

Physical and chemical properties, geochemistry of condensates from the deposits of the middle Jurassic Maloyamalskoe field (West Siberia) and adamantanes in them

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Abstract. According to geochemical hydrocarbon indicators (the concentration ratios for the composition of the C₄-C₉ hydrocarbons, n-alkanes and acyclic isoprenanes, C₁₀-C₁₃ adamantanes, steranes, terpanes and aromatic compounds) and carbon isotope composition, the condensates of the Maloyamalskoe deposit correspond to the terrestrial genotype. The hydrocarbon maturity indices (the sterane and terpane isomer ratios, maturity indices calculated from aromatic composition) indicate that hydrocarbon fluids formation in sediments occurs under conditions of the oil generation window. The adamantane and its alkyl-substituted derivatives identified in the studied condensates.

Keywords: geochemistry, condensate, hydrocarbons, adamantanes, West Siberia

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The obtained geochemical data on adamantanes and their distribution in condensates from the MY field, and their genetic classification are included into highly topical comprehensive studies which aim to establish the factors controlling natural synthesis of diamantoids and their abundance in the petroleum systems.

Adamantane and its derivatives, in themselves, are bridged tricyclic hydrocarbons (HCs). Owing to the unique properties imparted by their diamond-like structure, these hydrocarbons have found wide industrial application. Diamantoid hydrocarbons are currently produced mainly by chemical synthesis. Despite their high density, adamantanes are concentrated in distillate fractions, which, given their high thermal stability, makes them important components of jet fuels. The kerosene fractions of oils and condensates are therefore seen as a natural source of low-molecular-weight compounds of this series. Petroleum fluids rich in adamantane hydrocarbons are associated with the shallow occurring Cenomanian sediments with low reservoir temperatures in the northern West Siberia

(fields: Russkoe, Pangodinskoe, Van-Yeganskoe, North-Komsomolskoe) (Kashirtsev et al., 2013). Oils and condensates are generally biodegraded in these deposits. Results of the experimental studies (Baklanova et al., 2017), have shown that during rectification, the biodegraded West Siberian Cenomanian naphthenic oils enriched with adamantanes can yield kerosene fractions with low freezing point (70°C) and density of 0.905-0.912 g/cm³ that meet the GOST (Russian State Standards) requirements for jet fuels.

Experimental

The research was conducted on 5 samples of stabilized condensates from Middle Jurassic beds (Yu₂₋₃, Yu₄ and Yu₆; wells # 3005 and 3010 at the Maloyamalskoe field). The sampling depth ranges from 2,264 to 2,366 m, formation temperatures are between 69 and 80°C.

Discovered in 1975, the Maloyamalskoe (MY) gas condensate field is situated in the southern part of the South Yamal oil-and-gas-bearing region within the Yamal petroliferous province (Brekhuntsov, Bityukov, 2005). Stratification of the Middle Jurassic deposits section and structural map for the top of Yu₂ bed are shown in Fig. 1 and 2. As many as eight exploration wells were drilled on the MY field periphery. The Mesozoic-Cenozoic sedimentary cover thickness varies between 2,600 and 2,840 m. Paleozoic bedrocks exposed by four wells are

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composed of green and dark grey to greenish shales. There are three hydrocarbon pools identified within the field: one gas accumulation (PK₁ bed of Cenomanian stage (K₂)) and two gas-condensate accumulations in the Yu₂₋₃ and Yu₄ beds (Bathonian stage, J₂).

A hydrocarbon pool within the Yu₂₋₃ beds comprising a bigger half of the total gas reserves is ranked the largest. Evidences of gas presence derived from the well test results are also reported from the Yu₆ bed (J₂) (Bajocian stage) composed of fine-grained, dense, strongly cemented sandstones with rare mudstone interlayers in its lower portion. The physical parameters of the Yu₂₋₃ and Yu₄ beds are as follows: its lithology is represented by light gray fine-grained sandstones with interlayers of dark gray, dense silty-clayey rocks (Fig. 1); effective gas-saturated thickness is about 22 m; concentrations of stable condensate vary from 156.33 to 162.27 g/m³. The formation pressure is from 23.21 to 24.92 MPa, which is equal to hydrostatic pressure. The gas-condensate pools are anticlinal (Yu₂₋₃ beds) and massive (Yu₄) and are sized

