

MDBT estimation ratio for transformation organic matter ratio in Bazhenov Formation of Western Siberia (Tomsk Oblast, Russia)

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Abstract. The Bazhenov Formation is the main source rock in the West Siberian Basin, because of high organic-rich Bazhenov black shales, with a total organic carbon (TOC) content of 10-15wt.% generally. Based on Rock-Eval pyrolysis data, the initial generative potential for a significant part of West Siberian Bazhenov Formation organic matter (OM) is from 10 to 60% expended. Most West Siberian oils are in the Bazhenov Formation due to very high oil potential (initial hydrogen index = 710mgHC/gTOC) and widespread regional distribution). Vitrinite reflectance (Ro) does not correctly indicate the transformation ratio (TR) of the OM in Bazhenov black shales. However, GC-MS analysis of extracts indicated a good correlation between some molecular maturity and Rock-Eval maturity parameters. Molecular maturity parameters based on naphthalenes and phenanthrenes are not applicable for Bazhenov Formation OM. While the parameters based on 4-methyldibenzothiophene and 1-methyldibenzothiophene ratio (4MDBT/1MDBT) is applicable in estimating the hydrocarbon potential of Bazhenov Formation black shales and, consequently, provides more reliable information about marine OM TR than does Ro. The 4MDBT/1MDBT ratio is more consistent and precise than pyrolysis data. Therefore, it is more applicable in the case of scarcity of core samples throughout the whole formation.

1. Introduction

One of the main questions in petroleum exploration is the quantity of generated hydrocarbons in this or that new area. So, the following parameters should be taken into consideration: type and thickness of the source rock, TOC value, residual hydrogen index (HI), initial hydrogen index (HI₀), and TR.

The first three parameters are not problematic. However, it can be difficult to determine the initial generative potential of source-rock OM, i.e. generative potential before entering the oil window (phase).

The simplest approach is to find areas, where OM is not involved in the starting stage of oil generation, i.e. areas with thermal immature source rock. However, this is practically impossible, especially in those areas where OM is already in the active oil generation phase (oil window).

One can refer to the kerogen type documented in research literature. According to the case studies on the West Siberian Basin by Lopatin et al. [1] and Peters et al. [2], the Bazhenov black shales contain marine Type II kerogen. Classical Type II kerogen is characterized by the value 627 mg HC/g TOC [3].



If HI and TR of OM are known, then H_{IO} is calculated: while Ro calculates TR [3]. In this case, however, Ro does not always indicate the transformation degree of OM. Some problems in Ro determination are the low- quality polished samples and incorrect population selection of vitrinite. Ro determined by various laboratories commonly differs due to the above-mentioned factors [4]. Moreover, it is very difficult to measure Ro in marine kerogens, such as those in Bazhenov Formation, where vitrinite is absent. Obviously, no direct measurement of Ro for oils is possible.

Thus, this paper provides an alternative geochemical parameter based on molecular composition of extracts for Ro in the Bazhenov source rock. Similar investigations were performed for source rocks in different sedimentary basins [5-7], where molecular parameters were calibrated against Ro. Many molecular parameters are used for maturity evaluation of source rocks and oils, while (some are limited by a certain maturity level) a maturity level may limit some of them [8, 9] or even organic facies affect the application of these parameters [10]. Thus, molecular maturity parameters must be selected and calibrated for each OM type and sedimentary basin. They must indicate the hydrocarbon potential of the source rock (Rock-Eval pyrolysis data).

2. Geological setting

West Siberian Basin, one of the largest basins in the world, contains more than 3500 m Mesozoic and Cenozoic sedimentary rocks, and has a relatively simple geologic structure. There are big oil & gas pools, occurring throughout the stratigraphic section from Paleozoic to Upper Cretaceous.

Literature data [2, 11] and geochemical analyses [12-14] of oil, gas and rock samples indicate at least three source rocks in this basin. The Bazhenov Formation is the major oil source rock in Western Siberia and about 90 % of originated oil in it [1,15].

The Bazhenov Formation is located in the south, center, and north parts of the West Siberian platform, covering about 1 million km² in area. The base of the formation is Early Tithonian, while the top is Early Berriasian [16]. The Bazhenov Formation is a classic source rock consisting of black and brownish-black deep-marine carbonate-siliceous shales with high quality OM. TOC contents range from 5 to 20wt.% and up to 35wt.% in the central part of the West Siberian Basin [1]. The Bazhenov Formation is characterized by many anomalous parameters, including high natural radioactivity, high electrical resistance, low density, and high trace element content. The formation varies in thickness from 20-50m in the central part and up to 10-30m in peripheral part.

In a significant part of the West Siberian Basin, the Bazhenov Formation is within the oil window zone. In the central part of this basin it is no more than 25% of the initial generation potential, while more extensive conversion has occurred only in areas of major faults.

Oil pools related to OM in the Bazhenov Formation occur throughout the stratigraphic section, as types and lithology of overlying and underlying rocks are highly variable (figure 1) and hydrocarbon migration conditions from the source rock are also different. In the eastern part of the West Siberian Basin, the Bazhenov Formation is overlain by Neocomian marine shale of Kulomzin Formation (about 300m thick), providing an efficient seal. Below the Bazhenov Formation are the Georgiev and Vasyugan Formations, consisting of alternating mudstone, siltstone, coal and sandstone with good reservoir properties.

