



Article

Underground Upgrading of the Heavy Crude Oil in Content-Saturated Sandstone with Aquathermolysis in the Presence of an Iron Based Catalyst

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Citation: Sitnov, S.A.; Mukhamatdinov, I.I.; Feoktistov, D.A.; Onishchenko, Y.V.; Sudakov, V.A.; Amerkhanov, M.I.; Vakhin, A.V. Underground Upgrading of the Heavy Crude Oil in Content-Saturated Sandstone with Aquathermolysis in the Presence of an Iron Based Catalyst. *Catalysts* **2021**, *11*, 1255. <https://doi.org/10.3390/catal11101255>

Academic Editor: Ioannis V. Yentekakis

Received: 16 September 2021

Accepted: 15 October 2021

Published: 19 October 2021

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Abstract: Increasing the efficiency of thermal recovery methods is an important and relevant task. This study is devoted to reducing heavy components (resins and asphaltenes) and quality improvement of heavy oil by catalytic hydrothermal treatment. The object of this study is a bituminous sandstone sample from the Ashal'cha reservoir. The catalytic (iron tallate) hydrothermal simulation was carried out under reservoir conditions (200 °C, 30 bar). The composition and physicochemical characteristics of the products were studied using elemental and SARA analysis, MALDI, GC-MS, FT-IR. Moreover, the extracted rock is analyzed in XRD and DSA (Drop Shape Analyzer). The introduction of catalyst in combination with a hydrogen donor reduces the content of resins by 22.0%wt. with an increase in the share of saturated hydrocarbons by 27%wt. The destructive hydrogenation leads to a decrease in the sulfur content of upgrading products. This is crucial for the oil reservoirs of the Tatarstan Republic, as their crude oils are characterized by high sulfur content. According to the wettability data, the hydrophilicity of the rock surface increases due to inhibition of the coke formation after the introduction of the catalytic complex. Thus, the oil recovery factor can be increased due to the alteration of the oil-wetting properties of reservoir rocks.

Keywords: aquathermolysis; catalyst; heavy oil; sandstone; properties; thermal conversion; H-donor; iron tallate; oil extracts

1. Introduction

Steam treatment remains the most popular method for improving the recovery efficiency of unconventional hydrocarbons, particularly high-viscosity oils, among other enhanced recovery methods. Despite this, it is relevant to investigate technologies of increasing the efficiency of steam treatment using catalytic systems that can significantly reduce the viscosity of hard-to-recovery oils.

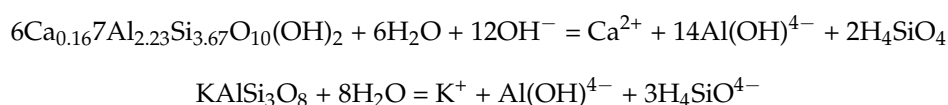
In the literature, change in soil properties under the influence of thermal factors in the environment of water vapor and rock minerals is referred to as aquathermolysis and considered for modeling the transformation processes of hydrocarbons in the sedimentary strata using thermal methods for increasing oil recovery [1–3].

It is equally important to study the upgrading of heavy oil under the influence of steam when various mineral components are presented in the surrounding reservoir rocks [4–8].

Experimental data confirm the hypothesis of the possibility of catalytic reactions in oil reservoirs using naturally occurring materials—oil-bearing rocks (sandstones, clays, basalts) as catalysts [9,10].

According to [11], the oil reservoir comprises sands, clays, and non-clays rocks, mainly including quartz, feldspar, and clay minerals, such as montmorillonite. During injection of

steam at high temperature into the reservoir formation, montmorillonite and feldspar take part in the following chemical reactions [12,13];



It is assumed that the interaction of the Al^{3+} ion with the formed acid H_4SiO_4 occurs, which leads to the formation of surface hydroxyl groups with high acidity, which increases the catalytic activity of the medium [14].

In the presence of quartz, the process of formation of substances with a lower molecular weight, particularly aromatic compounds and saturated hydrocarbons, is intensified; high molecular weight products are predominantly formed using calcite [15].

The research [16] investigates the influence of various clay and non-clay minerals present in carbonate formations (limestone and three different minerals—bentonite, kaolinite, and zeolite) on the process of steam distillation of samples of degassed high-viscosity oils for 40 h. Based on the determination of density, viscosity, and group composition of oil by the SARA method, it is found that all minerals have catalytic activity; kaolinite turned out to be the most effective—as a result of the process, the content of light components increased. In addition, the steam distillation effect is more pronounced in limestone interlayers than sandstone samples [17]. However, hydrothermal reactions in clay minerals significantly deteriorate the reservoir properties of formations, causing a decrease in porosity and permeability [18,19].

In [20], structural changes in the composition of residual oil from the Middle and Upper Devonian sediments of the Romashkinskoye field of different ages were studied under conditions close to the reservoir in a flow-through system.

Due to the aquathermolysis process, the content of hydrocarbon fractions in the extracts (extracted from the rocks) increases, alcohol-benzene resins, asphaltenes, total sulfur, vanadyl porphyrins, and other complexes containing heavy metals decreases. In the composition of biomarker hydrocarbons, the content of tricyclic terpanes increases with a simultaneous decrease in the proportion of steranes and pentacyclic triterpanes. The content of pregnane increases relative to C27 α -sterane, as well as rearranged steranes relative to steranes of regular structure [21].

In [22], the influence of rock-forming minerals such as calcite, dolomite, kaolin clay and manganese oxide on the physicochemical properties of heavy oil during steam treatment of the reservoir formation is considered. It was found that the destruction of high-molecular oil compounds occurs on the surface of mineral supplements with a large surface area, capable of exhibiting catalytic properties. As a result, a monomolecular surface layer with a reduced entropy of adsorbed molecules is formed on the surface of mineral supplements. This shifts the equilibrium towards the thermal decomposition reactions of $-\text{C}-\text{C}-$ bonds by a radical chain mechanism. In addition, the increasing temperature in the absence of high pressure reduces the possibility of their adsorption on the surface of the supplements.

In [23], the authors carried out physical modeling of aquathermolysis of high-viscosity oil in the presence of mineral components of carbonate rocks—dolomite and calcite. Based on the analysis of the group composition and IR spectroscopy, it was found that in the presence of calcite, a significant effect is achieved in reducing the proportion of resins and asphaltenes due to the destruction of the least stable C-S-C bonds. According to the gas chromatography results, it was established that the thermal transformation of bitumoids led to an increase in the proportion of hydrocarbons in the homologous series C19–C30. The analysis of geochemical coefficients showed a high degree of maturation of organic matter of thermally transformed bitumen in a model system with dolomite.

