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Effect of Temperature on Kerogen Transformation and Hydrocarbon Generation in Bazhenov Formation (Western Siberia, Russia) Rocks During Hydrous Pyrolysis

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Abstract: The aim of this investigation is to determine the role of temperature in hydrocarbon generation in Bazhenov formation source rocks, as hydrothermal processes in situ are supposed to be the main contributor to kerogen transformation in Western Siberia. Laboratory modeling of organic matter isothermal transformation in powdered and extracted samples by hydrous pyrolysis at 300 °C, 325 °C, 350 °C, 375 °C, and 400 °C for 24 h was performed. Heated samples were analyzed via pyrolysis, and hydrocarbons were investigated by GC and GC-MS. Results show that more than 90% of the kerogen generation potential was utilized. The amounts of liquid and gaseous products reached 82 and 126 mg of hydrocarbon/g TOC, respectively. The volume of generated gas increased while the maximum production of liquid decreased with temperatures over 350 °C. The biomarker composition of liquid products at different temperatures was similar. The characteristics of kerogen and the product composition had a high correlation with the parameters for samples naturally formed in situ under an elevated heat flow. More subtle chemical analyses are required to determine the effects of kerogen's chemical structure and the rock mineral composition on oil and gas generation.

Keywords: Bazhenov formation; hydrous pyrolysis; pyrolysis; kerogen; organic matter conversion; oil and gas generation; biomarker analysis; Western Siberia

1. Introduction

Oil and gas source rocks are key objects in hydrocarbon (HC) systems. They play a fundamental role in the processes of hydrocarbon generation. The result reflected in the amount and composition of hydrocarbon compounds will be determined by the nature of the organic matter, the composition of the source rocks, as well as the heat flux and the duration of its action. There have been many studies performed to investigate the transformation of kerogen (a solid organic substance insoluble in organic solvents [1]) into liquid and gaseous hydrocarbon compounds. They are based on the analysis of the composition of formation fluids in source rocks. The patterns of fluid characteristics' dependence on the type and maturity of organic matter were determined. One of the most representative results is shown in the Biomarker Guide [2,3].



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Kerogen's properties are a governing feature for the process of oil and gas generation. Kerogen is divided into three types according to its elemental composition or Rock-Eval pyrolysis data [4]. The kerogen types correspond to different origins. Type I is formed from a lacustrine–algal residue and has a high H/C ratio and pyrolysis hydrogen indexes higher than 700 mg HC/g TOC. Type II kerogen is formed mainly from marine plankton. It is characterized by a lower H/C ratio, a larger number of cyclic structures, oxygen-containing groups, and fewer aliphatic structures compared to type I kerogen. The hydrogen index for immature ones is in the range of 300–700 mg HC/g TOC. Through a geological history, with an increase in geothermal heating, the structure of kerogen begins to transform, and hydrocarbons are formed. The type of kerogen directly affects the ratio of its conversion products and their composition. Meanwhile, the arrangement of aromatic and aliphatic rings, different functional groups in the kerogen structure, varies depending on the original organisms, conditions of sedimentation, and subsequent lithogenesis. Thus, the pathways of kerogen transformation and hydrocarbon composition will vary [5]. This means the same type of kerogen can vary quite significantly depending on the investigated region [6]. Nowadays, the existing data can generally be used to predict the kerogen conversion ratio and amount and the composition of generated products marginally, and quite exactly only for highly researched basins. Additionally, source rocks may be exposed by elevated heat flows associated with the movement of heated fluids along faults in tectonic fault zones [7]. Based on the above transformation processes, studies should take place at the exact objects.

Laboratory modeling methods are used to investigate kerogen transformation and oil and gas generation. There have been a variety of experiments on heating kerogencontaining rocks under different conditions performed for many shale formations around the world: the Green River formation (UT, USA) [8–10], the Aarip Basin in Brazil [11], specimens from the Sargelo formation in Iran [12], rocks from the Ordos Basin in northwestern China [13,14], rocks from the Sichuan Basin in southern China [15], the Bohai Basin in eastern China [16], rocks from the Kinshu Basin in southern China [17], and several others. The key methods are heating samples in gold tubes, pyrolysis in an open system, and hydrous pyrolysis in a closed system. Meanwhile, all experiments have been self-consistent with their own methodology. Pyrolysis research has been performed for almost all formations of the world, and the results are comparable, but the kerogen structure for at least one specific formation of the world is poorly studied. The results of oil and gas generation modeling for the same type of kerogen in different basins may contradict each other, which indicates the kerogen transformation process's complexity. The process might be affected by variations in the kerogen's chemical structure, the mineral matrix composition and structure, the sample preparation approach (whether pulverization or extraction was performed), and the conditions of the experiment. A secondary cracking of the formed products can play an important role in the process. Therefore, to determine the characteristics of organic matter, studies for each new object should be performed.

Most investigations on kerogen transformation in Russia were performed for the Domanic formation source rocks of the Volga and Ural provinces and the Bazhenov formation of Western Siberia. Under temperature exposure, generation potential was released, and different hydrocarbon compositions were obtained [18–21]. In these studies, fluid generation was investigated in sufficient detail, but only in some rare cases were the conclusions on the kerogen structure and its changes during maturation drawn [20,22]. Thus, the results do not demonstrate kerogen's variability and its transformation dynamics through geological evolution. The data for the Bazhenov formation kerogen alteration are limited. The influence of the complex lithological composition of the sediments [18,23], the uneven distribution of macerals across the section and lateral area [24], differences in generation at various stages of the catagenesis [25], the role of bitumen present in the rocks, and the possibility of hydrocarbons removal from the reaction zone are discussed in very few research investigations.

The goal of the study is to assess the effect of temperature on the Bazhenov formation's kerogen transformation using a characteristic sample from the central part of Western Siberia. Under the same heating time, with the absence of hydrocarbon compound influences and differences in the mineral matrix structure, divergences in the process under 300–400 °C could be determined. For this purpose, a model isothermal experiment on the pulverized and extracted rock sample with immature type II kerogen in a closed system was set up. The kerogen pyrolysis parameters and generated fluids' composition were compared with the same parameters of a rock sample and the hydrocarbons from the Bazhenov section in a nearby area, where organic matter achieved the middle of the oil window. The results will show whether hydrothermal processes affect hydrocarbon generation in the main source rocks of Russia and serve as a starting point for kerogen structure and characteristics investigations, to determine their role in hydrocarbon systems.