In the western part of the basin, the Georgiev and Vasyugan Formations are replaced with Abalak Formation sediments, consisting of marine shale. However, Neocomian sediments occur as regressive sandstones, the so-called "clinoform complex" in the Achimov Formation. These sandstones have good reservoir properties and, simultaneously, provide migration paths for Bazhenov hydrocarbons to Aptian-Albian shallow-marine terrigenous reservoirs.

Furthermore, in high catagenesis zones lacking favorable conditions for hydrocarbon migration, some oil pools may occur in nontraditional reservoirs within the source rock itself in the Bazhenov Formation (e.g. Salym oilfield region).

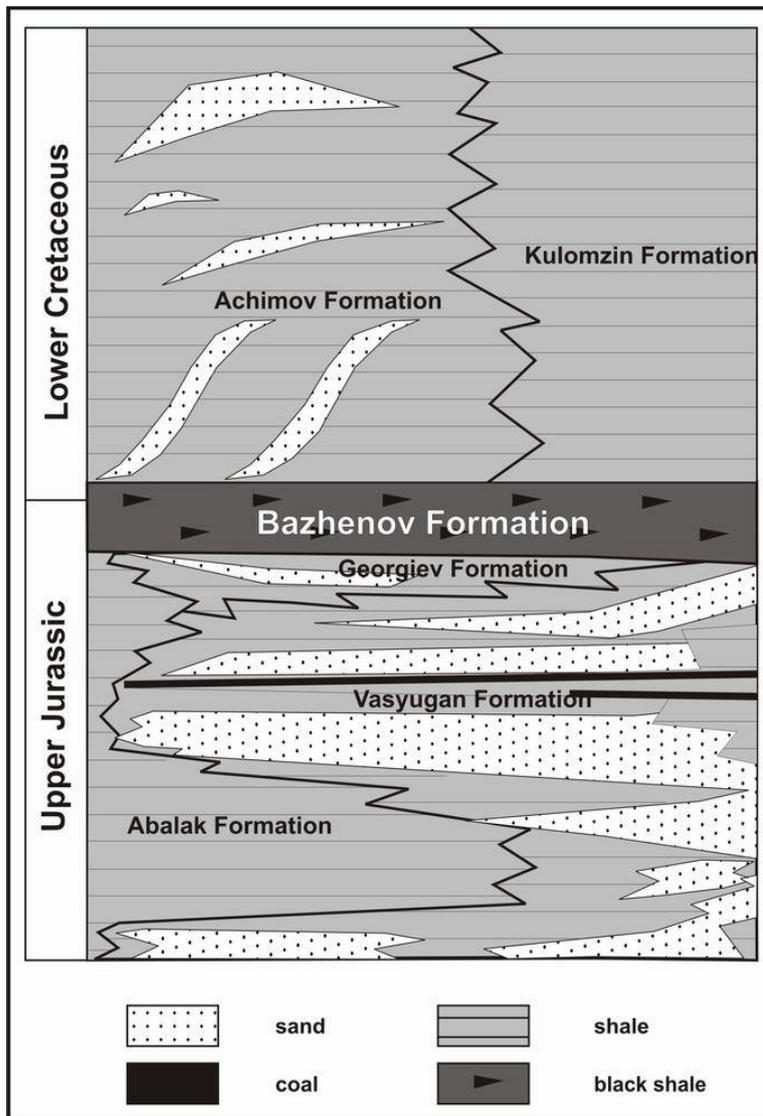


Figure 1. Generalized lithology column of Upper Jurassic and Lower Cretaceous section for the studied area.

3. Samples and methods

The above-mentioned study investigated the Bazhenov Formation black shale core samples, Upper Jurassic coals (the Vasyugan Formation), and oils related to OM in the Bazhenov Formation. More than 1500 core samples from over 100 wells in the Bazhenov Formation were investigated (figure 2). Samples were obtained from within 1-m spacing of each well throughout the Bazhenov Formation. Samples with average values from each well were used for correlation.

All crushed core samples were washed and dried beforehand and pyrolysis was carried out in Rock-Eval 6 Turbo design (with two infrared cells). The programmed temperature for pyrolysis was at 300°C (3min), 25°C/min up to 650°C, and for oxidation at 300°C (1min), 20°C/min up to 850°C (5min). Therefore, transformation ratio is given by [17]:

$$TR = \frac{1200 \cdot (HI_0 - HI)}{HI_0 \cdot (1200 - HI)} \cdot 100\%$$

Crushed rock and coal samples were subjected to chloroform solvent extraction in Soxhlet apparatus for over 1 hour. Deasphalted crude oils and source rock extracts (bitumens) separated into

saturated hydrocarbons, aromatic hydrocarbons, and resins in a silica gel column. These fractions were eluted with hexane, benzene, and benzene: methanol (1:1v/v), respectively.

GC-MS analyses of total extracts and oils, as well as, their fractions were carried out with Hewlett Packard 6890/5973 instrument in 30-m HP-1-MS column. The programmed oven temperature was at 45°C (3min) to 310°C (30min) at 3°C/min, in a helium atmosphere, where flow rate was 0.7ml/min. Their areas were calculated on the basis of biomarker peak ratios. In some publications the recognition of appropriate biomarkers and component ratio calculations from mass fragmentograms have been described [9,18]. A.N. Fomin (Institute of Geology, Russian Academy of Sciences, Siberian Branch, Novosibirsk) and N.V. Lopatin (VNII Geosistem, Moscow) defined Ro.