However, in the presence of rock, the catalytic potential from the point of view of heavy oil upgrading is not fully revealed. At the same time, scientists in [16] found that although minerals have catalytic activity during thermal action in a water vapor environment, due to depletion in hydrogen, along with an increase in viscosity and density, the chemical

composition of residual oil also changes. Namely, the proportion of high molecular weight asphaltenes significantly increases.

Many scientists are investigating the transformation of organic matter in water vapor and catalytic systems, including various hydrogen donors [24–26]. This is due to the possibility of intensifying cracking and hydrogenolysis reactions and, consequently, an increase in the degree of viscosity reduction due to the breaking of C–S bonds in high molecular weight components. In addition, catalytic agents will facilitate the release of hydrogen from naphthenic aromatic compounds that are part of the oil directly in the formation [27,28].

According to [29,30], the hydrogen content can significantly affect the composition of the products formed during fluid hydrocracking in a heated reservoir. In the absence of hydrogen, pyrolysis of heteroatomic compounds and polycyclic aromatic hydrocarbons results in the generation of hydrocarbon fluids, including double bonds and radicals. The use of hydrogen makes it possible for the reactions of hydrogenolysis, hydrogenation, and hydrocracking to occur, which reduces the formation of unsaturated double bonds and the polymerization of generated hydrocarbons [31].

In [32], the transformation of heavy oil in the sandstone formation in the presence of an H-donor and oil-soluble catalyst precursor based on a transition metal iron in a water vapor condition was studied. Based on the results of determining the group chemical composition, it was found that the use of a catalyst (2.0% of the mass per mass content of the oil extract in the rock) ensures the transformation of resins by 24% at 250 °C. Moreover, the use of catalyst provides conversion of asphaltenes at 300 °C resulting in a reduction of asphaltenes content to almost “trace” amounts at this temperature. Intensifying destructive processes of breaking heteroatomic bonds in resin and asphaltene molecules contributes to light liquid hydrocarbons generation.

In [33], the effect of kaolin and aluminum oxide (as a rock-forming supplement) in the presence of nickel compounds and poly- α -olefins as hydrogen donors on the thermal catalytic conversion of heavy oil at a temperature of 360 °C in a reducing atmosphere at various pressures in the reactor was investigated. It was found that during the thermobaric process, in the presence of Al_2O_3 , Ni, and poly- α -olefins (at 8 MPa), reactions of the destruction of resinous components, both normal and branched aliphatic substituents in asphaltene molecules prevail. As a result, a redistribution of n-alkanes towards homologs with a lower molecular weight leads to a decrease in the viscosity of heavy oil. Using kaolin in reducing atmosphere and pressure decrease leads to a decrease in the quality of the final product (reduction in aromatic content) and an increase in the yield of lube and low-boiling fractions. Furthermore, it was found that the studied metal complexes with various ligands can penetrate not only into the pore space of the rock but also into asphaltenes, which allows them to catalyze the enrichment of heavy oil under conditions of hydrothermal reaction [10,34].

Thus, this research aims to test an oil-soluble iron-based catalyst in the in-situ upgrading of heavy oil as a reagent that enhances the catalytic effect of rock minerals in reservoir conditions during the development of Permian deposits.

2. Materials and Methods

2.1. Experiment Design

The scheme of the experiment is shown in Figure 1.

2.2. Materials

The objects of study:

- Initial oil extract and oil extracts after steam treatment (extracted from oil-saturated sandstone);
- extracted rock samples;

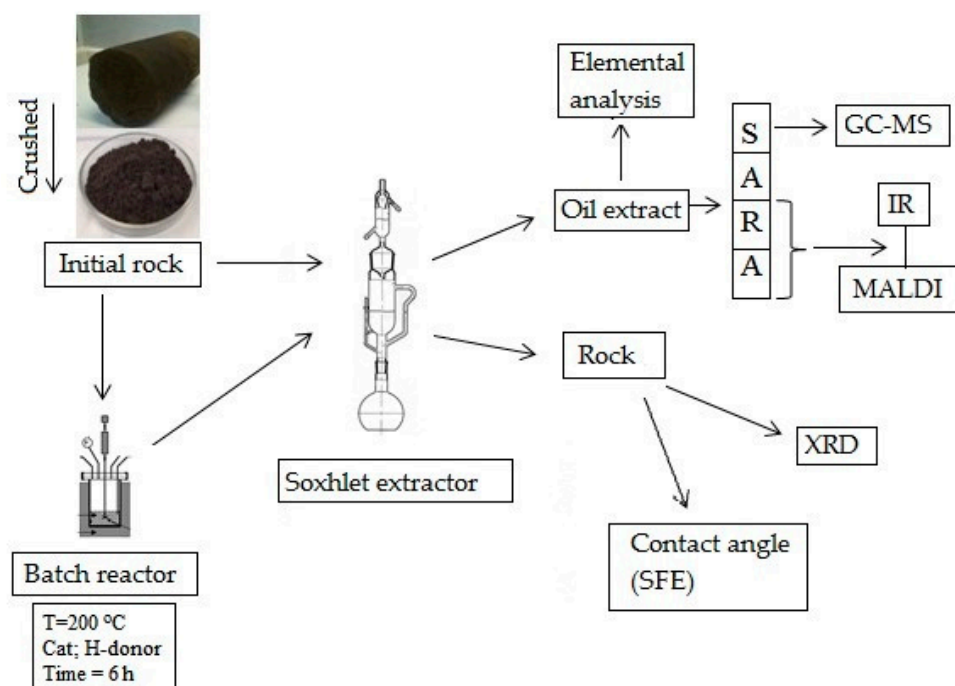


Figure 1. Scheme of the experiment.

Rock samples were sampled from well No. 106 (Ashal’cha field, sampling interval 174.4–177.6 m). Rock samples have undergone steam treatment under the conditions of catalytic and non-catalytic aquathermolysis and the addition of a hydrogen donor.

The characteristics of the oil extract are presented in Table 1.

Table 1. Group composition (SARA) and elemental analysis of oil extract from the initial crushed core.