2. Materials and Methods

2.1. Geological Characteristics of the Object

The investigated wells are located in the West Siberian petroleum basin (Figure 1). In the structure of the West Siberian basin, the Mesozoic–Cenozoic sedimentary cover and the Paleozoic basement are distinguished. The sedimentary cover is composed mainly of terrigenous rocks. The target interval of the study is confined to the Volgian (J3vol) deposits—the Bazhenov formation, represented by clayey, siliceous high-carbon rocks (Figure 1). A lithological and stratigraphic column for the Mesozoic age and Paleozoic basement of the region under study was constructed based on previous investigations [26]. The Bazhenov formation was deposited in deep-sea marine environments during an extensive transgression that began in Oxfordian time (J3o) [27,28].

In the section of the Bazhenov formation, six units can be distinguished, which combine rocks with similar lithological characteristics. The first unit is composed of clay-flint rocks. The second one is similar in mineral composition to unit I but differs in numerous finds of bivalve mollusk shells. The third unit is composed of kerogen–clay–silicon varieties with interlayers and radiolarite lenses. Radiolaritic interlayers are usually unevenly carbonated and partially recrystallized. The first three units are combined into a Bazhenov lower subformation (LB). The fourth unit is represented by clay–silicon–kerogenic varieties with numerous shells of bivalves and ammonites. The fifth unit is composed of kerogenic– siliceous–argillaceous varieties with numerous nodules and interlayers of carbonates. There is also carbonate in the matrix, partly associated with the content of carbonate skeletons of coccolithophores and calcispheres. The sixth unit is composed of siliceous–argillaceous varieties with a high content of pyrite, up to 30%, as well as numerous contractions of pyrite. In the section of the Bazhenov formation, this unit is periodically replaced by the upper transition zone (UTZ) to the overlying sediments.



Figure 1. Location of wells (**right**) and the studied interval in the section of the sedimentary cover (**left**).

2.2. Materials

Core samples from wells A and B (Figure 1), drilled at a distance of over 50 km from each other, were used as test materials; 99 pyrolytic studies were performed on extracted samples and 89 tests were performed by X-ray fluorescence spectroscopy (XRF). For well B, 107 pyrolytic studies and 110 XRF analyses were performed. After that, one sample was selected from well A, for which a set of experiments on hydrous pyrolysis was carried out with further analysis of the released hydrocarbons and a study of changes in the pyrolytic characteristics. The results were compared with a similar sample from well B, for which the characteristics of bitumen from the pore space were also studied using the GC–MS method (Section 3.4 below).

2.3. X-Ray Fluorescence Spectroscopy (XRF)

The initial samples were crushed to a size of <0.074 mm, after which glassy discs were made from them by melting the calcined sample material with the addition of lithium borate (10:1) at a temperature of 1200 °C in gold–platinum crucibles in the MiniFuse induction melting furnace (Philips, The Netherlands). The molten material was poured onto a gold–platinum mold heated to a temperature of 700 °C, in which it was completely cooled and solidified to obtain a glassy preparation in the form of a disc with a glossy surface.

Further analysis was carried out using the Axios mAX Advanced vacuum X-ray fluorescence spectrometer (PANalytical, Almelo, The Netherlands). The results were

processed in software (SuperQ-5.0, Almelo, The Netherlands). In addition, weight loss on ignition (LOI) was assessed. For this purpose, the change in the weight of the test sample was measured before and after the calcination of sample powders in a muffle furnace at a temperature of 1000 $^{\circ}$ C for 1 h.

The results obtained were used to calculate the mineral-component model; thus, the standard mineral composition of the rocks was obtained [29]. The general approach was described previously [30–32]. In this work, we used conversion to the most common minerals described for the Bazhenov formation: clay, apatite, barite, albite, pyrite, siderite, dolomite, calcite, quartz, and chalcedony (silica) [33]. In addition, the content of organic matter (OM) was determined on the basis of pyrolytic studies. All results were combined and displayed on geological and geochemical plates built using Techlog software version 2021.1.1 (Schlumberger, Paris, France).

2.4. Pyrolysis

To characterize the initial organic matter and to study the changes in kerogen after the removal of bitumen, pyrolysis of samples was carried out by the Rock-Eval method [34] on HAWK Resource Workstation equipment (Wildcat Technologies, Humble, TX, USA). A weight of 30 mg was used for the analysis. The processing of the obtained pyrolytic spectrum was carried out using HAWK-Eye software version r:8364 (Wildcat Technologies, Humble, TX, USA).

As part of the work, the parameters S2 (mg HC/g rock) and T_{max} (°C) were measured. The S2 parameter shows the amount of kerogen contained in the rock, and T_{max} is determined by the temperature at which the maximum formation of S2 occurs; this parameter is a measure of the maturity of the rock sample [34]. Among the calculated parameters, the hydrogen index (HI) was used. The HI (mg HC/g TOC) changes with the increase in the maturity of organic matter. Total organic carbon (wt. %) shows the total content of organic carbon in the sample. GOC (wt. %) and NGOC (wt. %) are generative and non-generative organic carbon. These parameters show the amount of organic carbon involved in the formation of hydrocarbon compounds or the part of kerogen with a complicated structure that can only be burned with oxygen to produce CO and CO₂. The measure of inaccuracy relative to the WT2-HAWK-STD reference material was ±10% for the S2 and HI measurements, ±2 °C for T_{max} , and ±5% for TOC, GOC, and NGOC. The calculations of the other pyrolytic parameters, given in the Supplementary Materials, are also described in detail [34].

2.5. Hydrous Pyrolysis

The sample selected for hydrous pyrolysis was preliminarily rubbed. All bitumen was removed by Soxhlet extraction using alcohol–benzene (1:1). The extracted sample was divided into 5 equal parts and immersed in an autoclave (Comvics, Moscow, Russia). Seventy mL of distilled water was added to the powdered samples. The autoclaves were lowered into a tube furnace preheated to the desired temperature for 24 h. The heat was set using an OWEN TPM-10 PID controller (Owen, Russia) using a chromel–aluminum thermocouple with an accuracy of ± 5 °C. The temperatures of the experiments were 300 °C, 325 °C, 350 °C, 375 °C, and 400 °C, determined as the Bazhenov formation kerogen transformations window [18].