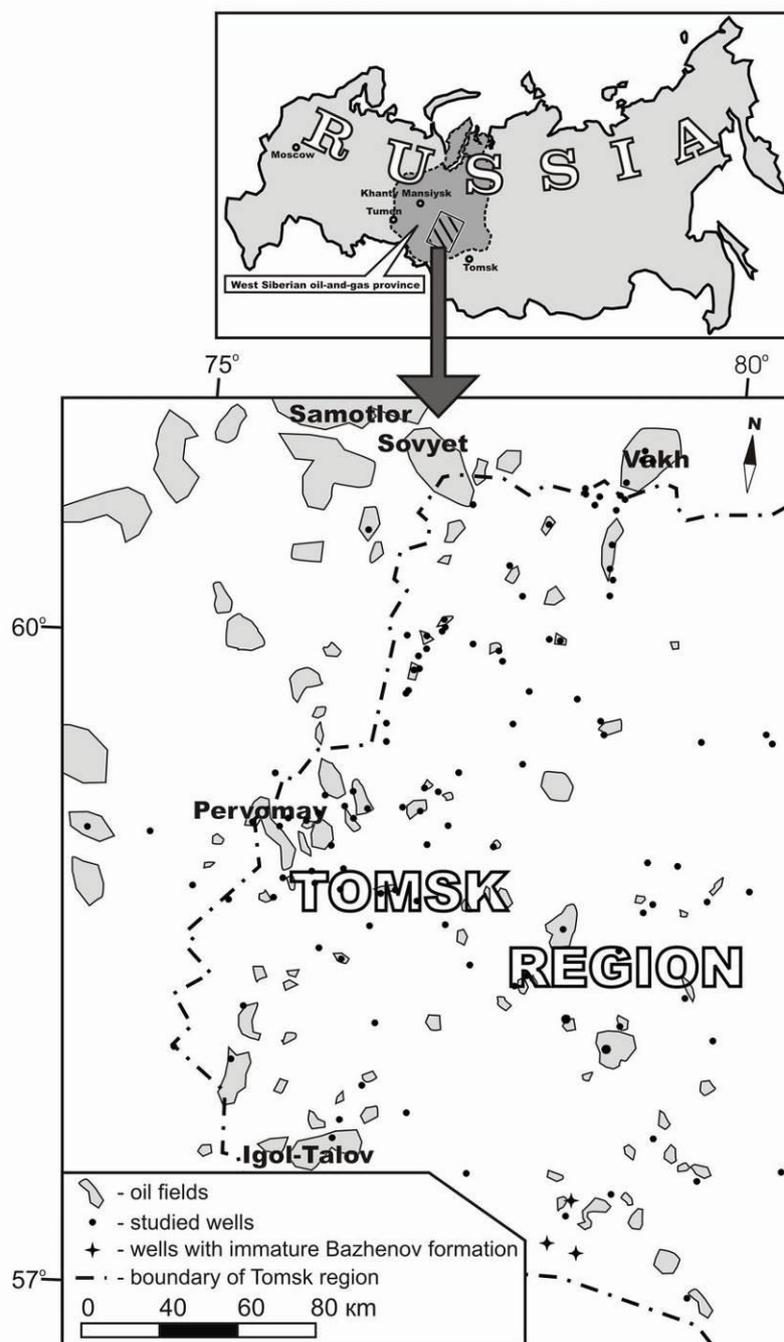


Figure 2. Map- location of the studied area.

4. Results and discussion

Rock-Eval pyrolysis data for Bazhenov Formation rock samples indicate that current HI ranges from 120 to 770mg HC/gTOC. Consequently, if it is assumed that HI₀ is 627mg HC/gTOC [3], then TR negative value is determined, although there exist oil fields in this region. Therefore, HI for some Bazhenov Formation rocks should be higher than for typical Type II OM.

In this case, Ro can be applied to determine TR [3], though Ro does not objectively indicate the OM thermal maturity in the Bazhenov Formation (figure 3). This is obvious from the fact that Ro precisely characterizes thermal maturity of Type III OM in coals of Upper Jurassic deposits rather than the thermal maturity of Type II OM in the Bazhenov Formation.