Sample	SARA Fractions, wt. %							
	Saturates		Aromatics		Resins		Asphaltenes	
Initial core extract	36.1		34.0		23.8		6.1	
	Elemental analysis, wt. %							
	C	H	N	S	O	H/C		
	86.68	11.69	0.41	0.49	0.73	1.618		

2.3. Catalytic and Non-Catalytic Aquathermolysis Modeling in Batch Reactor

Laboratory modeling of steam treatment was carried out in a 300 mL autoclave reactor. The reactor was equipped with a temperature and pressure control and recording system (Parr Instruments, Moline, Illinois, USA). The model system was a mixture of crushed bitumen sandstone and water at a mass ratio of 10:1, which had undergone steam treatment at a temperature of 200 °C in a nitrogen atmosphere. The catalyst precursor and the hydrogen donor were introduced at 2.2 wt% and 1.0 wt% for oil, respectively. The operating pressure was maintained at 2.2 MPa. The duration of the experiment was 6 h after the process stabilization. Oil-soluble iron tallate was used as a catalyst [35], while a hydrogen donor solvent was used as described in [36]. The temperature of 200 °C was selected following the average reservoir temperature during the development of the Ashal’cha field using steam treatment methods, in particular, the SAGD technology.

After the thermal processes, all aquathermolysis products from the model system (Table 2) and the initial rock sample are extracted by a warm mixture of organic solvents in Soxhlet extractor: chloroform, benzene, and alcohol are taken in equal ratios to obtain oil extracts.

Table 2. Model system.

Sample Number	Subject of Research
1	Initial rock extract
2	Product of the non-catalytic aquathermolysis
3	Product of the catalytic aquathermolysis
4	Product of the catalytic aquathermolysis with hydrogen donor

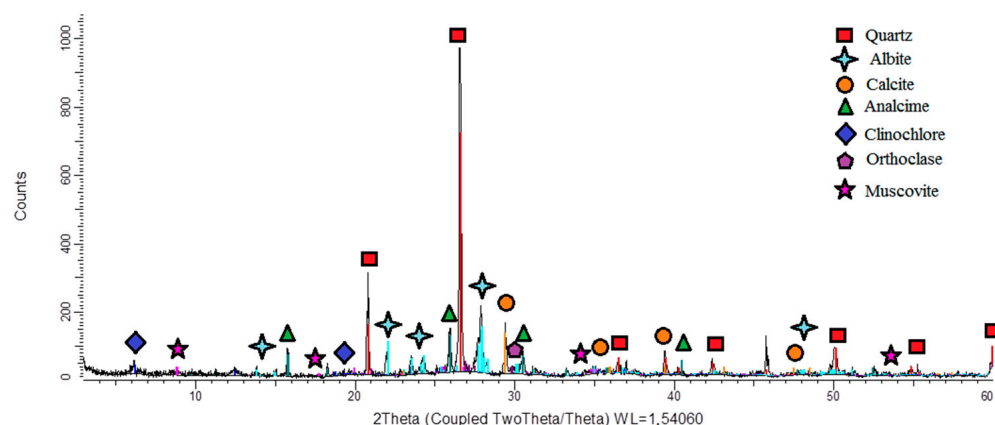
The term «initial rock extract» refers to the crude oil extracted from the untreated crushed rocks by a mixture of solvents such as chloroform, benzene, and alcohol.

After extraction, the phase composition of the sandstone rock was investigated using X-ray diffraction, and interfacial parameters were determined (contact angle and surface free energy (SFE) at the interface between the studied rock—wetting liquid—inert gas (nitrogen).

2.4. Methods for Studying Rock Samples

The X-ray diffraction analysis (XRD) was accomplished using a Shimadzu XRD-7000S automatic powder diffractometer with a nickel monochromator with a step of 0.008 nm and 3 s point exposure, in combination with a Bruker D2 PHASER and CuK α radiation with a wavelength of $\lambda = 1.54060$ nm.

Figure 2 shows the results of determining the phase composition of the original rock after extraction.

**Figure 2.** Phase composition of the original rock.

The main rock-forming minerals of the rock sample are silicates and aluminosilicates. The sample consists of 33% quartz (SiO_2) and 35% albite ($\text{Na} [\text{AlSi}_3\text{O}_8]$)—sodium feldspar of magmatic origin.

The remaining mineral composition accounts for approximately equal shares of minerals such as calcite (CaCO_3), analcime ($\text{Na} [\text{AlSi}_2\text{O}_6] \cdot \text{H}_2\text{O}$)—a mineral from the group of aqueous zeolites, orthoclase ($\text{K} (\text{AlSi}_3\text{O}_8)$)—potassium feldspar, and clinocllore ($\text{Mg}_5\text{Al}(\text{AlSi}_3\text{O}_{10})(\text{OH})_8$, phyllosilicate of magnesium and aluminum with hydroxyl, and muscovite ($\text{KA}_{12}(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$)—aluminosilicate of potassium and aluminum with hydroxyl.

The contact angle and SFE were determined using a KRUSS DSA 100 (Germany) at the interface: studied rock—wetting liquid—inert gas (nitrogen) at atmospheric conditions. SFE was calculated based on the polar and dispersed components, the values of which were obtained from the data of the contact angle when the surface is wetted with water and diiodomethane (non-polar substance). The polar and dispersed components show the presence of hydrophilic and hydrophobic areas on the surface, respectively, and the corresponding nature of wettability. Using a press, tablets were prepared from the extracted rock for all experiments, including the original sample, except for sample No. 3—using a catalyst without a hydrogen donor. Considering the appropriate drop geometry, the

method for determining the contact angle (polynomial, length-height, conical segment, circle, Jung-Laplace, distance between points) was selected.

2.5. Oil Extracts Analyses

Extracts from formations were investigated by the set of physical and chemical methods.

The elemental analysis of oil extracts before and after experiments was measured by elemental analyzer PerkinElmer 2400 Series II.

The study of the chemical group composition of oil extracts was followed by obtaining maltene and asphaltene fractions. Asphaltenes were obtained by precipitation—adding an excess of n-hexane to the extract at a ratio of 1 g of extract: 40 mL of n-hexane [37]. In its term, maltene was separated into 3 groups by the SARA method (saturates, aromatics, and resins) as per ASTM D 4124-09 and state standards, Russian federation 32269-2013. The fractionation was performed in a glass chromatography column by subsequent elution with aliphatic (hexane for saturates) and aromatic hydrocarbons (toluene for aromatic and toluene + methanol for resins) from adsorbent, previously dehydrated neutral aluminum oxide at 450 °C for 3 h [38,39].