After the experiment was completed, the autoclave was cooled with running water, and a gas sample was taken through a system of special tubes into a penicillin flask filled with a saline solution. The total volume of the gas formed was recorded by the volumetric method with an accuracy of 2.5 mL.

After gas extraction, the autoclave was opened, and 10 mL of pentane (chemical grade purity, Ekos-1, Moscow, Russia) was poured in, dissolving the released light synthetic oil on the walls of the autoclave and the water surface, after which the water and light oil were separated using a dividing funnel. The sample powder was extracted and dried at room temperature to a constant mass. Heavy synthetic oil was collected from the walls of the autoclave with alcohol–benzene. The amount of light and heavy synthetic oil was determined by the weight method with an accuracy of 0.00005 g after removing the solvent by evaporation at room temperature.

2.6. Gas Chromatography of Hydrocarbons

The analysis of released hydrocarbons in gases was carried out on the analytical complex of a "Chromatech-Crystal 5000" chromatograph (CHROMATEC, Yoshkar-Ola, Russia) with a flame-ionization detector (FID). The calculation of the concentrations of gas components was carried out by peak areas. For calibration, concentrations in certified gas mixtures containing both saturated and unsaturated hydrocarbon compounds were used (Monitoring, Saint Petersburg, Russia). The results were processed using the Chromatec-Analytic program (CHROMATEC, Yoshkar-Ola, Russia).

2.7. Gas Chromatography-Mass Spectrometry (GC-MS)

Biomarker parameter analysis was performed for light and heavy synthetic oil samples from hydrous pyrolysis experiments, as well as for bitumen from the well B comparison sample. To extract light hydrocarbon compounds from the open pores of the comparison sample, hot extraction was used in a Soxhlet apparatus using pentane (Ekos-1, Moscow, Russia) according to the international standard ASTM D5369-93 [35]. Extraction was completed when the bitumen concentration in the solution of the cooled Soxhlet apparatus reached less than 0.000625%. Because pentane is a non-polar solvent, it does not affect the polar resin–asphaltene compounds that can block the pore space to form sealed pores. Upon completion of pentane extraction, the extract was collected, and the sample was re-placed in the Soxhlet apparatus, where extraction with alcohol–benzene was performed. The analysis method is described in more detail in the article by Tikhonova et al. [36,37].

The determination of biomarker hydrocarbons was carried out on an Agilent 8890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) connected to a 5977B mass spectrometric detector (Agilent Technologies, USA) with an Inert plus ionization source. The separation was carried out on a 60 m \times 0.25 µm \times 0.25 µm capillary GC column (Agilent Technologies, Santa Clara, CA, USA). Samples of the studied fluids were preliminarily separated by SARA analysis [38]. To determine the molecular composition of synthetic oils and bitumen, studies were carried out for saturated and aromatic fractions. The desired compounds were identified on certain mass fragments using MassHunter Qualitative Analysis software version 10 (Agilent Technologies, Santa Clara, CA, USA).

3. Results

3.1. Characteristics of Wells

In well A, 28 m of the Bazhenov formation were penetrated, including LB, IV, and V units, as well as the UTZ (Figure 2). For XRF analyses of well A samples, see the Supplementary Materials, Table S1. In the LB, the amount of siliceous material is approximately the same and averages 48–50 wt. %. In some intervals, the values reach 70–90 wt. %. The amount of clay material does not achieve 25 wt. %, and the average value is 15 wt. %. The content of organic matter (OM) in the LB is mostly the same and averages 15 wt. %. In the lower part of the LB, there is a single layer with a high content of carbonate material, containing 77 wt. % of calcite and 18 wt. % of dolomite. In the IV unit, the content of OM

increases, equal to an average of 25 wt. %. The number of clays is on average 17 wt. %, and the content of siliceous material is about 37 wt. %. In some interlayers, an increased content of carbonates (up to 32 wt.%) and pyrite (about 12 wt.%) was determined. The V unit is characterized by an increased content of carbonate material, in some interlayers reaching 60–80 wt.%. The amount of silica and clay minerals is 32 wt.% and 20 wt.%, respectively. The UTZ is composed of siliceous–argillaceous varieties and is characterized by low values of OM content.



Figure 2. Geological and geochemical plate of well A. Red frame, a sample selected for further research.

According to the results of pyrolytic measurements after extraction, the S2 parameter in the LB of well A averages 43.5 mg HC/g rock. Average TOC values are about 7 wt.%. At the same time, in single-carbonate or high-siliceous interlayers, these parameters lower to approximately zero. Samples from the IV unit are the most enriched in OM and show similar values of pyrolytic parameters in the sample. The average value of S2 is 86 mg HC/g rock, and TOC is ca. 16 wt. %. At the same time, there are single layers with an OM content of up to 44 wt. %. The V unit is characterized by less homogeneity. The range of changes in S2 is from 5 to 108 mg HC/g rock, with an average of 48 mg HC/g rock, and TOC is 2–21 wt.%, with an average value of 10 wt. %. The T_{max} parameter varies in the range of 429–441 °C, the mean is 435 °C, and the HI is 284–856 mg HC/g TOC with an average of 460 mg HC/g TOC. TOC values in samples from the upper transition zone range from 1 wt. % to 3 wt. %, showing the smallest amount of OM for the entire section under study. Pyrolysis results after the extraction of samples from well A are shown in the Supplementary Materials, Table S3.

Well B penetrates 26 m of the Bazhenov deposits. These include LB, IV, and the lower part of the V units (Figure 3). For XRF analyses of well B samples, see Supplementary Materials, Table S2. The results of the studies showed that in the LB, the amount of siliceous material increases up the cut, reaching maximum values of 70–90 wt.%. The amount of clayey material naturally decreases, lowering from the values of 40–50 wt. % at the base of the section to values of 10–25 wt. % in its middle. In the upper part of the LB clayey material is practically absent. The content of OM in the LB is mostly the same and averages about 10 wt. %. There is a single interlayer of carbonate material containing about 60 wt. % dolomite and 12 wt. % calcite.