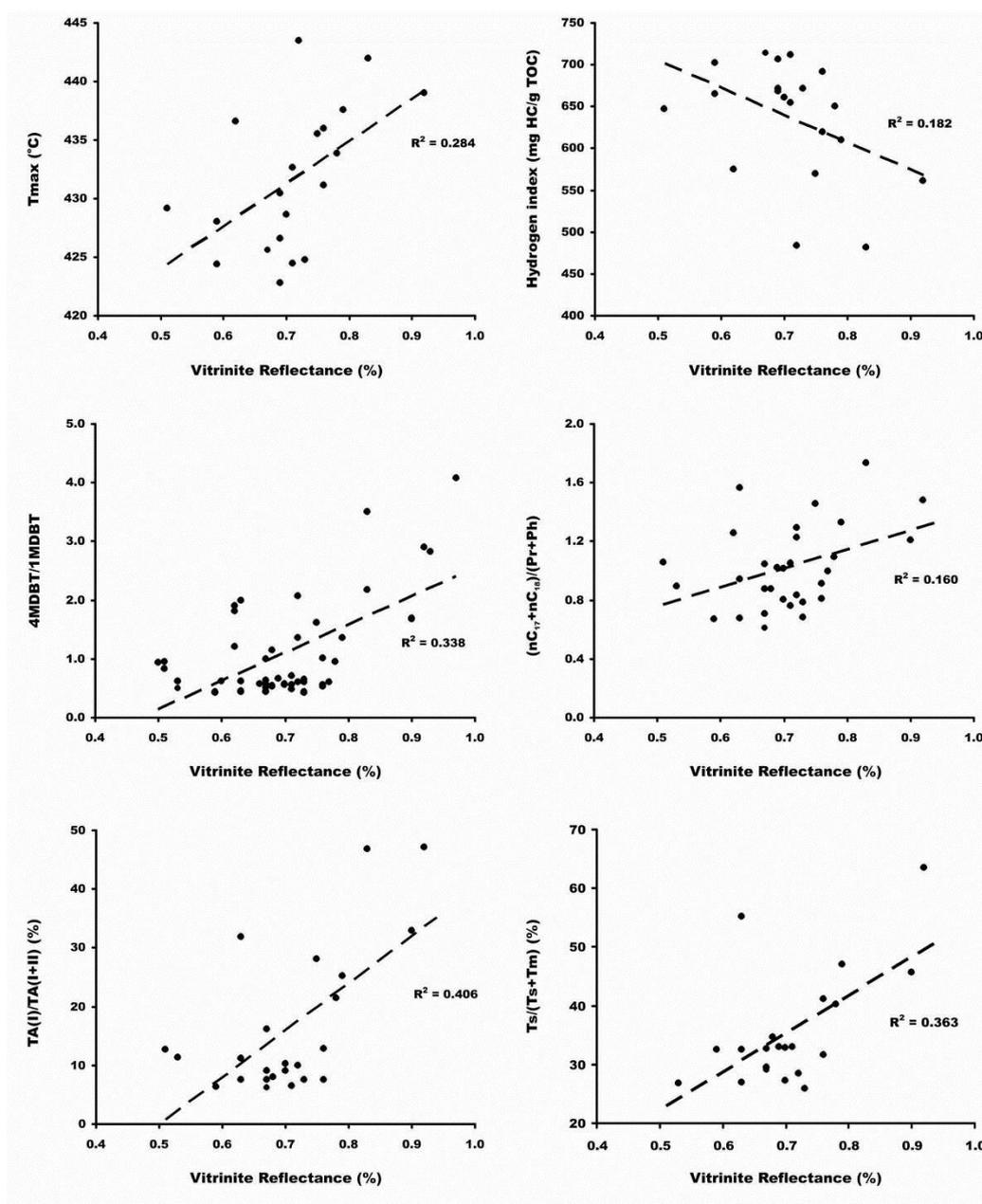


Figure 3. Rock-Eval 6 pyrolysis data for organic matter and molecular maturity parameters for Upper Jurassic Bazhenov Formation black shale extracts and Ro (%) of underlying Upper Jurassic coals.

Obtained Bazhenov Formation rock extracts were tested according to various parameters as described in Alexander et al. [19], Radke et al. [20], Peters et al. [9]. The parameters based on naphthalenes and phenanthrenes did not work out, (figure 4), probably as they indicate thermal maturity of Type III OM [6, 20-22]. Interestingly, a number of other parameters (4MDBT/1MDBT, TA (I)/TA (I+II), Ts/(Ts+Tm), (nC17+nC18)/(Pr+Ph)) increased with the increase of Ro [23]. However, the low level of thermal maturity corresponds to a significant distribution in values (figure 3). Furthermore, the relations between molecular parameters and Rock-Eval data are much more uniform with each other (figure 5,6), than with the Ro (figure 3). Two main reasons are: (1) all parameters characterize the state of OM in the source rock, and (2) the measurement error of molecular parameters is lower than that of Ro.