The structure-group composition of resin and asphaltene samples was studied by FTIR spectroscopy. IR spectra of resins and asphaltenes were recorded on a PERKIN ELMER Spectrum two with a UATR (Single Reflection Diamond) attachment in the range from 2000 to 450 cm^{-1} with a resolution of 4 cm^{-1} . In order to study the structure-group composition of the investigated products, the spectral coefficients were calculated, defined as the ratio of the optical density values at the maxima of the corresponding absorption bands: C1 = D1600/D720 (aromaticity); C2 = D1710/D1465 (oxidation); C3 = D1380/D1465 (branching); C4 = (D720 + D1380)/D1600 (aliphaticity); C5 = D1030/D1465 (sulfurization index) using a baseline in the 2000–450 cm^{-1} spectrum. The first coefficient is aromaticity due to stretching vibrations of $\text{C}=\text{C}_{\text{arom}}$ bonds of aromatic rings. Oxidation of (C2) is associated with the presence of carbonyl groups (CO); the structure of paraffin chains can be estimated by their branching (C3) CH_3/CH_2 . The fourth factor is aliphaticity $(\text{CH}_3 + \text{CH}_2)/\text{C} = \text{S}_{\text{arom}}$, and it shows the proportion of methyl and methylene groups to aromatic, whereas C5 shows the proportion of sulfoxide groups.

The matrix-assisted laser desorption/ionization (MALDI) method was applied to determine the molecular mass of resins and asphaltenes. The research was conducted on a Bruker mass spectrometer of the Ultraflex III TOF/TOF series with the time-of-flight analyzer. 2,5-Dihydroxybenzoic acid was used as the matrix

In addition, chromatograms of the fraction of saturated hydrocarbons of the extracts before and after thermocatalytic treatment were recorded using a chromatomass-spectrometric system, including a Chromatek-Kristall 5000 gas chromatograph with an ISQ mass-selective detector, Xcalibur software for processing the results. The chromatograph is equipped with a capillary column 30 m long and 0.25 mm in diameter. Gas flow rate (helium)—1 mL/min. Injector temperature—310 °C. The thermostat temperature program—a temperature rise from 100 to 300 °C at a rate of 3 °C/min followed by an isotherm until the end of the analysis. The voltage of the ion source is 70 eV, the temperature is 250 °C. Compounds were identified using the NIST electronic library of mass spectra and according to literature data [40].

3. Results

3.1. Elemental Analysis of Oil Extracts

The initial extract's elemental composition (C, H, N, S) and the experimental products after catalytic and non-catalytic aquathermolysis were determined (Table 3).

Table 3. Elemental analysis of the oil extract before and after experiments.

Subject of Research	Content, wt. %					H/C
	C	H	N	S	O	
1	86.68	11.69	0.41	0.488	0.73	1.618
Aquathermolysis products						
2	84.14	11.19	0.48	0.472	3.72	1.596
3	83.22	11.28	0.59	0.436	4.47	1.626
4	81.81	11.69	0.59	0.343	5.57	1.715

The study results of the elemental composition indicate a slight decrease in the H/C index in the non-catalytic experiment compared to the initial sample No. 1. This is since the destruction of heteroatomic bonds occurs during steam treatment. However, in the absence of an additional source of hydrogen, the oil system is additionally compacted. Even though carbon is declining, the H/C ratio is also declining. The introduction of a catalyst (sample No. 3) and a catalyst with a hydrogen donor (sample No. 4) increased the hydrogen content. This was because of the involvement of H-hydrogen in the aquathermolysis reaction and the provision of a catalyst for the transfer of hydrogen from naphthene-aromatic compounds that make up oil. In addition, the comparison between experiments with and without a catalyst reflected a more realistic picture of steam treatment directly in the field with and without catalyst injection. In this case, experiments in the presence of a catalyst provided an increase in the H/C ratio when compared directly with the non-catalytic experiment.

During the catalytic process, a redistribution of heteroatoms in the samples occurred, resulting in an increase in nitrogen and a decrease in sulfur contents. This is due to the process of “binding” of free sulfur as a result of the destruction of carbon-heteroatom bonds and the formation of hydrogen sulfide and metal sulfides. Metal sulfides are formed at a certain temperature from the introduced precursors in the presence of sulfur-containing compounds that are catalysts for the hydrogenolysis reaction [41]. The amount of oxygen was calculated from the difference relative to the rest of the elements. Therefore, the tendency towards an increase in the oxygen content is explained by a decrease in the proportion of carbon relative to the initial extract.

3.2. SARA Analysis of Oil Extracts Samples

Table 4 shows the results of the SARA analysis.

Table 4. SARA analysis of the oil extract before and after aquathermolysis.

Subject of Research	Composition. %			
	Saturates	Aromatics	Resins	Asphaltenes
1	36.1	34.0	23.8	6.1
Aquathermolysis products				
2	37.1	31.9	23.0	8.0
3	40.1	30.1	22.8	7.0
4	49.7	26.2	17.8	6.3

It can be seen from the table that an increase in the content of asphaltenes is observed during non-catalytic aquathermolysis. Sandstone demonstrates acidic properties, which contribute to both cracking and polymerization reactions. The absence of a hydrogen source in the system leads to the formation of high molecular weight products. The catalyst favors reactions with the transfer of hydrogen from the naphthene-aromatic components contained in the hydrogen donor with donor-hydrogen properties to free radicals [42]. This ensures their saturation and prevents their recombination, which is reflected in a decrease in the proportion of resins and asphaltenes compared to the non-catalytic exper-

iment. The separation of alkyl substituents from resins and asphaltenes molecules due to the destructive hydrogenation process led to an increase in the content of saturated hydrocarbons by 27.2%. The additional introduction of a hydrogen donor improved the effect of reducing resins and asphaltenes content (compared to non-catalytic experience, on average, by 22.0%) due to the complete closure of the formed free radicals as a result of the aquathermolysis reaction.

3.3. IR-Spectroscopy of Resins and Asphaltenes

Spectral coefficients of resins and asphaltenes of the studied oil extracts, calculated based on IR spectra (Figures 3 and 4), are presented in Tables 5 and 6.