Figure 3. Geological and geochemical plate of well B. Red frame, sample selected for comparison.

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In the IV unit, the contents of clayey material and carbonates increase. The average amount of clay is 19 wt. %, the amount of OM varies in the range from 10 to 23 wt.% and averages 18 wt.%, and the amount of carbonate materials is 3 wt.%, with the exception of individual interlayers with a carbonate fraction of 29–48 wt.%. The content of siliceous material is about 44 wt.%. At the beginning of the V unit, the amount of silica and clay minerals decreases, and the amount of the carbonate component increases and reaches 20–25 wt.%, and in the unique layer, the value is equal to 92 wt.%. The amount of silica varies in the range of 30–37 wt.%, and the amount of OM decreases to the values of 12–16 wt.%.

Pyrolytic measurements of samples from well B after extraction show an average S2 value of about 23 mg HC/g rock for samples from the LB, and TOC of 7 wt. %, while at the very bottom of the section, there is practically no OM. The IV pack is characterized by higher concentrations of OM. The S2 parameter ranges from 3 mg HC/g rock to 50 mg HC/g rock, with an average value of about 16 mg HC/g rock, and TOC of 2–15 wt.%, with an average of 12 wt.%. In samples taken from the V unit, the average S2 value equals 23 mg HC/g rock, and TOC is 9 wt.%. The lowest OM content is observed for the samples with the highest amount of carbonate. The mean T_{max} is 443 °C and the HI is 295 mg HC/g TOC. Pyrolysis results after the extraction of samples from well B are shown in the Supplementary Materials, Table S4.

Two samples, from wells A and B, were selected from the IV unit, as it contains the highest amount of OM in both wells. The samples have a similar composition and belong to clayey–kerogenic–siliceous rocks. The experiments on the OM transformation during hydrous pyrolysis were performed with the sample from well A, and the sample from the more mature well B was used for comparison of the natural and laboratory transformation. The pyrolytic parameters of these samples are presented in Table 1.

Well	S2, mg HC/g Rock	TOC, wt. %	Tmax, °C	HI, mg HC/g TOC	GOC, wt. %	NGOC, wt. %
А	170	24.2	429	701	14.6	9.7
В	61.8	14.7	436	421	5.4	9.3

Table 1. Pyrolytic parameters of samples selected for the study of oil and gas generation processes.

3.2. Characteristics of Kerogen

Measurement of the pyrolytic parameters of the extracted samples after multitemperature experiments of hydrous pyrolysis allowed the recording of the thermal evolution of kerogen (Table 2). With an increase in the heating temperature, the value of the S2 parameter after extraction, which characterizes the generation potential of kerogen, decreases. After 24 h under 300 °C, about 43% of the kerogen potential was realized; at 325 °C, 91%; at 350 °C, 85; and at 375 °C and 400 °C, almost the entire potential was converted into hydrocarbons. The amount of TOC in the experiments decreased by 32% at 300 °C, and in the rest, by about 53%. At the same time, the amount of generative organic carbon decreased, reaching a value of about zero at high temperatures, and the proportion of non-generative organic carbon, on the contrary, increased. All pyrolytic parameters are presented in the Supplementary Materials, Table S5.

Heating Temperature, °C	S2, mg HC/g Rock	TOC, wt. %	T_{max} , °C	HI, mg HC/g TOC	GOC, wt. %	NGOC, wt. %
Initial sample	170	24.2	429	701	14.6	9.7
300	96.5	16.5	434	586	8.3	8.2
325	16.1	11.3	450	141	1.5	9.9
350	22.2	11.4	445	195	3	9.39
375	2.5	11.4	578	21	0.3	11.1
400	1.1	11.7	603	9	0.2	11.5

Table 2. Pyrolysis results of extracted samples after hydrous pyrolysis for 24 h.

The OM maturity parameters (Tmax and HI) show the degree of maturation increase for the studied samples. The T_{max} parameter at 325–350 °C increased from 429 °C to 445–450 °C, and the HI decreased from 701 mg HC/g TOC to 141–195 mg HC/g TOC. Experiments at higher temperatures resulted in values of 578–603 °C and 9–21 mg hydrocarbon/g TOC for T_{max} and HI, respectively. The data indicate that the kerogen has passed through the oil window and entered the gas window.

3.3. Composition of Hydrocarbons in Gaseous Products

The specific yield of gaseous hydrocarbons increased from 0.2 mg HC/g TOC at 300 °C to 82 mg HC/g TOC at 400 °C (Table 3). At the same time, there was a lower hydrocarbon yield at a temperature of 350 °C than at 325 °C. The presence of supercritical water in the system led to a sharp increase in the specific gas yield in the experiments under 375 °C and 400 °C.

Heating Temperature, °C	Specific Yield C1, mg HC/g TOC	Specific Yield C ₂ –C ₆ , mg HC/g TOC
300	0.1	0.1
325	4.1	10.3
350	2.5	6.4
375	21.4	51.5
400	31.8	50.2

Table 3. Specific hydrocarbon gas yield during hydrous pyrolysis experiment.

The distribution of normal alkanes and their homologues in the gas mixture is shown in Figure 4. With an increase in temperature, there is an increase, both in the total amount of hydrocarbons and, separately, methane and C₂–C₆ gases. The ratio of methane to other gases is almost the same in the temperature range of 325–375 °C. The number of isoalkanes is less than their normal homologues. These distributions correlate well with the composition of natural gases produced in the gas fields. At the same time, the composition of gas products after heating at 300 °C differs; the ratio of ethane and propane is much higher. In the composition of gaseous products after heating at 400 °C, an increase in the share of methane was recorded. Results of the GC analysis of HC synthetic gas after heating are shown in the Supplementary Materials, Table S6.



Figure 4. Composition of hydrocarbon gases synthesized under different temperatures.