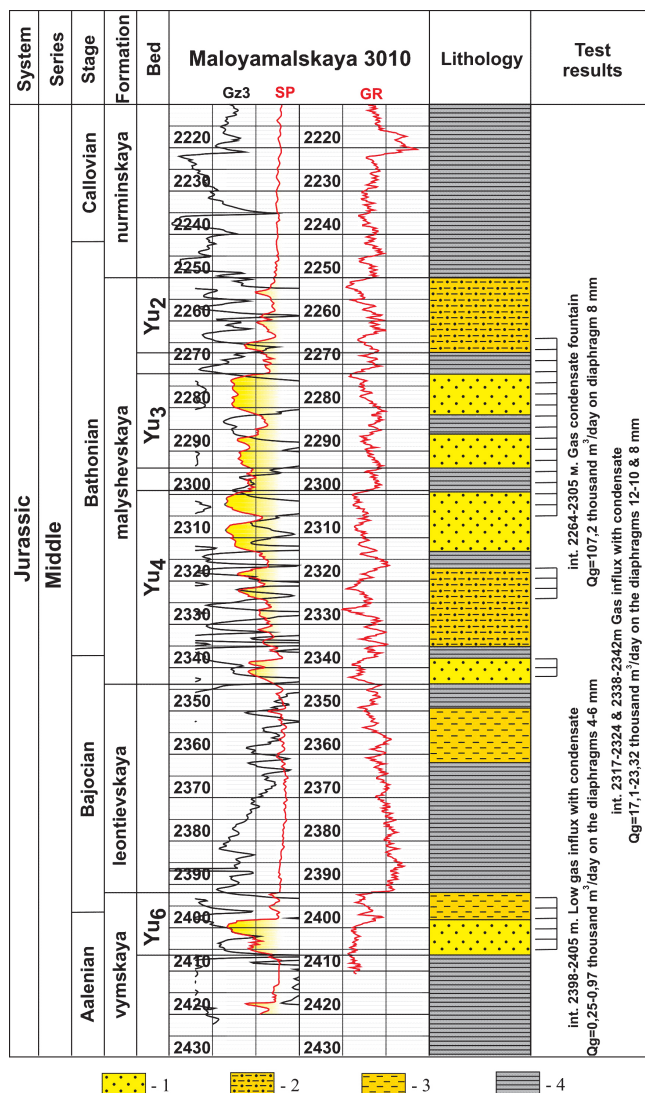


Fig. 1. Subsurface structure of Jurassic deposits in Maloyamalskaya well – 3010. Legend: 1 – sandstone; 2 – siltstone; 3 – clayey siltstone; 4 – mudstone.

10-14 by 32-34 km (extent) and 120-150 m (height) (Brekhtunsov, Bityukov, 2005). The gas-water contact (GWC) is reported at elevation of -2,361 m a.s.l. (Fig. 2).

The physical and chemical properties (density, viscosity, fractional composition) of condensates were determined by State standard (GOSTs) techniques.

The distributions of low boiling HCs and adamantanes were analyzed using chromatograms for total ion current (TIC) of unfractionated condensates obtained by the “Hewlett Packard 5890” gas chromatography-mass spectrometry GC-MS system with the highly efficient mass-selective detector Agilent MSD 5972, and ChemStation computer system for data registration and processing. Liquid sample (1 µl) introduction in the GC system was carried out in the split mode with a 10 µl SGE syringe. The samples were split into individual components using a DB1 capillary quartz column (length: 60 m, inner diameter: 0.254 mm, stationary phase: 100 % dimethylpolysiloxane, thickness: 0.25 µm). The carrier gas (helium) flow rate was 1 ml/min; injector temperature: 290°C. Individual HCs were identified based on retention times, by comparing the obtained mass-fragmentograms with the spectra available from the NIST-05 library and published data (Petrov, 1984; Bagrii, 1989; Gordadze, 2008; Giruts et al., 2014, etc.). Relative abundances of C₄-C₉ hydrocarbons were derived from a relationships between the area of a respective peak on the TIC chromatogram and sum of areas of the peaks for the identified compounds. Relative contents of adamantanes are equal to ratios between the areas of mass spectral peaks on the m/z 136, 135, 149, 163 mass chromatograms and total areas of peaks registered by the GC-MS system during the unfractionated sample analysis.

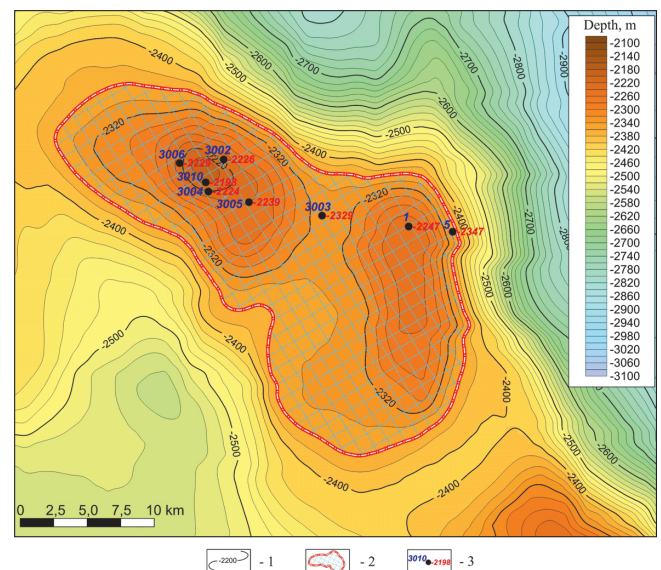


Fig. 2. Structural map for the top of producing reservoir of Yu₂ bed from the Maloyamalskoe field. Legend: 1 – isolines for the top of Yu₂ bed; 2 – unified contour line delineating hydrocarbon deposit within the Yu₂₋₃ and Yu₄ beds; 3 – wells that penetrated Middle Jurassic deposits.

The composition of aromatic hydrocarbons (benzene and naphthalene series) of unfractionated condensates was analyzed using the GC-MS method on a quadrupole "Shimadzy" GSMS-QP5050 system with automatic registration of data in the database and improved interpretation of GSMS. The chromatograph is furnished with GC capillary column DB-5MS (length: 30 m; 0.32 mm in diameter). The analysis was performed in the programmed-temperature mode (80-290°C, 2°C/min), with final temperature being maintained constant during 25 minutes. The carrier gas is helium. The ionizing voltage is 70 eV, the MS source temperature is 250°C. Both SCAN and SIM modes (Shimadzu software) were used in the data collection and processing. The compounds were identified by comparing the obtained mass spectra with those available from the NIST and WILEY libraries.