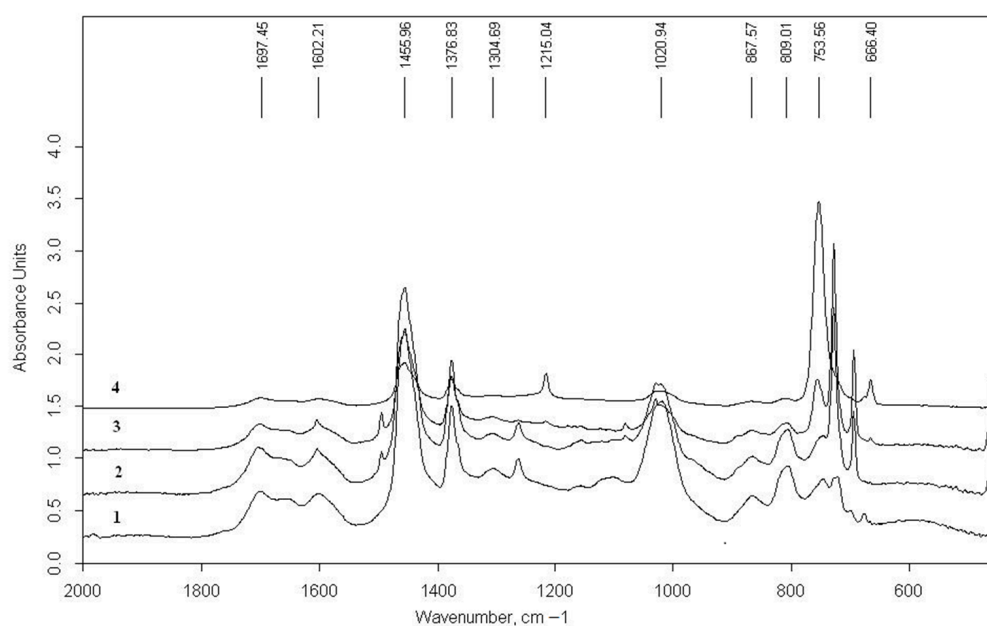


Figure 3. IR spectra of resins of oil extracts.

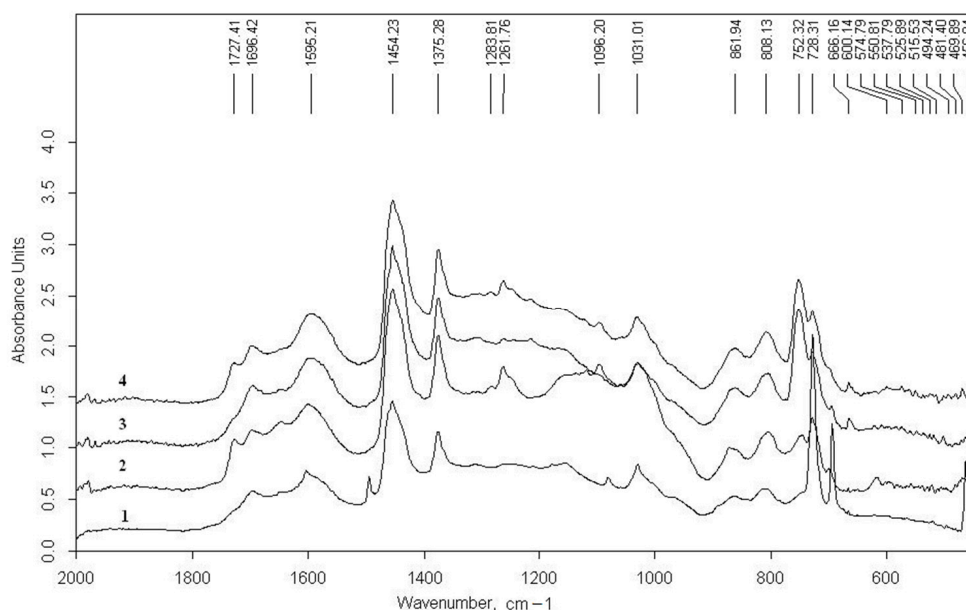


Figure 4. IR spectra of asphaltenes of oil extracts.

Table 5. Results of IR spectral analysis of resins.

Spectral Coefficients	Subject of Research			
	1	2	3	4
C ₁	0.72	0.24	0.15	0.04
C ₂	0.22	0.23	0.22	0.22
C ₃	0.63	0.64	0.62	0.62
C ₄	4.37	7.05	9.31	25.45
C ₅	0.65	0.53	0.43	0.37

C₁ = D₁₆₀₀/D₇₂₀ (aromaticity); C₂ = D₁₇₁₀/D₁₄₆₅ (oxidation); C₃ = D₁₃₈₀/D₁₄₆₅ (branching); C₄ = (D₇₂₀ + D₁₃₈₀)/D₁₆₀₀ (aliphaticity); C₅ = D₁₀₃₀/D₁₄₆₅ (sulfurization index).

Table 6. Results of IR spectral analysis of asphaltenes.

Spectral Coefficients	Subject of Research			
	1	2	3	4
C ₁	1.18	0.33	0.94	0.97
C ₂	0.30	0.35	0.31	0.28
C ₃	0.77	0.78	0.75	0.76
C ₄	2.63	4.63	2.73	2.76
C ₅	0.63	0.54	0.43	0.42
C ₆	0.38	0.45	0.28	0.28

C₁ = D₁₆₀₀/D₇₂₀ (aromaticity); C₂ = D₁₇₁₀/D₁₄₆₅ (oxidation); C₃ = D₁₃₈₀/D₁₄₆₅ (branching); C₄ = (D₇₂₀ + D₁₃₈₀)/D₁₆₀₀ (aliphaticity); C₅ = D₁₀₃₀/D₁₄₆₅ (sulfurization index); C₆ = D₈₈₀/D₇₅₀ + D₈₂₀ (condensity).

According to the results of IR spectroscopy, the structural changes in the molecules of resins and asphaltenes were characterized by a similar orientation, depending on the conditions taken to influence the initial extract in the rock. All considered samples showed that the aromaticity coefficient decreased (this can be seen from the decreasing intensity of absorption bands at 1600 cm^{−1}) with an increasing trend in the aliphatic index for the fractions of resins and asphaltenes (for resins to a greater extent). A significant effect (C₄ increases almost six times) was achieved during the aquathermolysis of oil in the presence of a mixture of a catalyst and a hydrogen donor. This was due to destructive processes in the molecules of resinous-asphaltene compounds that led to the formation of smaller condensed structures, the separation of alkyl substituents, and an increase in the length of alkyl chains. As a result, there is a decrease in the branching index of fragments of n-paraffin hydrocarbons [43]. A decrease in the degree of aromaticity due to thermocatalytic processes indicates a decrease in the stability of the colloidal state of resins and asphaltenes and, possibly, aggregation of asphaltenes to coarser particles up to precipitation from the system [43]. The oxidation coefficient, as expected, does not change since the process of steam treatment proceeds in the system of an inert gas-nitrogen. An equally important change should be considered a noticeable decrease in the sulfurization index, characterizing the content of -SO groups, which is the reason for reducing sulfoxides to sulfides and hydrogen sulfide. This indicates the intensification of the hydrogenolysis reactions of carbon-heteroatom bonds.

