa at 420°C.

Hot extraction with chloroform was applied on core material before and after exposure to thermal effect in a Soxhlet extractor. The extract's composition (SARA analysis) was determined by liquid-adsorption chromatography on aluminum following the methodology recommendations developed by VNII NP, ASTMD4124-09 and GOST 32269-2013.

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

## Results and Discussion

The group composition of products of hydrothermal experiments obtained in sub- and supercritical water at various temperatures is presented in Fig. 1. The initial sample of Domanic shale rock is characterized by a high content of high-molecular hydrocarbons: asphaltenes (29.0 wt %) and resins (37.0 wt %). The content of saturate (14.8 wt %) and aromatic (19.2 wt %) hydrocarbons are low. During hydrothermal treatment of Domanic shale rock in subcritical conditions ( $T=320^\circ\text{C}$  and  $P=17$  MPa) compared with the original rock, there is an increasing concentration of aromatic hydrocarbons to 22.7 wt % and asphaltenes up to 32.9 wt %.

However, the content of resin decreased to 27.1 wt % in contrast with the initial rock sample.

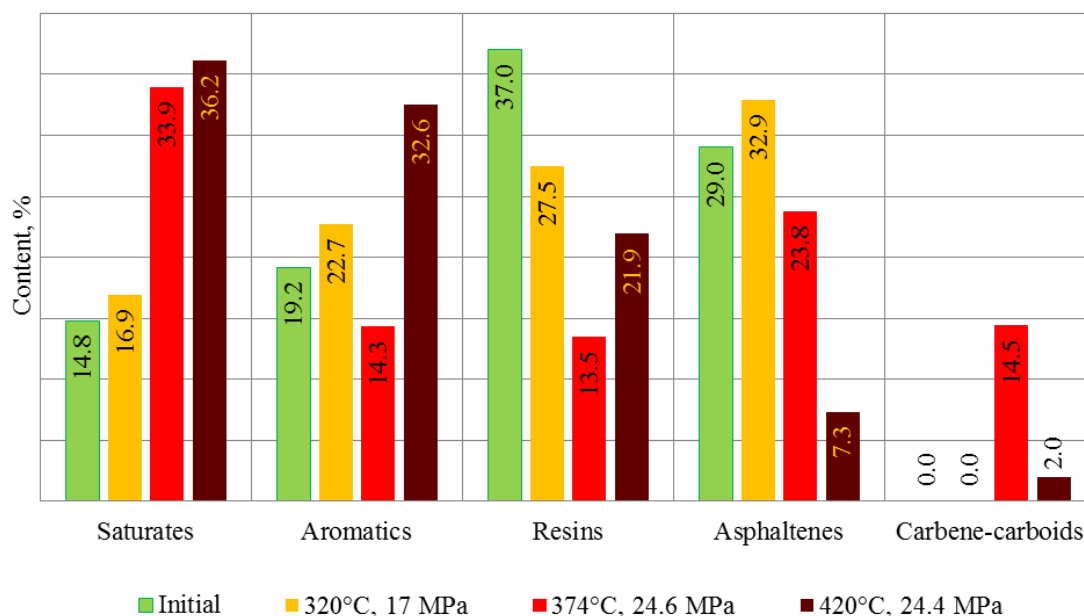
The supercritical condition of 374°C and 24.6 MPa has a special influence on the destruction of resins, the content of which is greatly reduced to 65%. The composition of the products of the experiments increases newly formed saturated hydrocarbons from 14.8 to 33.9 wt %.

Increasing the temperature of supercritical water up to 420°C reduces the content of asphaltenes and resins due to transition of hydrocarbons into saturate (36.2 wt %) and aromatic structures (32.6 wt %).

In the products of hydrothermal experiments obtained in supercritical water at 374°C and 420°C, the formation of insoluble high-carbon substances such as carbene-carboids is observed.

This indicates the occurrence of the processes of destruction of asphaltenes and high molecular weight fragments of kerogen through the least stable heteroatomic bonds with the formation of both saturated and aromatic hydrocarbons and products of compaction such as carbonaceous substances.