3.4. Liquid Hydrocarbon Products

The specific yield of light synthetic oil at 300 °C is 1.3, and at 325 °C it is 44.2 mg HC/g TOC (Table 4, Figure 5). At the same time, a further increase in temperature to 375–400 °C leads to a decrease in the proportion of released hydrocarbon fluids to 21.3 and 8.9 mg HC/g TOC, respectively. The yield of heavy synthetic oil rises up to the temperature of 350 °C, reaching 83.7 mg HC/g TOC. Further, there is a decrease in the heavy products to 33.6 mg HC/g TOC at 400 °C.

Specific Yield of Light Specific Yield of Heavy Heating Temperature, °C Synthetic Oil, mg HC/g Synthetic Oil, mg HC/g TOC TOC 300 1.3 13.7 325 44.2 54.5 350 42.4 83.7 375 21.3 57.5 400 8.9 33.6



 Table 4. Specific yield of synthetic oil during a hydrous pyrolysis experiment.

Figure 5. Specific yield of light and heavy synthetic oils.

The results of oil generation were investigated by the comparison of the synthetic oils and the extracts' molecular composition. For this purpose, biomarker parameters were used, which made it possible to characterize the lithological composition of the oil and gas source rocks and the nature of the organic matter and its maturity, as well as the sedimentary conditions, in particular, whether they were marine or continental and oxidizing or reducing. Parameters characterizing the sedimentary conditions and lithological composition of rocks include Pr (i-C19 berth)/Ph (phytan i-C20), C29 ($17\alpha(H)$,21 $\beta(H)$ -norgopan)/C30 ($17\alpha(H)$,21 $\beta(H)$ -gopan), t24 (C24H44 tricyclic terpan)/t23 (C23H42 tricyclic terpan), t26 (C26H48 tricyclic terpan)/t25 (C25H46 tricyclic terpan) and H31R ($17\alpha(H)$, $21\beta(H)$, 22(R)-homogopan)/C30 ($17\alpha(H)$, $21\beta(H)$ -gopan), H35S/H34S (H35S-17α(H),21β(H),22(S)-pentaxisgogogopan, H34S-17α(H),21β(H),22(S)tetrakisgogogopan), dia/(reg + dia)C27. The nature of organic matter is characterized by the parameters Pr/C17, Ph/C18, (t28 + t29)/C29 (t28-C28H52 tricyclic terpan, t29-C29H54 tricyclic terpan), t23/H30. The parameters used as maturity parameters are Ts/(Ts + Tm), Ts/C30, H32S/(S + R) (ratio of two epimers (20R and 20S) 17α (H),21 β (H) bisnorgogopan), $bb/(aa + bb)C29 (bb/(aa + bb)C29 = (29\beta\beta R + 29\beta\beta S)/(29\alpha\alpha S + 29\alpha\alpha R + 29\beta\beta R + 29\beta\beta S))$ and aa20S/(S + R)C29 (ratio of two epimers (20R and 20S) 24-ethyl- 5α (H), 14α (H), 17α (H) cholestan). These parameters are widely used in organic geochemistry [39–42]. The mass fragments with different m/z ratios for all the synthesized products from the rock sample of well A and extracts from the samples of well B are shown in Figures S1-S60.

The results of GC-MS analysis showed that according to most biomarker parameters, light and heavy synthetic oils practically do not differ much from each other. Significant discrepancies were detected in the ratios of some peaks of the terpanes group (Figure 6). All mass fragments for the synthetic oil and bitumen from the comparison sample are presented in the Supplementary Materials, Figures S1–S60.



Figure 6. Changes in the ratios of hydrocarbons' biomarkers in light (pentane) and heavy (alcoholbenzene) synthetic oils.

The values of biomarker parameters for light and heavy synthetic oils are shown in Table 5. To check how statistically significant the differences in the compositions of light and heavy oils are after heating, the mean, dispersion, and standard deviation for all extracts were calculated based on the assumption that the change in parameter values is subject to the normal distribution. It was found that a strong dispersion was observed only for the Pr/Ph, t26/t25, and H35S/H34S ratios (0.55, 0.49, and 0.26, respectively). This is mainly due to the fact that a number of synthetic oils lack light n-alkanes and their isoprenoids. Terpane compounds were below the detection limit in some products, which significantly affected the statistics. Otherwise, the generated fluids have a similar composition.

Well	Α							В				
Heating Temperature, °C	3	00	3	25	3	50	3	75	4	00		-
Product Type	Light SO	Heavy SO	Open Pores Bitumen	Blocked Pores Bitumen								
Pr/Ph	-	2.55	0.77	-	0.14	-	-	-	-	-	0.03	0.42
Pr/C17	-	0.66	0.12	-	0.10	-	-	-	-	-	0.37	0.58
Ph/C18	-	0.33	0.13	-	0.15	-	-	-	-	-	0.39	0.46
C29/C30	0.65	0.74	0.70	0.82	0.76	0.68	0.70	0.86	0.74	0.77	0.62	0.55
t24/t23	0.91	0.88	0.85	0.79	0.75	-	0.91	1.05	0.85	0.97	0.67	0.59
t26/t25	2.54	1.86	2.28	2.20	2.27	-	2.20	2.14	2.30	2.04	1.23	1.40
(t28 + t29)/C29	0.21	0.28	0.23	0.52	0.20	-	0.21	0.47	0.19	0.44	0.50	0.54
H31R/C30	0.15	0.41	0.15	0.44	0.17	0.44	0.16	0.51	0.15	0.47	0.36	0.43
t23/H30	0.04	0.06	0.05	0.14	0.05	-	0.04	0.09	0.04	0.09	0.31	0.25
H32S/(S+R)	0.56	0.56	0.55	0.62	0.55	-	0.57	0.55	0.56	0.55	0.57	0.57
H35S/H34S	-	0.89	-	0.88	0.58	-	0.69	1.40	0.65	1.34	1.09	1.21
Ts/(Ts + Tm)	0.63	0.47	0.63	0.39	0.61	0.34	0.64	0.51	0.62	0.44	0.52	0.47
Ts/C30	0.15	0.15	0.15	0.16	0.15	0.19	0.15	0.20	0.14	0.20	0.30	0.22
dia/(reg + dia)C27	0.16	0.23	0.16	0.21	0.16	0.20	0.17	0.18	0.16	0.20	0.23	0.22
bb/(aa + bb)C29	0.47	0.58	0.44	0.56	0.47	0.57	0.47	0.59	0.58	0.56	0.63	0.54
aa20S/(S + R)C29	0.30	0.41	0.37	0.33	0.35	0.38	0.40	0.40	0.57	0.41	0.41	0.36

Table 5. Biomarker parameters of synthetic oils (SOs).