The condensity of asphaltenes also significantly changes due to the decompaction of their structure and partial destruction and hydrogenation of C–C bonds in the presence of a catalyst and a mixture of a hydrogen donor and a catalyst.

3.4. MALDI Spectroscopy of Asphaltenes

According to the MALDI mass spectra (Figure 5), the average molecular weight of asphaltenes in the initial extract is 1088; asphaltenes of the products of non-catalytic and catalytic aquathermolysis are 1064, 1052, and 1000, respectively; the average molecular weight of the resins practically does not change 273 ± 0.5.

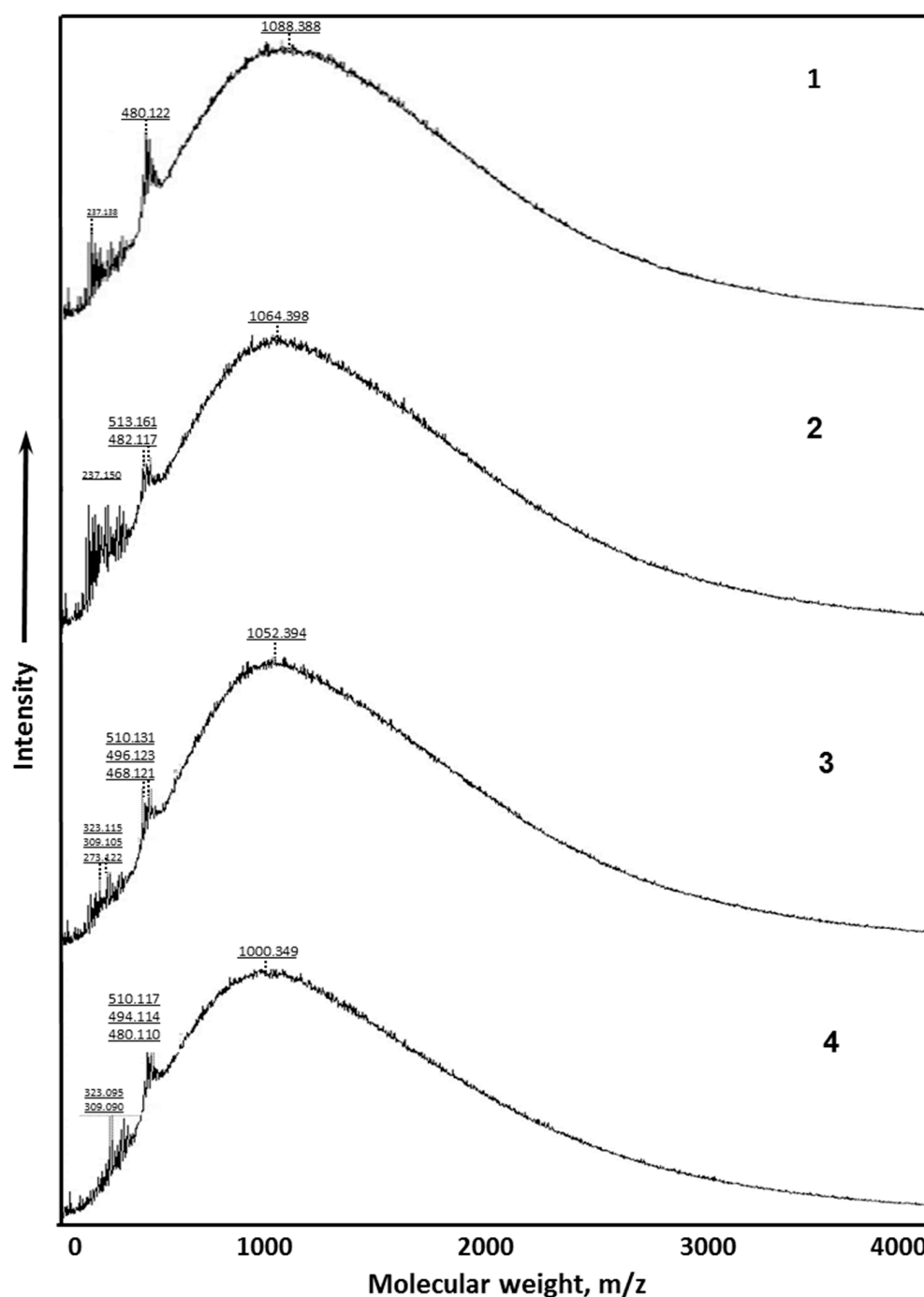


Figure 5. MALDI mass spectra of asphaltenes of samples of extracted extracts: initial (1) and experimental products (2,3,4).

The decrease in the average molecular weight of asphaltenes was explained by the destruction of the least strong carbon-heteroatom bonds in the molecules of the latter and by the detachment of alkyl substituents during catalytic aquathermolysis in the presence of a hydrogen donor. This correlated with the decrease in aromaticity recorded by IR spectroscopy data and the group composition results by the SARA method. However, according to the SARA analysis, the asphaltene content of aquathermolysis products is always higher than the values of the initial extract, with a decrease in the proportion of resins (see Table 4). This may be because the asphaltenes of this oil contain an insignificant amount of C-S bridging bonds, and the decrease in molecular weight occurs mainly due to the separation of alkyl substituents from asphaltene molecules as a result of thermocatalytic

action. Thus, there is no transition from larger “molecules-continents” of asphaltenes to small “molecules-archipelagos,” which could pass into the resin fraction, which is reflected in the high content of asphaltenes in the test products. In addition, large fragments of resins pass into the asphaltene fraction and blocks due to the interaction of side alkyl substituents of asphaltenes and resins [44].