The further study of asphaltenes and coal matters (carbene-carboids) was performed using IR Fourier Spectroscopy. The IR spectra of high-molecular products were compared by optical density at maximum corresponding absorption bands: formation of alkane at 720  $\text{cm}^{-1}$  (methylene group  $\text{CH}_2$ ), 1380  $\text{cm}^{-1}$  and 1465  $\text{cm}^{-1}$  ( $\text{CH}_3$  methyl and  $\text{CH}_2$  methylene group); aromatic compounds at 1600  $\text{cm}^{-1}$  (C=C bond); oxygen containing compounds in carbonyl groups of acids at 1710  $\text{cm}^{-1}$ , in ester carboxyl groups at 1740  $\text{cm}^{-1}$  and sulfoxide groups 1030  $\text{cm}^{-1}$  [9].

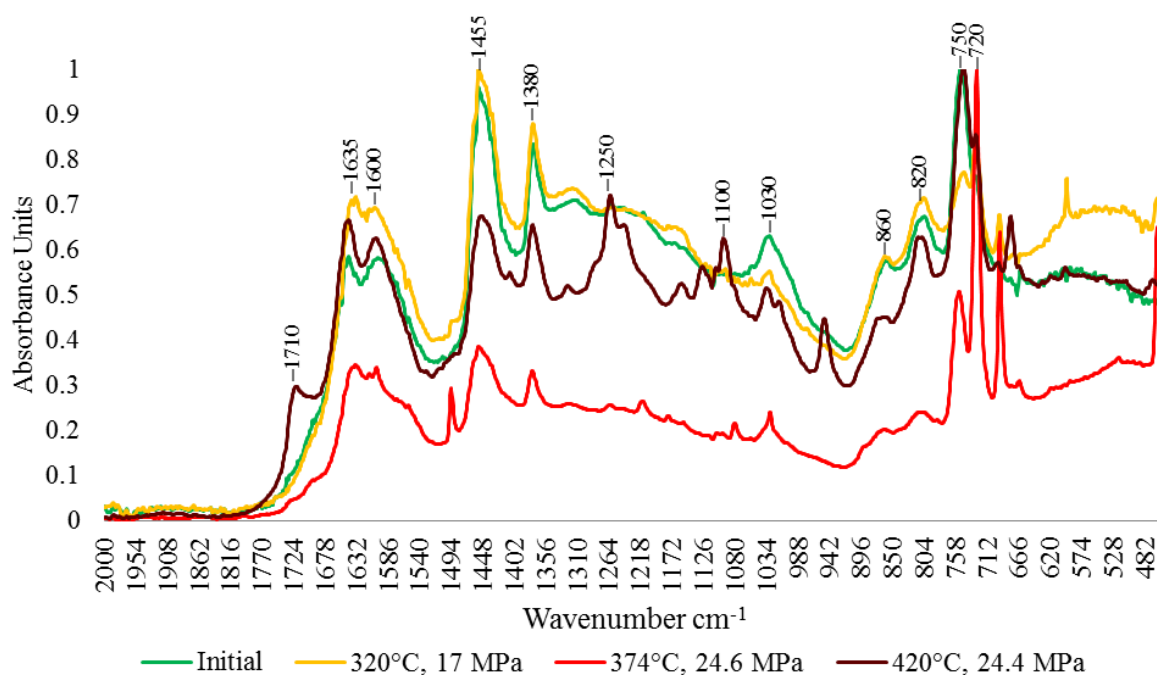


**Fig. 1.** SARA-analysis of the initial extract and extracts after the transformation of Domanic shale rocks at sub- and supercritical conditions (320, 374 and 420 °C)