High-molecular-weight cyclic HC biomarkers of the paraffin-naphthene fractions and aromatic compounds of the naphthenoaromatic fraction were studied by GC (Maestro 7820 AGC System gas chromatograph (Agilent Technologies); normal and isoprenoid alkanes) and by GC-MS (the system including a Hewlett Packard 5890 gas chromatograph with an Agilent MSD 5972 high-performance mass-selective detector and a ChemStation HPG 1034 computer system for data acquisition and processing; steranes, terpanes, arenes). The hydrocarbon fractions were isolated from the gasoline-free condensates by methods of liquid adsorption chromatography.

Relative contents of each type compounds was determined from a relationship between its total intensity and total area (sum of all the peaks) for all of the identified compounds.

In addition to the indicators of the C₄-C₉ hydrocarbons distribution, the geochemical fingerprinting involved the carbon isotope composition data (δ¹³C, determined using DELTA V Advantage mass spectrometer, with the analysis results normalized to the VPDB international reference standard for carbon isotope).

Physical and chemical characteristics of samples, distribution of hydrocarbons and geochemical classification of condensates

The studied condensates have low densities (in the range from 722.4 to 778.0 kg/m³, averaging 744.4 kg/m³) and kinematic viscosity of about 1 mm²/s (at 20°C), with the initial boiling points being explicitly low (averaging 53°C within the range from 41°C to 81°C). These consist by more than 70 % vol. of gasoline fractions (i.b.p. < 200°C).

The condensates are dominantly represented by hydrocarbons (>99 % wt. per condensate), with very low amounts of resinous-asphalt components. The concentrations of methane-naphthenic hydrocarbons

show a 3-fold increase vs. aromatic HCs. However, despite the prevalence of methane-naphthenic HCs, condensates contain a good part of aromatics (> 15 %) (both per gasoline and condensate fractions).

The studied samples are characterized by heavy carbon isotope composition (varying from δ¹³C of -27.4 ‰ to -25.6 ‰), which suggests their predominantly terrestrial (i.e. resulting from land sediment transport to the aquatic environment) genotype (Tissot, Welte, 1981; Kontorovich et al., 1986; Peters et al., 2005, etc.).

GC-MS chromatograms of unfractionated condensates showed a shift of n-alkanes concentration peaks towards the low-molecular-weight region (n-C₆), which is usual for this type of hydrocarbon fluids, whereas abundance of n-C₁₁ (undecane) proved the highest only in one condensate from the Yu₄ bed (Fig. 3). However, group composition of C₄-C₉ hydrocarbons identified in the samples and their genetic markers attest to their single genetic type. Given that the presence of light alkanes appears slightly less than that of cyclanes, the alkanes/cyclanes ratio varies from 0.76 to 0.98, respectively. As is the case with calculated the overall amount of condensate per group composition, elevated concentrations of light arenes (> 14 % per sum of identified C₄-C₉ HCs) (Table 1) are observed in the studied samples, thereby distinguishing them from typical West Siberian petroleum fluids (Goncharov, 1987; Rudkevich, 1988; Fursenko, 2014).

In all of the studied Maloyamalskoe condensates, methylcyclohexane is reported in maximum concentrations (Fig. 3). This signature is illustrated by the C₇ HCs distribution trigonogram (Fig. 4a), where the studied samples are grouped in the region characteristic of petroleum fluids of the terrestrial genotype (Odden et al., 1998; Huang et al., 2014). Proceeding from the trigonogram, the genetic classification correlates with genetic indicators by composition of light hydrocarbons (Σcyclopentanes/Σcyclohexanes; ethylbenzene/Σxylenes; n-heptane/methylcyclohexane) (Table 1) (Goncharov, 1987; Peters et al., 2005; Fursenko, 2014, etc.). The source of the studied condensates is inferred to be single, which is confirmed by the dimethyl-substituted pentanes distribution and the toluene/n-heptane parameter (Fig. 4b) (Halpern, 1995).

C₁₄-C₃₅ n-alkanes and C₁₃-C₂₅ acyclic isoprenanes were identified by GC-MS method in the composition of methane-naphthenic fraction of the studied condensates characterized by high values of Pr/Ph ratio (> 3) and odd/even index (CPI) (>> 1) (Table 2). The n-C₂₇/n-C₁₇ ratio varies from 0.06 to 0.10. Such low values are dictated by low concentrations of high-molecular-weight n-alkanes, which is associated with redistribution of hydrocarbons by their molecular weight provoked by the processes of hydrocarbon phase separation (retrograde condensation) inherent in the formation of gas-condensate