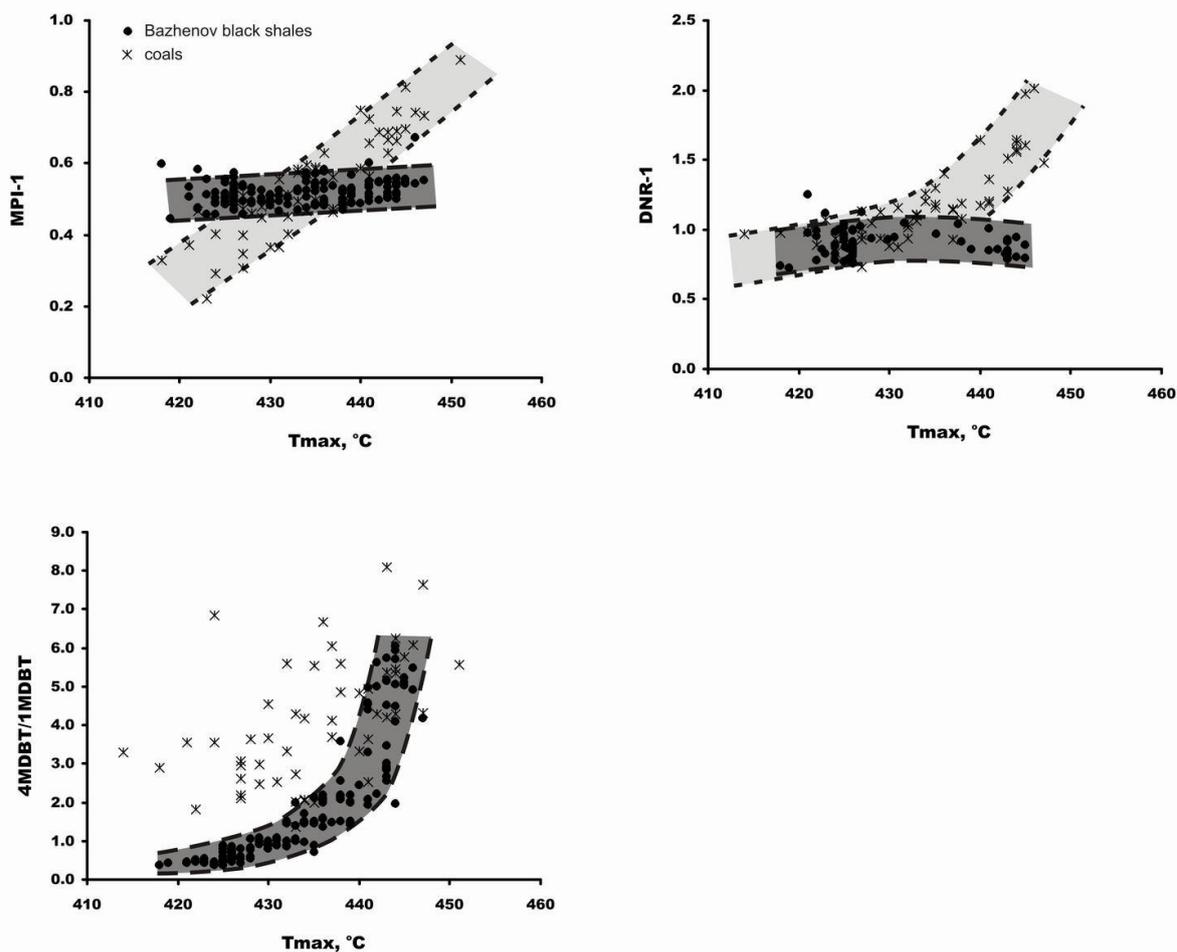


Figure 4. Molecular parameters vs. Tmax for Upper Jurassic Bazhenov Formation black shales and Jurassic coals.

Methylphenantrene Index 1 (MPI-1) = $1.5 \times (2\text{-MP} + 3\text{-MP}) / ((P \times 0.69^a) + 1\text{-MP} + 9\text{-MP})$, using m/z 178 and 192, ^aGCMS data corrected to FID response [21];

Dimethylnaphthalene Ratio 1 (DNR-1) = $(2,6\text{-DMN} + 2,7\text{-DMN}) / 1,5\text{-DMN}$, using m/z 141 response [19].

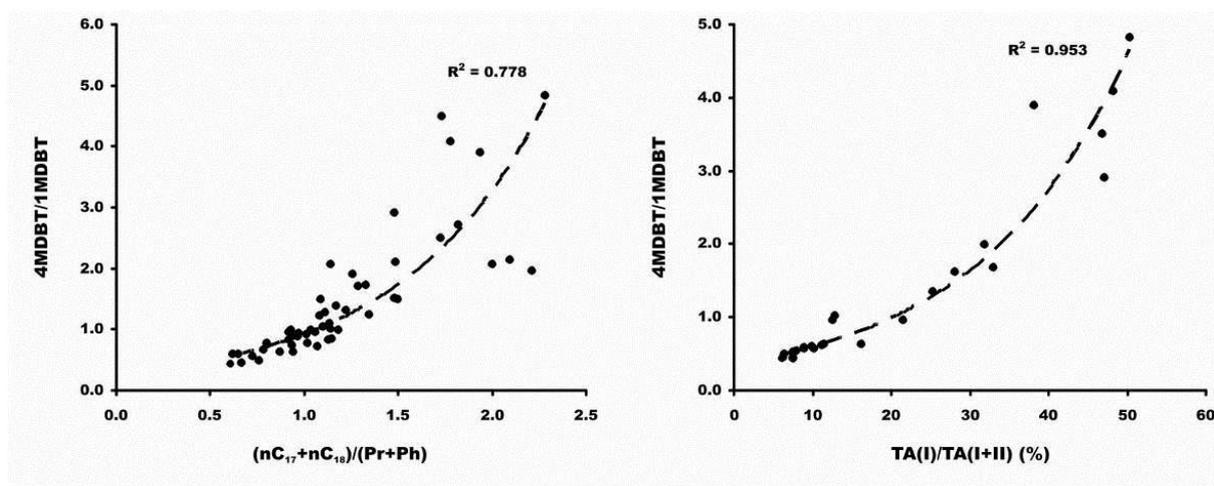


Figure 5. Relationship between molecular maturity parameters for Upper Jurassic Bazhenov Formation black shale extracts.