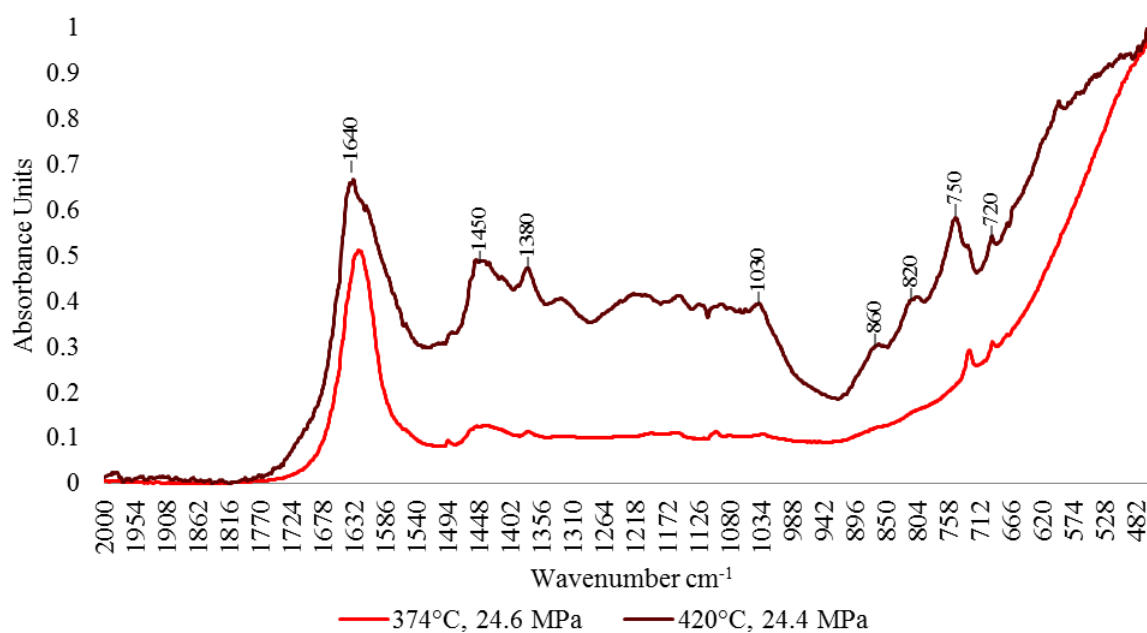
The spectrum of asphaltenes after treatment at 320°C (Fig. 1) is almost similar to the spectrum of initial asphaltenes. However, it differs strongly from the spectra of asphaltenes after 374°C in the higher intensity of absorption band, which is specific for aromatic structures (1600 and 900-730  $\text{cm}^{-1}$ ). In the given spectra, there is no absorption band for carbonyl structures (1710  $\text{cm}^{-1}$ ). The increase in intensity of 1450-1455, 1380  $\text{cm}^{-1}$  absorption bands is observed. It indicates an increase in the content of aliphatic structures of asphaltenes.

The IR spectra of asphaltenes from products at 420°C is characterized by a sharp increase in the intensity of the absorption band at 1250  $\text{cm}^{-1}$ , 1100  $\text{cm}^{-1}$ , which indicates the presence of an oxygen-containing group in esters and alcohols. The intensity of aromatic groups in the range of 900-730  $\text{cm}^{-1}$  is due to the vibration of four hydrogen atoms that are attached to the aromatic ring. In the given region, the intensity of absorption band was significantly decreased in contrast with the initial asphaltenes and the experiment after 320°C. The greatest decrease in the intensity of aromatic triplets in the range of 900-730  $\text{cm}^{-1}$  is observed in the spectra of asphaltenes after the transformation of Domanic rock in supercritical water at 374°C. The increase in intensity of 1710, 1030, 500-400  $\text{cm}^{-1}$  absorption bands indicate the increase of oxygen containing groups in their structure. Oxidative cracking processes are ongoing.