4. Discussion

4.1. Kerogen Transformation

Strata of the sections of the studied wells, A and B, have a fairly characteristic composition for the Bazhenov formation sediments [43]. Pyrolytic parameters show a wide range of values, with the largest amount of organic matter for the IV unit. The HI and Tmax indicate the kerogen to be a type II marine type. The wells are located close to each other, and with the same depth (60 m) the maturity of the kerogen should be the same. Pyrolysis data determine the OM maturity as the beginning of the oil window in well A and the middle of the oil window in well B. Such a gradient can be caused by hydrothermal processes, whose influence has been confirmed for the investigated region [44]. To confirm the exact effect of such processes, more geological and geophysical studies are necessary. Nevertheless, the transformation of OM under hydrothermal conditions is a pending issue, as the process of oil and gas generation within hydrothermal treatments should be investigated. Also, the significance of the differences in the OM transformation chemical processes during the gradual immersion of the sedimentary stratum and a hydrothermal treatment is unknown.

The hydrothermal treatment under subcritical conditions for 24 h performed in the investigation led to an almost complete change in the kerogen structure. The S2-TOC graph shows that the characteristics of the samples after heating form a linear trend with the samples treated under 375 °C and 400 °C with a slight deviation (Figure 7). The point for the well B sample is located almost in the middle, between the results for samples

heated to 300 °C and 350 °C. As the maceral composition of the samples is the same according to the coal petrography, it can be assumed that the initial characteristics of the samples were similar, and the kerogen transformation in well B could be accounted for by hydrothermal processes.



Figure 7. S2-TOC diagram with pyrolysis parameters for heated well A samples and initial well B sample after extraction. The red line indicates the trend of organic matter transformation during maturation.

Changes in kerogen maturity after heat exposure, shown in the modified van Krevelen diagram (Figure 8), are consistent with the kerogen transformation trend for the West Siberia basin [45]. Figure 8 represents the kerogen characteristics after heating up to 350 °C, indicated between two yellow lines that show the geological kerogen maturation trend for the region. Samples, after exposure to supercritical water, show higher T_{max} values and actually enter the gas window. The well B sample characteristics are between the values of samples heated to 300 °C and 350 °C. The temperatures of 375–400 °C allow simulation of the transformation of kerogen from the beginning to the end of the gas window. In the Bazhenov formation of well B, the hydrothermal treatment provided lower energies.

According to the pyrolysis data, the kerogen transformation at 325 °C compared to 350 °C was more significant. This is confirmed by a larger amount of released gas. Since all the experiments were carried out on the same pulverized sample, and the quartering method was used, the components' distribution heterogeneity in the powder should not have played a significant role. At the same time, it is known from previous studies that Bazhenov source rocks' kerogen in the region is represented by various macerals, among which the liptinite group and various zooclasts are distinguished [46]. Previous studies of natural and artificially transformed samples of the Bazhenov formation have shown that these macerals are transformed unevenly with the growth of maturation [46,47]. Therefore, it can be assumed that the difference in the results obtained is due to the different ratios of individual macerals in the divided sample. Since the macerals that form kerogen have plasticity and do not separate from inorganic minerals, it is possible that even during quartering, samples contain different amounts of macerals.



Figure 8. Modified van Krevelen diagram with the results of the experiments. The numbers are the temperature values of the hydrous pyrolysis.

The other possible reason is that heavy heteroatomic hydrocarbon compounds can convert to an insoluble state. After the main phase of oil formation is completed, asphaltenes can condense into kerogen-like structures [48]. Such processes were specified in the ultradeep Jurassic and Triassic sediments in Western Siberia [49]. Under high-temperature exposure, condensation of asphaltenes into coke can occur due to the rearrangement of polycyclic aromatic rings [50]. At the same time, during maturation, the secondary cracking of heavy bitumen into lighter hydrocarbons can occur, while some of the bitumen transforms into so-called pyrobitumen, with an increase in the non-generative kerogen content [11]. Pyrobitumen has been found in many oil-and-gas-bearing provinces where overripe organic matter was established [51–54]. A thermal event accompanied by the igneous rocks' introduction or hydrothermal fluid transfer can affect the formation of pyrobitumen [55–57]. However, the chemical process of pyrobitumen formation is not fully understood. It is associated with the generation and further transformation of crude oil and directly depends on the amount of various fractions in the generated products [58]. As under 350 °C, the kerogen reaches the end of the oil window, and gas starts forming, the asphaltenes formed by the kerogen cracking could condense back into kerogen-like structures. This process can explain the change in the ratio of generative to non-generative organic carbon within the same total organic carbon content at different heating temperatures.

4.2. Synthetic Gas Composition

The differences in the volume of synthetic gases may indicate the influence of pressure on the process. It can be assumed that the kerogen cracking at 325 °C and 350 °C requires the same activation energy for bond disruption. Then, the higher temperature would lead to the process's precipitation and a faster pressure increase. According to the Le Chatelier principle, the system will tend to reduce the additional pressure, slowing down the ongoing reactions and reducing the amount of new products. An increase in temperature to the supercritical conditions leads to newly kerogen cracking processes and liquid products' secondary cracking activation. As a result, more gas and less light and heavy synthetic oil are formed. At the supercritical conditions, the pressure may play a less relevant role, as the solubility of hydrocarbon compounds in water increases.

4.3. Synthetic Oil Composition

The total specific yield of light and heavy synthetic oil increases from 300 °C to 350 °C, and then the amounts decline. The decrease in the products' yield at higher temperatures can be caused by their secondary cracking. This is indirectly confirmed by the change in the methane to C_2 – C_6 hydrocarbons ratio, which increases markedly in the products formed at 400 °C (Figure 9). The ratio of methane to other hydrocarbon gases in all experiments except at 400 °C is approximately 0.4, while in the latter, it achieved a value of 0.6. Similar processes are described in article [59].



Figure 9. Changes in the C_1/C_2 - C_6 ratio during warm-up.