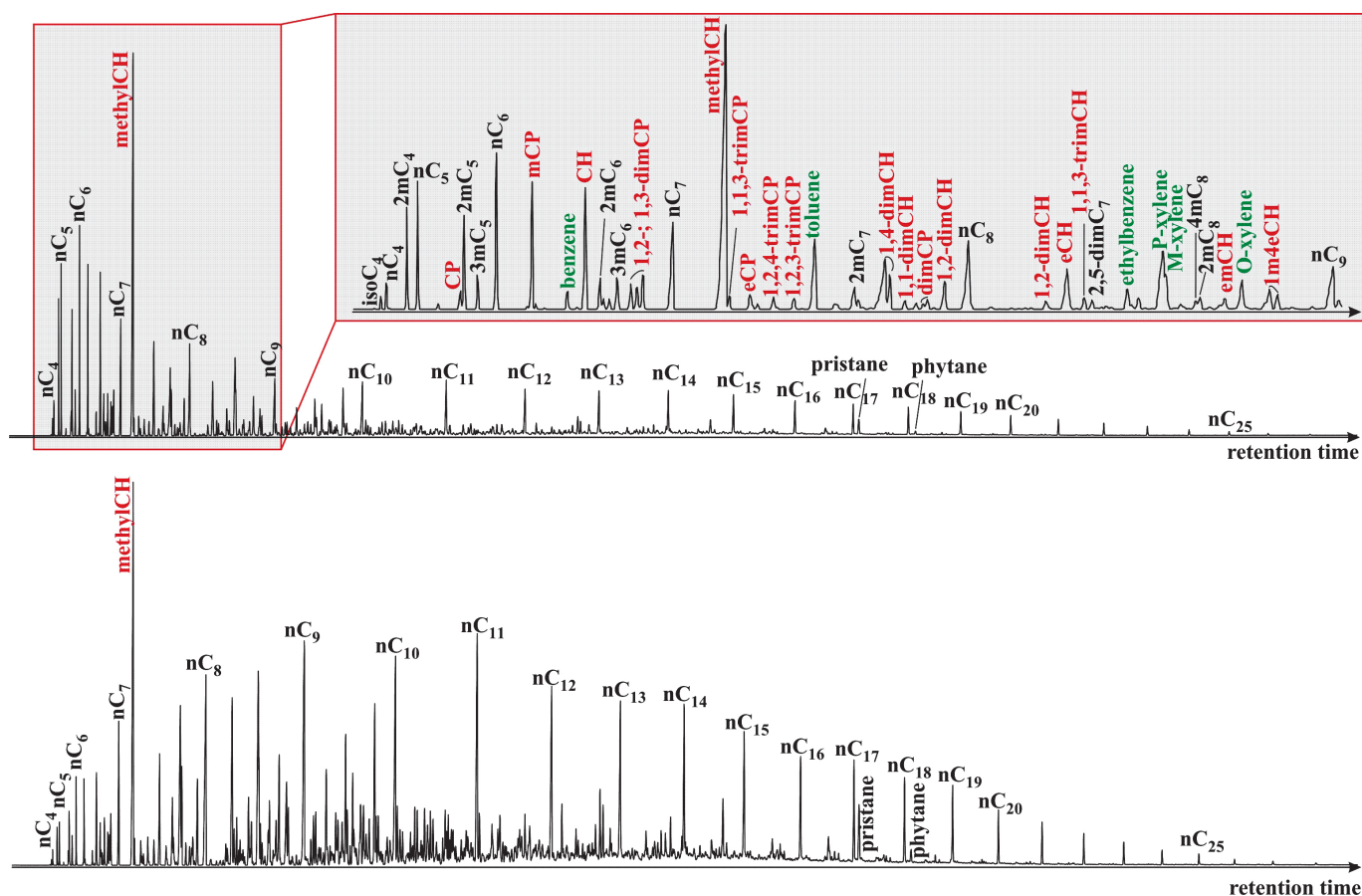


Fig. 3. TIC chromatograms for the studied condensates. Legend: CH – cyclohexane(s); CP–cyclopentane(s); m – methyl-substituted HCs; e – ethyl-substituted HCs; methylCH – methylcyclohexane; nC_4 – nC_{25} – C_4 – C_{25} n-alkanes

Bed	% per sum of identified C_4 – C_9 HCs							genetic indicators			
	Σ n-alkanes	Σ isoalkanes	Σ alkanes	Σ CHs	Σ CPs	Σ cyclanes	Σ aromatic HC	alkanes / cyclanes	n- C_7 / mCH	Σ CPs/ Σ CHs	ethylbenzene/ Σ xylenes
Yu ₂₋₃	20,87	16,87	37,74	30,65	16,00	46,65	15,62	0,81	0,22	0,52	0,18
Yu ₂₋₃ + Yu ₄	23,92	18,49	42,42	33,06	10,35	43,41	14,17	0,98	0,23	0,31	0,16
Yu ₄	17,71	17,95	35,66	32,48	14,43	46,91	17,43	0,76	0,20	0,44	0,18
Yu ₆	19,54	16,07	35,61	36,68	10,02	46,70	17,69	0,76	0,26	0,27	0,15
Yu ₄	20,81	15,79	36,60	33,87	6,65	40,52	22,87	0,90	0,25	0,20	0,16
						*aquatic genotype	>2	>1,2	>0,9	>0,3	
						*terrestrial genotype	0,75 - 1,50	0,3 - 0,8	<0,7	<0,2	

Table 1. Geochemical characteristics of the studied condensates inferred from the composition of C_4 – C_9 hydrocarbons. *genetic typing is according to (Fursenko, 2014)

pools (Starobinets, 1974; Chakhmakhchev, 1983; Reference Book of oil and gas geochemistry..., 1998). Note that the studied condensates are not subjected to biodegradation confirmed by the observed: molecular weight distributions of n-alkanes typical of unmodified petroleum fluids; predominance of the identified n-alkanes over acyclic isoprenes (pristane/n- C_{17} – 0.55-0.73; phytane/n- C_{18} – 0.17-0.24; n-alkanes/acyclic isoprenanes: 5.6-7.8) (Table 2). Besides, in-situ temperatures in the studied condensate reservoirs have prompted the environments unfavorable for bacteria

and fungi, and hence hydrocarbon biodegradation by microorganisms (Arefiev et al., 1978; Zabrodina et al., 1978; Philippi, 1977; Peters et al., 2005, etc.).