The spectra of carbenes-carboids (Fig. 2) obtained at temperatures of 374°C and 420°C do not have absorption bands of carbonyl group (1710  $\text{cm}^{-1}$ ), or esters (1740  $\text{cm}^{-1}$ ). The increase in temperature of supercritical water up to 420°C increases the absorption bands of 720-900, 1640 in spectral curve of high-organic matter, which is characterizes the aromatization degree; 1435, 1380  $\text{cm}^{-1}$  paraffinic degree and 1030  $\text{cm}^{-1}$  sulfurization degree.



**Fig. 2.** IR spectra of asphaltenes of initial extract and after the conversion of Domanic rock in sub- and supercritical water at 374 °C and 420 °C



**Fig. 3.** IR spectra of carbenes/carbides of initial extract and after the conversion of Domanic rock in sub- and supercritical water at 374 °C and 420 °C

The observed changes in the structure of asphaltenes and carbenes, carboids of the products of hydrothermal transformations of Domanic rock are reflected in the spectral indices presented in Table 1. For comparison of the products under study, the following spectral coefficients associated with the structural group composition were used: C1 = D1600/D720 (aromaticity), C2 = D1710/D1465 (oxidation), C4 = (D720 + D1380)/D1600 (paraffinicity) and C5 = D1030/D1465 (sulfurization) [10]. The values of spectral coefficients are presented in the table.

**Table 1.** The structural-group composition

Sample no.	Absorbance A at maxima of absorption bands at $\nu$ , $\text{cm}^{-1}$							*Spectral indices				
	1740	1710	1600	1465	1380	1030	720	C1	C2	C3	C4	C5
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
320°C	0.06	0.14	0.68	0.79	0.82	0.55	0.70	0.98	0.18	1.03	2.22	0.70
374°C	0.03	0.06	0.32	0.33	0.31	0.24	0.45	0.71	0.19	0.96	2.38	0.74
420°C	0.13	0.28	0.62	0.55	0.63	0.51	0.67	0.92	0.51	1.14	2.09	0.92
Carbenes and Carboids												
Initial	-	-	-	-	-	-	-	-	-	-	-	-
320°C	-	-	-	-	-	-	-	-	-	-	-	-
374°C	0.02	0.03	0.30	0.12	0.12	0.11	0.26	1.15	0.30	1.01	1.26	0.98
420°C	0.04	0.11	0.53	0.41	0.47	0.38	0.47	1.14	0.26	1.14	1.77	0.92

In asphaltenes of the initial samples, the content of aliphatic hydrocarbons is very low and high amount of aromatic structures. This is observed in the low value of paraffin (2.48) and high aromaticity value C1 (0.86). The thermal influences on the Domanic shale in sub- and supercritical conditions effects the intensity of aromatization process that can be observed by the increasing index of aromaticity up to 0.98 at 320°C and 0.92 at 420 °C. The aromatization process is carried out due to the deficiency of atomic hydrogen in the system that is necessary for hydration of generated reactive radicals. The indices are increased from 0.21 to 0.51 for oxidation (C2) and from 0.86 to 0.92 for sulfurization (C5) under hydrothermal influence at 420 °C.

## Conclusions

The investigations performed on the transformation products of high-organic Domanic shale rocks from Semilukskoe-Mendimskoe deposits of the Volga-Ural petroleum province using the IR-Fourier spectroscopy method revealed their composition and structure. With an increase in temperature to supercritical water conditions (374 and 420 °C), the formation of polymerization and condensation products of hydrocarbons (carbene-carboids) is observed. These carbonaceous substances, characterized by a high degree of aromaticity, are formed from asphaltenes or kerogen fragments as a result of the breaking of heteroatomic bonds with the separation of substituents. The highest content of carbenes and carboids is observed in the composition of the products of experiments obtained at 374 °C, apparently associated with intensive decomposition of kerogen of Domanic rock. With an increase in the experimental temperature to 420 °C, the formation of coaly matters is accompanied by oxidative destruction processes, which leads to a decrease in their content in the composition of liquid hydrocarbons.

The results of IR spectroscopy indicate the occurrence of oxidative cracking of hydrocarbons under supercritical water conditions: asphaltenes become more oxidized, and carbene-carboids more aromatic.

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