The values of studied biomarker parameters for the light and heavy synthetic oils demonstrate that the products are practically the same, with no influence from the heating temperature (Figure 10). The established similarities may be related to the mobility and stability of individual hydrocarbons, as well as to the absence of any mineral matrix catalytic effects as the sample was pulverized and the kerogen–mineral matrix contacts were broken. Nevertheless, light synthetic oils after all the experiments have a higher value of the t26/25 parameter in comparison with heavy ones, as well as a lower value of the H35S/H34S parameter. Such deviations may be explained by the inability to identify a sufficient number of specific biomarkers in the system in some cases, as was mentioned above. At the same time, in general, individual deviations still allow us to consider formed liquid products to be similar.



Figure 10. Average composition of synthetic oils and natural extracts from a more mature well.

Comparing the synthetic oils' biomarker parameters with the ones for the bitumen from the well B sample shows that the average composition of heavy oil is better correlated with natural hydrocarbons (Figure 10). The values of some parameters, such as C29/C30, t23/H30, and Ts/(Ts + Tm), in heavy oils are inherited from natural extracts of sample B. The maturity parameters Ts/(Ts + Tm) and bb/(aa + bb)C29 are the same for both synthetic oils and natural bitumen. The most significant discrepancies with natural extracts are detected in the parameters t26/t25 (higher in light synthetic oils), (t28 + t29)/C29 and t23/H30 (lower in both types of synthetic oil). Based on the results, two assumptions can be made. According to the literature, the parameters (t28 + t29)/C29, t23/H30 μ H35S/H34S are affected by high temperatures during hydrous pyrolysis [60]. Our previous experiments also demonstrated a significant alteration of the t26/t25 parameter under 300 °C and 350 °C. Also, such differences may be caused by the slight difference in the process of biomarker compounds' generation and fractionation during hydrous pyrolysis [2].

No changes in the maturity parameters after different heating temperatures were detected; meanwhile, kerogen characteristics changed significantly. It can be assumed that under hydrous pyrolysis conditions, all maturity biomarkers are separated with the initial structure or at the initial stages of kerogen transformation. The system lacks time at lower temperatures for isomerization of the compounds or corresponding parts of the kerogen structure. According to the literature, the homohopanes and steranes' isomerization reaction rate can be lowered due to high temperature and pressure effects. The influence of hydrous pyrolysis on these processes was shown by different researchers [60–65]. Similar results with no changes in biomarker parameters were shown for other oil-bearing formations. For example, liquid products from Brazilian basin rocks containing type I kerogen after the multi-temperature exposure in autoclaves demonstrate the same parameters, except the Pr/Ph ratio, through experimentation [11].

The use of pulverized samples allows for products to be removed from the reaction zone due to the absence of the structure effect (curvature of pore channels and their blocking by heavy high-molecular compounds), and they exhibit a reduced catalytic effect. The results of the GC–MS showed that the process of synthetic oil generation follows a similar scenario at different temperatures. At the same time, it is comparable to the process in natural organic-rich formations, which were exposed by increased heat flows. To investigate the effects of other factors on oil and gas generation, further investigations are necessary. Among them, kinetic studies of kerogen destruction by pyrolysis, experiments under other conditions (different exposure times and in a semi-open system), and experiments on non-extracted, non-pulverized rocks should be performed for the Bazhenov formation sediments.

5. Conclusions

The Bazhenov formation kerogen in the two investigated wells achieved different maturity levels. After hydrothermal treatment on an immature sample from well A under temperatures of 300 °C and 350 °C, the pyrolysis values and biomarker parameters were similar to the values for the mature well B sample. The experiments allowed us to establish that under subcritical conditions, in the presence of water, more than 90% of the kerogen generation potential can be converted into hydrocarbons in 24 h. The supercritical water treatment led to the transformation of OM and an increase in the proportion of non-generative organic carbon. The OM maturity increased in accordance with the natural Bazhenov formation kerogen transformation trend. Under temperatures of 375–400 °C, kerogen passes through the oil window and enters the gas window, which was confirmed by the amount of gas released in the corresponding experiments.

The similar composition of the liquid and gaseous synthetic hydrocarbon compounds suggests that neither the pore space structure nor the catalytic or inhibitory effects of the mineral matrix affect the results of the experiments with pulverized and extracted samples. Some high-molecular products can convert into gases as a result of secondary cracking, and some can convert to pyrobitumen, but the biomarker parameters do not change significantly. A comparison of the experiment results with the characteristics of the natural sample bitumen showed that in mature Bazhenov sections, hydrocarbons might form under hydrothermal treatment or other processes accompanied by increased heat flow.

The results of this study show that hydrous pyrolysis can be used to study the oil and gas generation processes. However, the data obtained are not enough to indicate the partial restoration of the structure of kerogen, which might play a key role. For this purpose, additional studies should be performed, including the separation of kerogen from the mineral matrix and its detailed analysis by various chemical and analytical methods. It is also necessary to determine the role of the mineral matrix and the rocks' structure in the processes of hydrocarbon generation, migration, and accumulation. Such data will significantly improve the accuracy of oil and gas prediction, not only in Western Siberia, but also worldwide.