3.5. GC-MS Analysis of Saturated HC

The analysis of the saturated hydrocarbon fraction was investigated using gas chromatography-mass spectrometry (GC-MS). Figure 6 shows chromatograms, and Table 7 shows the calculated values of the distribution of n-alkanes (saturated fraction of hydrocarbons) for the initial extract and the products of the experiments. The content of n-alkanes (in relative %) was calculated using the electronic library of mass spectra NIST from the corresponding peak area.

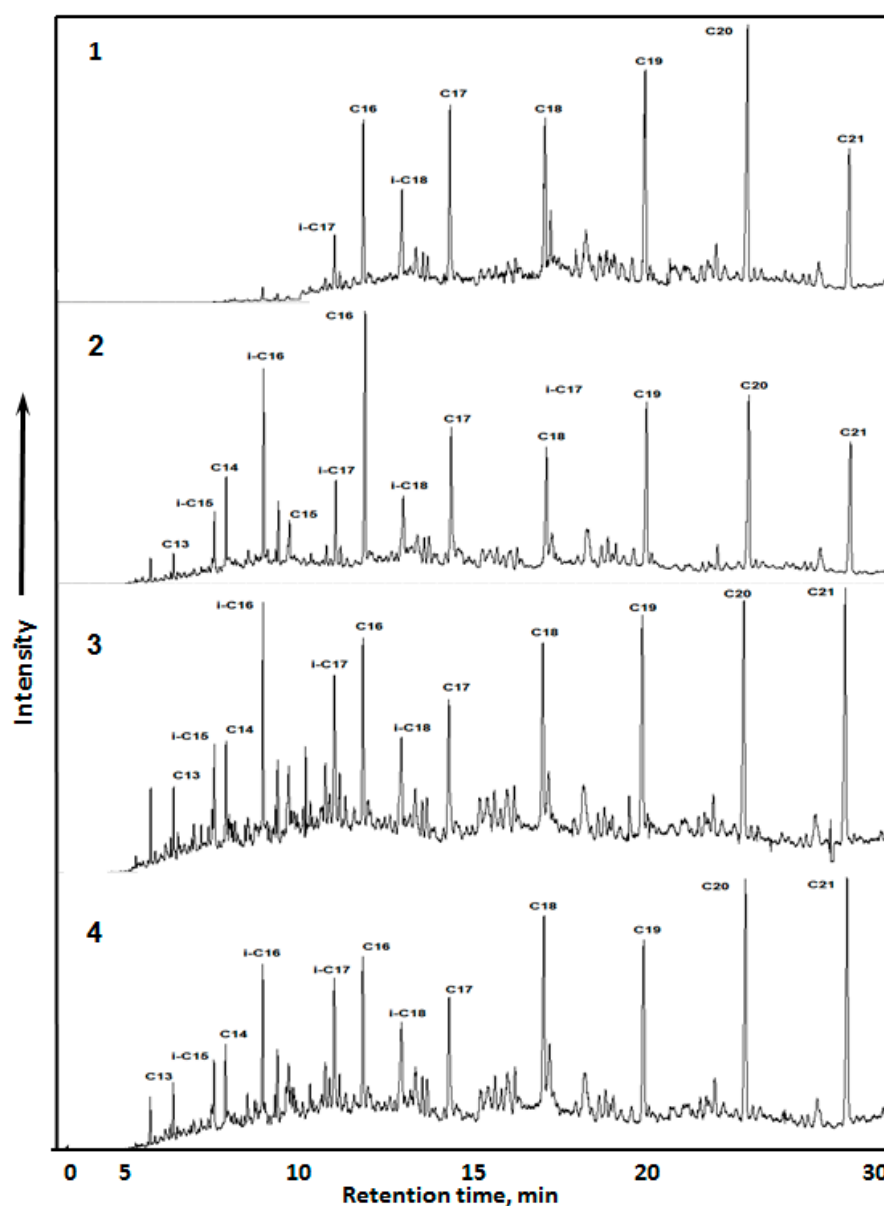


Figure 6. Chromatograms of the saturated fraction of the investigated samples of extracts: initial (1) and experimental products (2,3,4).

Table 7. Calculated values of the distribution of homologs of n-alkanes.

n-Alkan	Content, Relative %			
	Subject of Research			
	1	2	3	4
C12	0.0	0.2	0.2	0.4
C13	0.0	0.3	0.5	0.8
C14	0.1	3.3	3.4	3.5
C15	0.1	1.7	1.3	1.4
C16	10.2	20.3	9.1	10.4
C17	13.4	11.7	11.3	11.9
C18	14.1	10.1	14.3	13.0
C19	20.8	15.9	15.6	17.5
C20	25.8	20.4	21.6	20.8
C21	15.5	16.3	22.8	20.4

The fraction of saturated hydrocarbons of the initial extract is characterized by a low content of normal and iso-alkanes (Figure 6, (1)). The reason could be microbial processes (biodegradation) under thermobaric conditions of oil occurrence in the rock [45–47].

Compared with the Initial rock extract (Figure 6, (1)), in the non-catalytic experiment (Figure 6, (2)), the hydrocarbon composition of the saturated fraction of oil deteriorates—there is a decrease in homologs C17–C20; in this case, only the growth of C16 and C21 alkanes is observed, which can be attributed to the catalytic action of calcite [15,23,34].

Compared to the experiment without catalyst, a significant change in the content of normal alkanes and isoprenoids due to thermocatalytic treatment was observed. New lighter fractions of n-alkanes and isoprenoids are formed, characterized by a hydrocarbon spectrum of homologs of composition from C12 to C15. At the same time, the catalytic steam treatment led to an increase in the proportion of higher molecular weight n-alkanes C17–C21. As noted earlier, in the presence of a catalyst, the destruction processes of C–C and C–S bonds proceed more intensively, which is reflected in an increase in the proportion of the saturated fraction [48–50]. In addition, there is a possibility that coking occurs along with an increase in the proportion of asphaltenes during non-catalytic steam treatment. The high-molecular compounds formed in this case, according to some scientists [51], can capture free C15–C35 hydrocarbons and hold them; a decrease in the proportion of n-alkanes in the saturated fraction can be seen when examining the chromatogram of sample 2 (Figure 6 (2)). During pyrolysis in the presence of a catalyst, thermal destruction of these high-molecular components occurs (a decrease in the proportion of asphaltenes according to SARA data) and the release (thermal desorption) of captured saturated hydrocarbons (Figure 6 (3),(4)) [52]. All this correlated with the results of the SARA analysis.