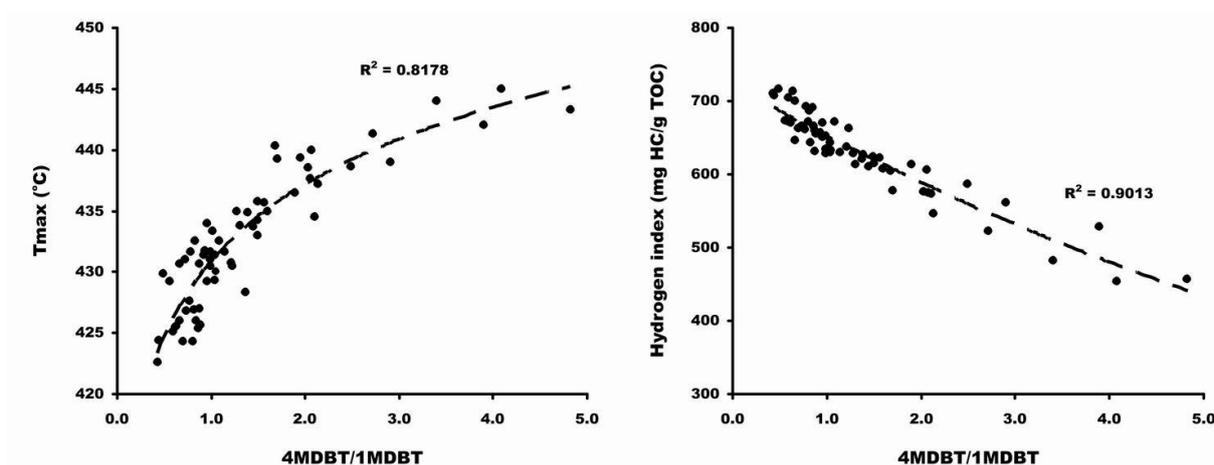


Figure 6. Rock-Eval 6 pyrolysis data vs. 4MDBT/1MDBT for Bazhenov Formation black shales.

Based on log characteristics, the Bazhenov Formation can be divided into four layers with different contents of OM, carbonates, clays and siliceous minerals [1]. In figure 7, molecular parameters change throughout the Bazhenov Formation in two wells having different thermal maturity levels. The 4MDBT/1MDBT ratio is the most stable parameter in the 10-15m thickness of both wells so, it can be stated that the maturity difference in such a small depth range is not possible. The variation limits of these parameters for all Bazhenov Formation samples in the studied area are detailed and shown in figure 8. The data show that R_o changes only two and a half times within the oil-window, while the molecular parameters change 5 or 8; while 4MDBT/1MDBT ratio changes to 55. However, at high thermal maturity levels, the biomarker content decreases, resulting in a sharp error increase. Therefore, 4MDBT/1MDBT and $(nC_{17}+nC_{18})/(Pr+Ph)$ are the most applicable in evaluating the thermal maturity level of OM in the Bazhenov Formation. So, their significant content (dibenzothiophenes and alkanes) in extracts and oil is important, but they are not trace contaminants. However, $(nC_{17}+nC_{18})/(Pr+Ph)$ ratio has a serious drawback as it partial depends on the TOC content [24].

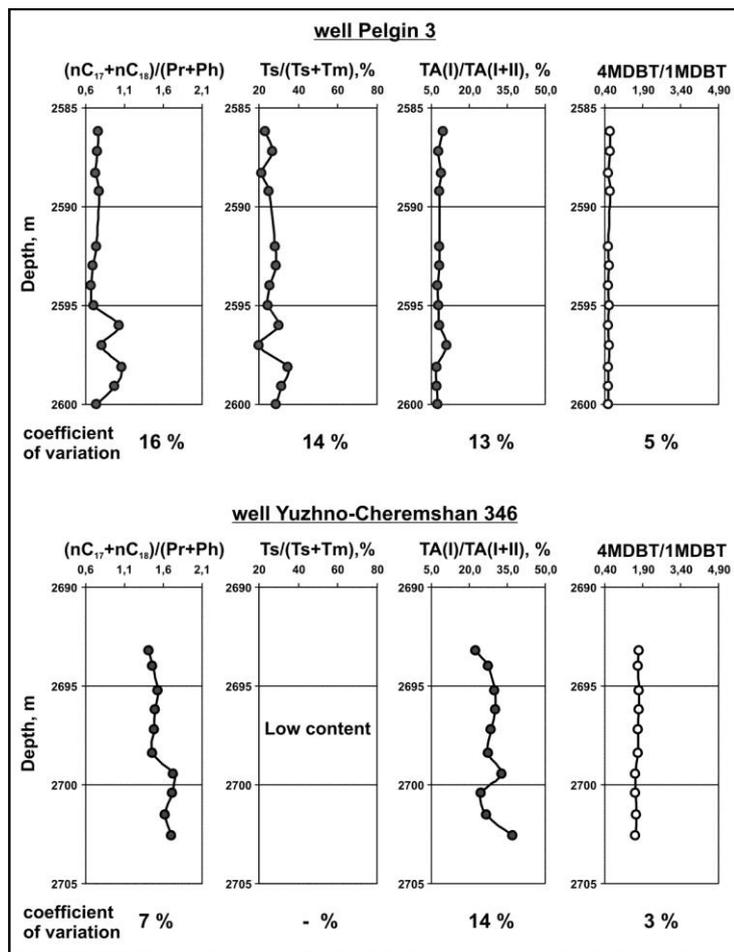


Figure 7. Variations of some maturity parameters through Bazhenov Formation in the well Pelgin-3 (low maturity) and Yuzhno-Cheremshan-346 (medium maturity)

$$\text{The coefficient t of variation} = \frac{\sqrt{\sum(X_i - X_{av})^2/n}}{X_{av}} \times 100\%$$

where, X_i is the parameter value; X_{av} is the average value; n is the number of values. The range of parameters is from minimum to maximum values of the parameters in the studied area (see Figure 8).

	main part of Western Siberia	Exception: "the hot zone" - Salym oil field	Sensitivity of parameters max/min
TR, %	5 20 40 60	80-90	
4MDBT/1MDBT	0.45 0.90 2.1 4.9	25	55
(nC ₁₇ +nC ₁₈)/(Pr+Ph)	0.6 1.0 1.5 2.1	3.0	5
TA(I)/TA(I+II), %	6.0 13 27 50	Low content	8
Ts/(Ts+Tm),%	26 35 50 80	Low content	2
Ro, %	0.51 1.00	1.2	2.5

Figure. 8. Variation limits of molecular maturity parameters for Bazhenov Formation black shales.