The GC-MS method enabled detection of polycyclic biomarkers (steranes and terpanes) in the saturated fractions of condensates. The steranes are dominated by ethylcholestane (C_{29}), with the cholestane group (C_{27}) being second in abundance, and, accordingly, $C_{29}/C_{27} > 1$. The diasteranes/regular steranes ratio being > 0.5 (Table 2), which was probably caused by a significant oxidation of the organic matter, i.e. the source

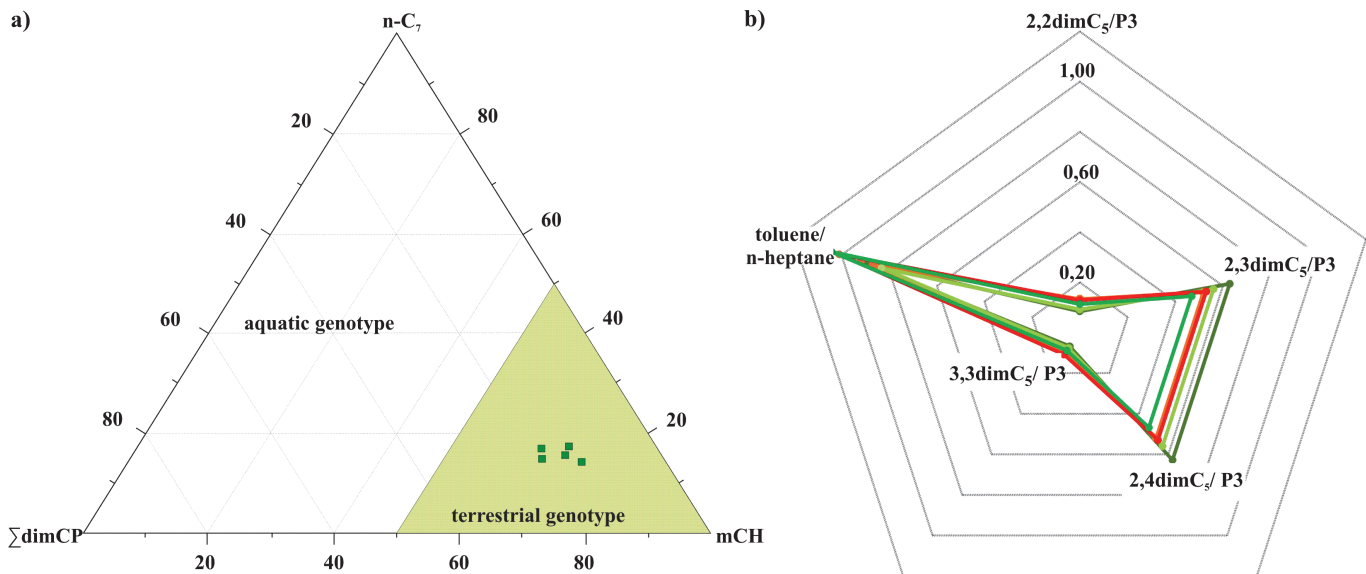


Fig. 4. Geochemical characteristics of the studied condensates inferred from the composition of C₇ hydrocarbons. (2,2-, 2,3-, 2,4-, 3,3-dimC₅ – dimethylpentanes; Σ dimCPs – sum of dimethylcyclopentanes; mCH – methylcyclohexane; P3 = 2,2dimC₅ + 2,3dimC₅ + 2,4dimC₅ + 3,3dimC₅)

Bed	n- Alkanes and acyclic isoprenanes						Steranes				Hopanes and tricyclanes		
	pristane/ phytane	pristane / n-C ₁₇	phytane / n-C ₁₈	n-алканы/ acyclic isoprenanes	n-C ₂₇ / n-C ₁₇	CPI	C ₂₉ / C ₂₇	dia-/ regular	C ₂₉		Ts/ Tm	C ₃₅ / C ₃₄	I _{TC}
									ββ(20S+20R) / αα20R	20S/ 20R			
Yu ₄	3,31	0,73	0,23	5,68	0,08	1,26	1,10	0,66	3,54	0,82	0,63	0,58	4,67
Yu ₂₋₃ + Yu ₄	3,06	0,70	0,24	5,61	0,08	1,26	1,55	1,64	4,38	1,09	0,77	0,15	9,33
Yu ₆	3,12	0,55	0,18	7,81	0,10	1,34	1,23	0,51	2,62	0,75	0,82	0,48	4,18
Yu ₄	3,53	0,62	0,19	6,26	0,07	1,29	2,04	1,71	3,65	1,05	0,59	0,23	11,83
Yu ₂₋₃	3,81	0,62	0,17	5,90	0,06	1,34	2,30	1,67	2,57	0,98	0,37	0,08	14,07