3.6. SFE Rock Samples

One of the most important parameters characterizing the reservoir rock is wettability. The specificity of the oil displacement process (e.g., polymer flooding, steam treatment, water flooding) depends on the wettability of the porous medium and residual oil saturation distribution. Figure 7 shows the average values of the contact angle at the interface: studied extracted rock—wetting liquid—inert gas (nitrogen) at atmospheric conditions. Table 8 shows the SFE values calculated based on the contact angle as the sum of the dispersed and polar components in the SFE.

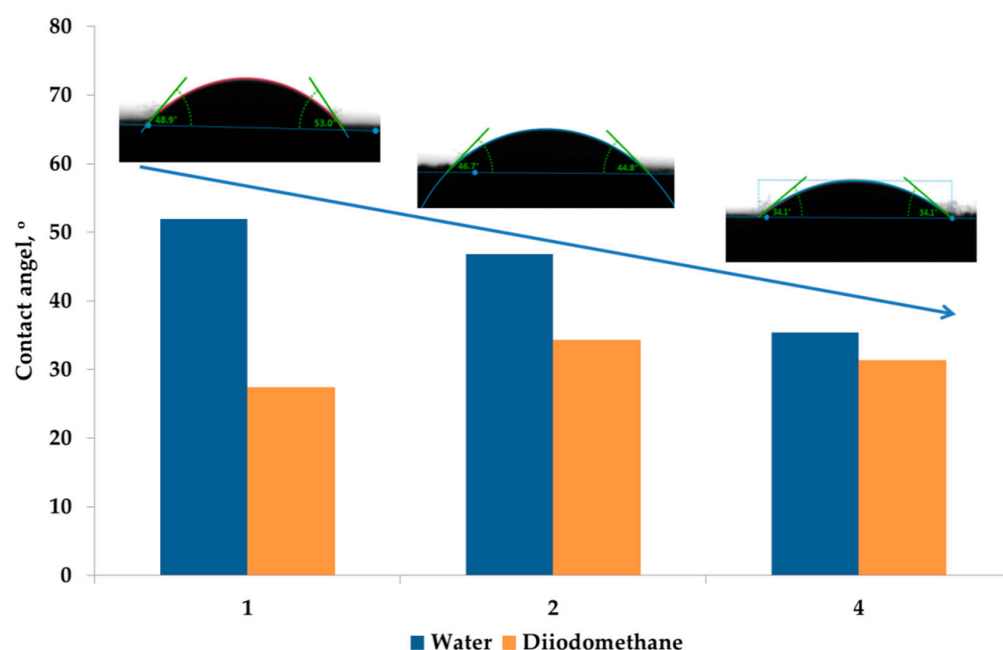


Figure 7. The results of measurements of the contact angle on the surface of the extracted initial sandstone and subjected to steam treatment.

Table 8. Results of mathematical calculation of the free energy of the surface of the extracted initial sandstone and subjected to steam treatment.

Parameter	Subject of Research		
	1	2	4
SFE, mN/m	60.1	61.4	68.3
Dispersed component, mN/m	45.3	42.5	43.7
Polar component, mN/m	14.8	18.9	24.6

Distilled water and diiodomethane were used as polar and non-polar wetting liquids, determining the surface's hydrophilicity (polar component) and hydrophobicity (dispersed component). The surfaces of the samples selected for the study were wetted in turn, respectively, with distilled water (blue line) and diiodomethane (yellow line). Since in this research, it was of interest to determine the contact angle on the initial rock sample, as well as to compare the non-catalytic and catalytic experiments in the presence of a hydrogen donor (since the commercial batch of the catalyst is just the catalyst system in the H-donor), sample No. 3 was not included in wetting studies.

In Figure 7, a photo of a wetting droplet corresponds to droplets of distilled water on the surface of the extracted rocks.

When comparing the extracted samples of the original sandstone (Sample No. 1), samples after non-catalytic aquathermolysis (Sample No. 2), and samples after catalytic aquathermolysis in combination with a hydrogen donor (Sample No. 4), there is a linear dependence of the increase in both the total free surface energy and its polar component. This indicates an improvement in the wettability of the rock with water.

One of the main requirements for chemical reagents during primary and secondary production stages is to improve the wettability of the rock with oil, that is, to hydrophobize the surface of the reservoir channels. In quartz rocks, the main adsorption centers are crystal lattice defects, which carry a negative charge [53]. Research [54] indicates that when oil contacts a reservoir rock under the influence of thermobaric factors over a long period of reservoir formation, the adsorption layer undergoes structural and chemical restructuring. In the rock zones contacted by oil, a solid film is formed, consisting of carbene-carbide products of oil transformation, with a thickness of about 0.5 microns. In our case, the

opposite effect of increasing the hydrophilicity of the surface was observed. This may be due to the combined effect of temperature, pressure, and the use of a catalyst based on transition metals, which ensures the transfer of hydrogen from the naphthenoaromatic component and effectively inhibits the formation of carbene-carbide compounds [41]. This prevents the closure of the hydrophilic active centers of the sandstone.

However, it should be noted that the aquathermolysis process presupposes the presence of high water cut in the produced oil due to steam condensation and the formation of a large volume of water. In our case, it would contribute to a more efficient oil production process due to the predominance of the wettability of rocks with water.

4. Conclusions

Based on the results of the assessment of physic-chemical characteristics (determination of group composition by SARA, MALDI and IR spectroscopy, elemental analysis, and gas chromatography), it can be concluded that the catalyst has a targeted effect on the destruction of the high-molecular compounds, such as resins and asphaltenes, with a significant positive effect on the generation of light hydrocarbons.

Using a complex of a catalyst and a hydrogen donor promotes the destructive hydrogenation process, leading to a decrease in sulfur content, which is important in the extraction and further processing of high-sulfur bituminous oils.

The study on the wettability of rocks revealed the effect of increasing the hydrophilicity of the surface associated with the combined effect of temperature, pressure, and the use of a catalyst based on transition metals. The combination of these processes ensures the transfer of hydrogen from the naphthene-aromatic component. As a result, it effectively inhibits the formation of carbene-carbide compounds, which favors an efficient oil recovery process due to the predominance of water wettability of rocks.

Author Contributions: Conceptualization, S.A.S.; methodology, I.I.M. and Y.V.O.; software, D.A.F.; resources, V.A.S.; writing—review and editing, A.V.V. and M.I.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by the Russian Science Foundation, Grant number 21-73-30023.

Conflicts of Interest: The authors declare no conflict of interest.

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