The above-mentioned parameter and systematic analyses of the Bazhenov black shales from different wells identified several zones with abnormally low parameters of thermal maturity level. Many parameters based on the biomarker composition indicate that OM has already reached the oil window level (table 1). But at the same time, the large collection of West Siberian oils has no samples with 4MDBT/1MDBT values below 0.8. So, it can be concluded that in these zones OM has not only

reached the oil window level but still retains its initial generative potential. Thus, the mean value of HI for these zones is 710mg HC/g TOC (table 2) and this HIo can be recommended for the Bazhenov Formation in the south-eastern part of Western Siberia. Though, it is much higher than is generally accepted for Type II OM.

Table 1. Maturity parameters of Bazhenov Formation rock extracts from the "cold zone" and some low maturity oils.

Extracts from samples of immature Bazhenov Formation black shales							
Depth, m	4MDBT/1MDBT	(nC ₁₇ +nC ₁₈)/(Pr+Ph)	TA(I)/TA(I+II) ^a , %	Ts/(Ts+Tm) ^a , %	20S/(20S+20R) SteraneC ₂₉ ^a , %	ββ/(αα+ββ) SteraneC ₂₉ ^a , %	Mor/Hop TerpanesC ₃₀ ^a
Archin 51, Ro=0.67 %							
2611.1	0.42	0.64	6.5	24.7	27.3	46.1	0.22
2612.7	0.38	0.50	5.3	29.6	21.6	39.4	0.20
2613.9	0.49	0.58	6.0	28.9	21.7	38.7	0.19
2614.9	0.44	0.64	5.9	31.6	20.9	36.7	0.21
2616.0	0.52	0.67	6.3	31.5	18.4	38.6	0.20
Kulgin 145, Ro=0.53 %							
2622.8	0.52	0.62	6.0	30.2	20.6	40.0	0.22
2623.8	0.47	0.64	6.2	35.7	17.9	37.4	0.22
2624.7	0.50	0.61	7.7	34.6	18.4	38.6	0.20
2625.7	0.46	0.74	5.5	32.5	24.9	40.6	0.19
2626.7	0.47	0.87	7.0	32.1	19.4	40.5	0.20
2628.1	0.53	1.10	6.4	32.9	17.1	38.8	0.19
Smolyanaya 3, Ro=0.59 %							
2613.7	0.42	0.68	7.6	19.0	32.1	46.0	0.19
2614.7	0.60	0.73	7.4	42.8	30.0	42.4	0.23
2616.8	0.42	0.54	6.1	35.9	32.2	42.0	0.21
2617.8	0.48	0.53	5.7	34.7	28.2	40.8	0.20
2618.7	0.39	0.63	5.2	36.0	24.6	40.8	0.18
2619.7	0.46	0.66	6.9	33.2	26.1	40.5	0.19
2620.7	0.46	0.72	6.4	31.4	26.3	41.8	0.19
2621.7	0.38	0.72	6.0	30.2	25.0	45.6	0.21
Low maturity oils (Vasyugan Formation, Upper Jurassic)							
Well ^b	4MDBT/1MDBT	(nC ₁₇ +nC ₁₈)/(Pr+Ph)	TA(I)/TA(I+II), %	Ts/(Ts+Tm), %	20S/(20S+20R) SteraneC ₂₉ , %	ββ/(αα+ββ) SteraneC ₂₉ , %	Mor/Hop TerpanesC ₃₀
1	0.84	1.05	8.3	56.0	30.0	54.0	0.14
2	0.84	1.02	11.3	44.5	48.1	62.3	0.15
3	0.88	1.14	11.7	43.4	31.8	49.0	0.11
4	0.92	0.96	11.6	47.0	44.3	61.7	0.16
5	0.92	1.05	9.9	39.0	47.7	58.9	0.11
6	0.95	1.02	7.6	47.0	50.2	75.5	0.09
7	0.96	1.11	9.6	55.0	46.3	57.5	0.19

4MDBT/1MDBT = 4-methyldibenzothiophene/1-methyldibenzothiophene; (nC₁₇+nC₁₈)/(Pr+Ph) = (n-heptahexadecane+n-oktahexadecane)/(pristane+phytane); TA(I) – sum of C₂₀ and C₂₁ TA-steroids; TA(II) – sum of C₂₆-C₂₈ (20S+20R) TA-steroids.

^a Parameters are described in Peters et al. [9]

^b 1 – Nizhnepervomay1; 2 – Lontyn-Yakh 70; 3 – Severo-Pervomay 2285; 4 – Zapadno-Vesenneye 241; 5 – Lontyn-Yakh 68; 6 – Uzhno-Festival 1; 7 – Kolotush 268.