Table 2. Main geochemical indicators of the hydrocarbon biomarker composition of the saturated fraction of condensates. I_{TC} is the tricyclane index (=2*Σ tricyclanesC₁₉₋₂₀/Σ tricyclanesC₂₃₋₂₆) (according to (Kontorovich et al., 1999)). CPI is ((n-C₂₅+n-C₂₇+n-C₂₉+n-C₃₁+n-C₃₃)/(n-C₂₆+n-C₂₈+n-C₃₀+n-C₃₂+n-C₃₄)+(n-C₂₅+n-C₂₇+n-C₂₉+n-C₃₁+n-C₃₃)/(n-C₂₄+n-C₂₆+n-C₂₈+n-C₃₀+n-C₃₂))/2 (according to (Bray, Evans, 1961))

of condensates. The C₂₉ steranes isomer ratios (maturity coefficients: ββ(20S+20R)/αα20R 20S and αα/αα 20R) of the studied condensates are found to be very close (2.62-4.38 and 0.75-1.09, respectively), enucleate the extent of steranes isomerization typical of the oil window (Petrov, 1984).

C₁₉-C₃₁ tricyclanes (cheilantanes) (41.33-59.18 % per sum of terpanes) predominate among the tri-, tetra- and pentacyclic tarpanes, while their abundance is approximately equal to hopanes and homohopanes (34.28-52.63 % per sum of terpanes), and tetracyclanes and moretanes are present in minor amounts. The elevated concentrations of tricyclanes comparable to the abundance of hopanes and homohopanes probably resulted from (by analogy with the n- and isoalkanes) the HC molecular weight redistribution during the formation of gas-condensate pools (Starobinets, 1974; Chakhmakhchev, 1983; Reference Book of oil and gas

geochemistry..., 1998). Analysis of the composition of identified hopanes and moretanes revealed that C₃₀ hydrocarbons concentrations are higher vs. C₂₉ HC, while C₂₇ and C₃₁-C₃₅ hopanes and moretanes are significantly fewer in number. Low C₃₅/C₃₄ ratios (< 1) suggest the formation of gas-prone source rocks in suboxidation environments, which is consistent with the Pr/Ph and diterpanes/regular steranes ratios (Tissot, Welte, 1981; Petrov, 1984; Peters et al., 2005, etc.). Tricyclanes (cheilantanes) are dominated by low-molecular-weight (C₁₉-C₂₀) homologues, whereas concentrations of C₂₁-C₃₁ HCs have shown multifold decrease. Accordingly, the tricyclane index values are high (I_{TC} >> 1). As such, its high values, according to (Kontorovich et al., 1999), can be seen as evidence of terrestrial genotype of the studied condensates. The Ts/Tm indicator value (0.37-0.82) and the ratio between the S and R isomers of C₃₁-C₃₃ homohopanes (S > R) suggest the formation

of condensates in the conditions of oil window (Petrov, 1984; Peters et al., 2005, etc.).

According to GC-MS analysis of unfractionated samples, among the aromatic hydrocarbons identified in the MY condensates the abundance of monoarenes (89.8-95.2 % rel.) is higher vs. biaromatic HCs (4.4-9.1 % rel.). Inasmuch as triaromatic compounds are present in minor amounts (0.05-0.16 % rel.), they were therefore investigated separately, within the aromatic fraction of condensates.

The composition of low-molecular-weight benzenes is dominated by toluene and dimethylbenzenes (xylenes). Among C_7 - C_{19} monoarenes, the maximum concentration accounts for n-alkylbenzenes (n-AB; 52.2-69.3 % rel.), which is followed in descending order by n-alkyltoluene (n-At; 18.3-34.0 % rel.), trimethylbenzenes (0-9.3 % rel.), tetramethylbenzenes (0-2.6 % rel.) and tetralines (naphthalene-substituted benzenes) (< 0.01 % rel.). The concentrations of long-chain n-AB and n-AT C_{11+} (0.8-1.1 and 0.9-2.3 % rel. respectively) are by an order of magnitude lower compared to low-molecular-weight alkylbenzenes and alkyltoluenes (C_7 - C_{10}) (52.2-69.3 and 18.4-34.0 % rel., respectively). The predominance of low-molecular over high-molecular monoarenes, as is the case with other hydrocarbons (e.g. n-alkanes), was most likely caused by their selective accumulation in the gas condensate mixtures, as the deposit formation proceeded.

Biarenes in the studied condensates are represented mainly by unsubstituted naphthalene (0.92-1.86 % rel.), as well as by mono- (1.64-3.29 % resp.), di- (1.30-2.82 % rel.), tri- (0.45-1.34 % rel.) and tetramethyl-substituted (0.06-0.15 % rel.) naphthalenes. Besides, the isolation of cadalene (0.01 % rel. or less) and fluorenes (0.03-0.08 % rel.) in the studied samples was successful.