Supplementary Materials: The following supporting information can be downloaded at https:// www.mdpi.com/article/10.3390/en18010023/s1, Table S1: Results of XRF analysis of major elements (%) of samples from well A; Table S2: Results of XRF analysis of major elements (%) of samples from well B; Table S3: Pyrolysis results after extraction of samples from well A; Table S4: Pyrolysis results after extraction of samples from well B; Table S5: Results of pyrolysis after extraction of samples for the study of OM conversion processes; Table S6: Results of GC analysis of HC synthetic gas after heating; Figure S1: Mass fragment m/z 57 for a sample of light synthetic oil after heating at 300 °C; Figure S2: Mass fragment m/z 191 for a sample of light synthetic oil after heating at 300 °C; Figure S3: Mass fragment m/z 217 for a sample of light synthetic oil after heating at 300 °C; Figure S4: Mass fragment m/z 218 for a sample of light synthetic oil after heating S5: Mass fragment m/z 259 for a sample of light synthetic oil after heating at 300 °C; Figure S6: Mass fragment m/z 275 for a sample of light synthetic oil after heating S5: Mass fragment m/z 276 for a sample of light synthetic oil after heating S6: Mass fragment m/z 577 for a sample of heavy synthetic oil after heating at 300 °C; Figure S6: Mass fragment m/z 191 for a sample of S7. Figure S6: Mass fragment m/z 276 for a sample of light synthetic oil after heating S7. Figure S6: Mass fragment m/z 577 for a sample of heavy synthetic oil after heating at 300 °C; Figure S7: Mass fragment m/z 577 for a sample of heavy synthetic oil after heating at 300 °C; Figure S7: Mass fragment m/z 577 for a sample of heavy synthetic oil after heating at 300 °C; Figure S7: Mass fragment m/z 577 for a sample of heavy synthetic oil after heating at 300 °C; Figure S7: Mass fragment m/z 577 for a sample of heavy synthetic oil after heating at 300 °C; Figure S7: Mass fragment m/z 191 for a sample of heavy synthetic oil after heating at 300 °C; Figure S8: Mass fragment m/z 217 for a sample of heavy synthetic oil after heating at 300 °C; Figure S9: Mass fragment m/z 218 for a sample of heavy synthetic oil after heating at 300 °C; Figure S10: Mass fragment m/z 259 for a sample of heavy synthetic oil after heating at 300 °C; Figure S11: Mass fragment m/z 57 for a sample of light synthetic oil after heating at 325 °C; Figure S12: Mass fragment m/z 191 for a sample of light synthetic oil after heating at 325 °C; Figure S13: Mass fragment m/z 217 for a sample of light synthetic oil after heating at 325 °C; Figure S14: Mass fragment m/z 218 for a sample of light synthetic oil after heating at 325 °C; Figure S15: Mass fragment m/z 259 for a sample of light synthetic oil after heating at 325 °C; Figure S16: Mass fragment m/z 57 for a sample of heavy synthetic oil after heating at 325 °C; Figure S17: Mass fragment m/z 191 for a sample of heavy synthetic oil after heating at 325 °C; Figure S18: Mass fragment m/z 217 for a sample of heavy synthetic oil after heating at 325 °C; Figure S19: Mass fragment m/z 218 for a sample of heavy synthetic oil after heating at 325 °C; Figure S20: Mass fragment m/z 259 for a sample of heavy synthetic oil after heating at 325 °C; Figure S21: Mass fragment m/z 57 for a sample of light synthetic oil after heating at 350 °C; Figure S22: Mass fragment m/z 191 for a sample of light synthetic oil after heating at 350 °C; Figure S23: Mass fragment m/z 217 for a sample of light synthetic oil after heating at 350 °C; Figure S24: Mass fragment m/z 218 for a sample of light synthetic oil after heating at 350 °C; Figure S25: Mass fragment m/z259 for a sample of light synthetic oil after heating at 350 °C; Figure S26: Mass fragment m/z 57 for a sample of heavy synthetic oil after heating at 350 °C; Figure S27: Mass fragment m/z 191 for a sample of heavy synthetic oil after heating at 350 °C; Figure S28: Mass fragment m/z 217 for a sample of heavy synthetic oil after heating at 350 °C; Figure S29: Mass fragment m/z 218 for a sample of heavy synthetic oil after heating at 350 °C; Figure S30: Mass fragment m/z 259 for a sample of heavy synthetic oil after heating at 350 °C; Figure S31: Mass fragment m/z 57 for a sample of light synthetic oil after heating at 375 °C; Figure S32: Mass fragment m/z 191 for a sample of light synthetic oil after heating at 375 °C; Figure S33: Mass fragment m/z 217 for a sample of light synthetic oil after heating at 375 °C; Figure S34: Mass fragment m/z 218 for a sample of light synthetic oil after heating at 375 °C; Figure S35: Mass fragment m/z 259 for a sample of light synthetic oil after heating at 375 °C; Figure S36: Mass fragment m/z 57 for a sample of heavy synthetic oil after heating at 375 °C; Figure S37: Mass fragment m/z 191 for a sample of heavy synthetic oil after heating at 375 °C; Figure S38: Mass fragment m/z 217 for a sample of heavy synthetic oil after heating at 375 °C; Figure S39: Mass fragment m/z 218 for a sample of heavy synthetic oil after heating at $375 \,^{\circ}$ C; Figure S40: Mass fragment m/z 259 for a sample of heavy synthetic oil after heating at 375 $^{\circ}$ C; Figure S41: Mass fragment m/z 57 for a sample of light synthetic oil after heating at 400 °C; Figure S42: Mass fragment m/z 191 for a sample of light synthetic oil after heating at 400 °C; Figure S43: Mass fragment m/z 217 for a sample of light synthetic oil after heating at 400 °C; Figure S44: Mass fragment m/z 218 for a sample of light synthetic oil after heating at 400 °C; Figure S45: Mass fragment m/z259 for a sample of light synthetic oil after heating at 400 °C; Figure S46: Mass fragment m/z 57 for a sample of heavy synthetic oil after heating at 400 °C; Figure S47: Mass fragment m/z 191 for a sample of heavy synthetic oil after heating at 400 °C; Figure S48: Mass fragment m/z 217 for a sample of heavy synthetic oil after heating at 400 °C; Figure S49: Mass fragment m/z 218 for a sample of heavy synthetic oil after heating at 400 °C; Figure S50: Mass fragment m/z 259 for a sample of heavy synthetic oil after heating at 400 °C; Figure S51: Mass fragment m/z 57 for light bitumen from the comparison sample; Figure S52: Mass fragment m/z 191 for light bitumen from the comparison sample; Figure S53: Mass fragment m/z 217 for light bitumen from the comparison sample; Figure S54: Mass fragment m/z 218 for light bitumen from the comparison sample; Figure S55: Mass fragment m/z 259 for light bitumen from the comparison sample; Figure S56: Mass fragment m/z 57 for heavy bitumen from the comparison sample; Figure S57: Mass fragment m/z 191 for heavy bitumen from the comparison sample; Figure S58: Mass fragment m/z 217 for heavy bitumen from the comparison sample; Figure S59: Mass fragment m/z 218 for heavy bitumen from the comparison sample; Figure S60: Mass fragment m/z 259.

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