Table 2. Some Rock-Eval 6 pyrolysis for wells from the “cold zone”

Depth, m	S1	S2	PI	TOC	Tmax	HI
Archin 51, Ro=0.67 %						
2611.1	4.1	49.2	0.08	7.1	423	692
2611.6	4.0	53.8	0.07	7.8	418	689
2612.7	3.4	60.3	0.05	8.4	424	720
2613.3	5.0	103.8	0.05	13.5	423	772
2613.9	3.2	68.9	0.04	10.0	422	692
2614.3	3.0	65.1	0.04	9.2	425	706
2614.9	3.4	71.7	0.05	10.3	424	697
2615.4	3.0	61.8	0.05	8.9	419	692
2616.0	3.7	84.4	0.04	11.6	422	727
Kulgin 145, Ro=0.53 %						
2622.8	2.9	60.0	0.05	8.4	425	718
2623.8	2.7	52.6	0.05	7.0	426	747
2624.7	1.6	28.5	0.05	4.1	425	692
2625.7	2.5	56.8	0.04	7.9	422	716
2626.7	3.1	75.6	0.04	10.5	421	722
2628.1	1.6	41.1	0.04	6.1	428	678
Smolyanaya 3, Ro=0.59 %						
2613.7	3.0	51.6	0.05	7.7	421	670
2614.7	3.4	52.6	0.06	7.6	425	694
2616.8	4.7	102.6	0.04	13.6	425	753
2617.8	3.8	73.3	0.05	9.7	424	756
2618.7	2.8	48.3	0.06	6.6	425	731
2619.7	2.3	37.5	0.06	5.4	425	690
2620.7	3.3	65.6	0.05	9.1	424	718
2621.7	3.1	56.1	0.05	8.4	424	672
2622.7	2.8	55.6	0.05	8.1	424	688
average	3.1	59.6	0.05	8.4	424	710
min-max	1.6 -5.0	28.5-103.8	0.04 - 0.08	4.1 - 13.6	418 - 428	670 - 772

S1 and S2 values in mg HC/g rock; PI=S1/(S1+S2) – production index; TOC – total organic carbon, wt.%; Tmax – temperature at which the maximum amount of S2 hydrocarbons is generated, °C; HI=S2/TOC – hydrogen index, mg HC/g TOC.

HIo makes it possible to determine TR and the dependent TR versus 4MDBT/1MDBT (figure 9). Figure 9 shows that 4MDBT/1MDBT determining TR gives a more precise depiction of the state of the OM than does Ro. Furthermore, TR determination by 4MDBT/1MDBT is often more simple and precise than when based only on pyrolysis results. It is difficult to find enough core samples to precisely characterize a source rock section. One or two samples are sufficient enough if 4MDBT/1MDBT changes insignificantly throughout the section and the variation coefficient are only 3-5% (figure 7). At the same time, there is a more detailed picture of thermal maturity and petroleum yield based on 4MDBT/1MDBT rather than on Ro. Due to the above-mentioned parameter the change in the petroleum yield can be established by four at a distance of 20km.

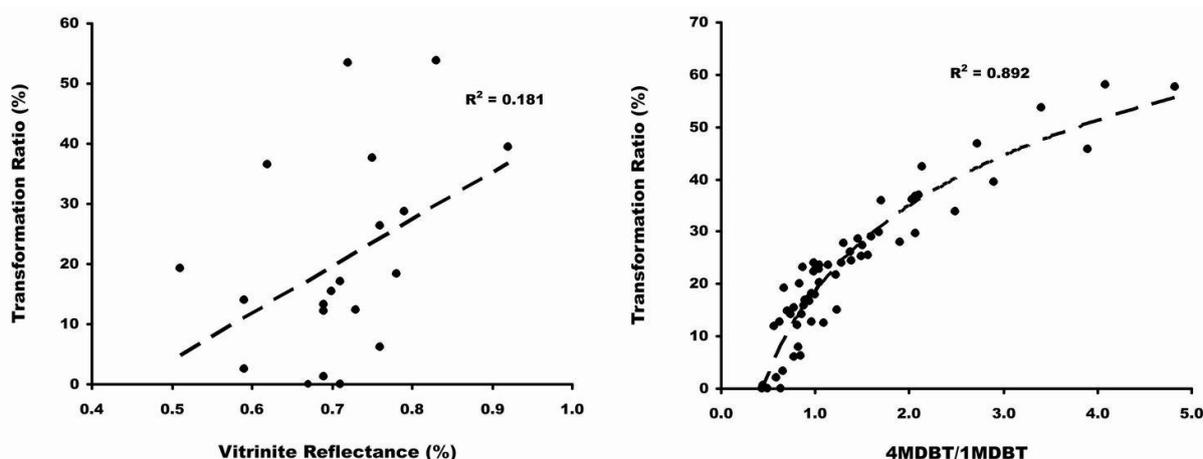


Figure 9. Transformation ratio vs. 4MDBT/1MDBT and R_o (%) for Bazhenov Formation black shales.

5. Conclusion

High sensitivity of 4MDBT/1MDBT parameter to changes in source rock thermal maturity makes it possible to evaluate areas of prospective oil and gas accumulations. Analysis of oils genetically related to the Bazhenov Formation in Western Siberia shows that 4MDBT/1MDBT value ranges from 0.80 to 18. However, oilfields with 4MDBT/1MDBT values of 0.80 – 0.90 occur very rarely and have small oil reserves. This is probable because of insufficient generated hydrocarbon amounts within catchments areas, which are necessary for larger oilfield formations. So, in the specific geological conditions of Western Siberia, 4MDBT/1MDBT values of 0.80 – 0.90 in Bazhenov Formation extracts could be considered as the minimal values of OM maturity when commercial oilfields are possible. Oils in larger oilfields in Western Siberia have 4MDBT/1MDBT ratios of 1.3 – 2.5.

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