The analysis of the individual composition of alkylnaphthalenes showed that all the condensates dominates unsubstituted naphthalene, as well as 2- and 1-methylnaphthalene. The established elevated concentrations of 1,2,5- and 1,2,7-TMN complexed by the presence of cadalene, suggest the terrestrial source of the investigated samples, and hence its accumulation in low reducing conditions (Armstroff et al., 2006; Perumal et al., 2008). The high values of naphthalene maturity indices (1.7-2.1; DNR2 ([2,6-(β,β)-+2,7-(β,β -) dmn]/1,5-(α,α -)dmn): 1.7-1.8; TNR6 ([1,3,7-(α,β,β -)+1,3,6-(α,β,β -)tmn]/[1,2,5-(α,β,α -)+1,2,4-(α,β,α -)tmn): 1.5-2.0)) attest to high maturation of the analyzed samples (Radke et al., 1986; Peters et al., 2005).

The composition of aromatic fractions of the condensates was investigated by the CMS method, involving phenanthrenes (91.80-93.97 % rel.), dibenzothiophenes (< 6 % rel.), mono- (< 1 % rel.) and triaromatic (< 1 % rel.) steroids. Such low concentrations of dibenzothiophenes suggest that

the source OM accumulated in the suboxidation conditions (Kontorovich et al., 2004; Peters et al., 2005, etc.), which is consistent with the respective parameters (Pr/Ph, diasteranes/regular steranes, C_{35}/C_{34} homohopanes) of the saturated fraction composition. Maturity indicators calculated from the composition of the identified arenes and dibenzothiophenes (DBT) (Table 3). Dibenzothiophene index (DBTI \approx 1), as well as the phenanthrene index (PI – 0,39-0,47), the ratios between triaromatic steroids (TASI: 0.28-0.60), the phenanthrenes ratios (1-methylP/P – 0.40-0.53; 3-methylP/P – 0.35-0.42; 9-methylP/P – 0.54-0.62, etc.) are largely associated with characteristics of the OM in the oil window (Radke et al., 1986; Kontorovich et al., 2004; Peters et al., 2005, etc.), which is comparable with the maturity indicators of steranes, terpanes and naphthalenes.

Bed	TAS/ MAS	P/ DBT	DBTI	PI	TASI
Yu ₄	0,53	17,51	1,00	0,41	0,37
Yu _{2,3} + Yu ₄	1,46	16,34	1,19	0,47	0,60
Yu ₆	2,28	16,85	1,01	0,44	0,28
Yu ₄	0,79	16,54	0,98	0,42	0,43
Yu _{2,3}	1,34	18,51	0,91	0,39	0,51

Table 3. Geochemical indicators inferred from the aromatic fraction of condensates. Legend: MAS is monoaromatic steroids; TAS is triaromatic steroids; P is phenanthrenes; DBT is dibenzothiophenes; DBTI is dibenzothiophene index ((2- + 3-methylDBT)/ Σ DBTs); PI is phenanthrene index (2-methylP/P); TASI is (TAS C_{20} + TAS C_{21})/ Σ TASs

Distribution of adamantane and its derivatives

The GCMS analysis of unfractionated condensates allowed to identify adamantane and its mono-, di- and trimethylsubstituted derivatives in their composition (Fig. 5). Unlike biodegraded oils from the Van-Yeganskoe, Russkoe and North-Komsomolskoe field (Kashirtsev et al., 2013), the investigated condensates showed no tetramethylsubstituted adamantanes, whereas among the ethylsubstituted adamantanes (with the exception of condensates from the Yu₆ bed), only 1- and 2-ethyladamantanes are observed (Fig. 4). Besides, diamantoid hydrocarbons which yielded no individual peaks on total ion current (TIC) mass-chromatograms (Fig. 5), showed up only on fragment ion scans (m/z 135, 136, 149, 163).

Accordingly, the abundance of adamantane HCs identified in the composition of the studied samples is low, not exceeding 0.1 % rel. (Table 4), which is an order of magnitude less, than in the South Tambeyskoye biodegraded condensates (Shevchenko et al., 2016). The dominance of disubstituted derivatives is slightly downplayed, as compared to monosubstituted, while the trisubstituted adamantanes are progressively decreasing.

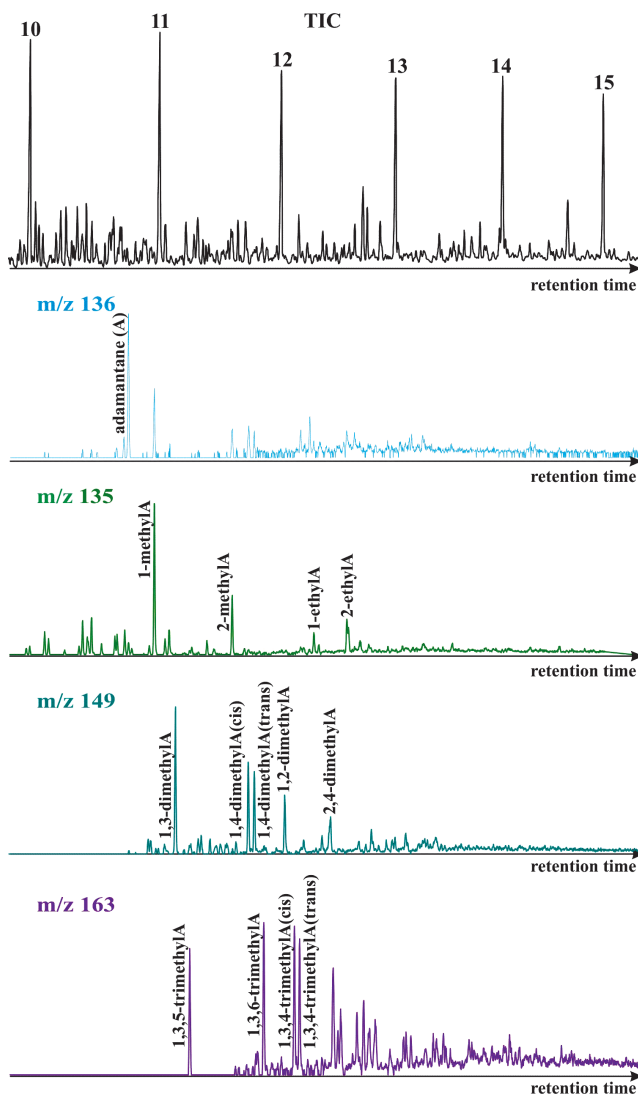


Fig. 5. Mass-chromatograms (TIC, m/z 135, 136, 149, 163) of diamantoid hydrocarbons identified in the Maloyamalskoe condensates (10-15 – n-alkane peakes from C₁₁ to C₁₅)

The abundance of unsubstituted adamantane is not more than 0.005 % rel. The adamantanes ratios derived from the studied samples differ slightly (Table 4), indicating a single source of the Maloyamalskoe condensates. By their molecular weight, the relative abundances follow in descending order: C₁₂ adamantanes, then C₁₁ and C₁₃, with the adamantane proper (C₁₀), as was noted above, culminating in lowest concentrations in the studied condensates. The ratios of adamantanes with different molecular weight in the Maloyamalskoe samples show striking similarity to these parameters in the Sredne-Vilyuyskoe condensates of the terrestrial genotype (Ivanova, 2010). It was shown previously (Schulz et al., 2001; Gordadze, 2008; Ivanov, 2010, etc.), that the relationships among methyl-substituted adamantanes differ significantly from equilibrium relations and tend to decrease with the increasing molecular weight. The studied condensates are no exception, which are characterized by: 1-methylA/(1-methylA + 2-methylA) > 1,3-dimethyl/(1,3-+1,2-+1,4-dimethyl) > 1,3,5-trimethyl/(1,3,5- + 1,3,6- + 1,3,4-trimethyl) (Table 4), as well as by the predominance of cis-isomers of dimethyl and trimethyl adamantanes over the trans-isomers.

Conclusions

Analysis of the distribution of major groups of the identified hydrocarbons along with the respective genetic parameters (composition of C₄-C₉ hydrocarbons; Pr/Ph; CPI; C₂₉/C₂₇ steranes; the ratios of tricyclic terpane (I_{tc}); C₃₅/C₃₄ homohopanes; low concentrations of dibenzothiophenes) complemented by the heavy carbon isotope composition, allow to infer that the investigated condensates from the Maloyamalskoe field were generated at the expense of lipid components of

Bed	Yu ₂₋₃	Yu ₂₋₃ + Yu ₄	Yu ₄	Yu ₆	Yu ₄
Content, % on condensate					
adamantane (m/z 136)	0,004	0,003	0,005	0,002	0,005
monosubstituted (m/z 135)	0,033	0,021	0,040	0,014	0,045
disubstituted (m/z 149)	0,037	0,022	0,044	0,017	0,048
trisubstituted (m/z 163)	0,012	0,008	0,016	0,006	0,019
Sum	0,086	0,054	0,105	0,039	0,117
Relations between identified adamantanes (A)					
C ₁₀ : C ₁₁ : C ₁₂ : C ₁₃	5:26:55:14	5:28:53:14	5:27:53:15	5:36:44:15	4:28:51:17
C ₁₁ / C ₁₃	1,86	1,92	1,85	2,33	1,73
C ₁₂ / C ₁₃	3,81	3,61	3,57	2,80	3,13
A/ (1-methylA + 2- methylA), %	17	19	17	15	14
1- methylA/ (1- methylA + 2- methylA), %	71	72	72	68	74
1- ethylA/ (1- ethylA + 2- ethylA), %	31	30	28	n/def.	31
1,3- dimethylA/ (1,3-+1,2-+1,4- dimethylA), %	37	37	37	35	35
1,3,5- trimethylA / (1,3,5- + 1,3,6- + 1,3,4- trimethylA), %	26	29	26	17	21
1,4- dimethylA (cis)/ 1,4- dimethylA (trans), %	1.10	1.15	1.20	1.12	1.16
1,3,4- trimethylA (cis)/ 1,3,4- trimethylA (trans), %	12.56	1.06	13.47	0.95	13.38

Table 4. Distribution of adamantane and its alkyl-derivatives identified in the studied condensates

the predominantly terrestrial organic matter accumulated in the suboxidation environments. The sterane/terpane isomer ratios, Ts/Tm ratios, as well as the maturity indicators of arenes and dibenzothiophenes derived from their composition suggest that these petroleum fluids composition formed in the conditions of the oil window. The source of some condensates being common is also corroborated by the relations between the identified diamantoid hydrocarbons. The observed significant abundances of diamantoid hydrocarbons in the Maloyamalskoe condensates have prompted an inference about potential discovery of petroleum fluids selectively enriched with adamantane and its derivatives in the shallow occurring reservoirs within the overlying Cretaceous deposits featured by low formation temperature (< 70°C) and intense biodegradation.

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