



Research article

Specific features of kinetics of thermal transformation of organic matter in Bazhenov and Domanik source rocks based on results of pyrolysis gas chromatography

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Abstract. Pyrolysis of organic matter with subsequent analysis of hydrocarbon composition of the resulting products allows obtaining multicomponent distribution spectra of the generation potential by the activation energies of reactions of kerogen transformation into hydrocarbons. Configuration of the spectra depends on the structure of kerogen and is individual for each type of organic matter. Studies of kerogen kinetics showed that the distribution of activation energies is unique for each oil source rocks. The kinetic model of thermal decomposition of kerogen of the same type, for example, marine planktonic (type II), can differ significantly in different sedimentary basins due to the multivariate relationship of chemical bonds and their reaction energy threshold. The developed method for calculating multicomponent kinetic spectra (four-component models are used) based on results of pyrolysis gas chromatography allows obtaining one of the most important elements of modelling the history of oil and gas generation in geological basins. Kinetic parameters of organic matter of oil and gas source rocks influence the onset time of generation and directly reflect differences in the composition and structure of different types of kerogens. The results of determining the kinetic parameters of two high-carbon source rocks occurring across the territory of three oil and gas basins are shown. Generation and updating of the data of kinetic models of certain oil and gas source rocks will increase the reliability of forecasting oil and gas potential using the basin modelling method.

Keywords: pyrolytic gas chromatography; kinetics; hydrocarbon generation; kerogen; pyrolysis; activation energy; oil; gas

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Introduction. According to the sedimentary-migration theory [1-3], the origin of oil and gas is associated with organic matter (OM) of plants and living organisms buried together with mineral components in sedimentary basins. This theory is confirmed by results of modern fine chemical analyses that allow recording the presence of purely biogenic molecules in oils (biomarkers or chemofossils). After sedimentation, diagenetic and early catagenetic transformation, OM is first decomposed by microorganisms to molecules of carbohydrates, proteins and lipids, then it is gradually transformed from a biopolymer into a geopolymer (kerogen) by polymerization and condensation [2, 4]. At this stage, the composition and oil and gas generation potential of kerogen form depending on composition of the source biomass and the conditions of OM burial in sediments. During further transformation at the stages of catagenesis, where the main factors influencing the transformation of OM are temperature and time, kerogen is subject to destruction with formation of hydrocarbons (HC) [1, 3, 5].

Mathematical modelling of oil and gas formation processes is associated with development of pyrolytic studies of OM, which is currently the main tool for investigating the generation characteristics of source formations [6-8]. Quantitatively, the process of kerogen destruction with formation of



various hydrocarbon compounds is described by the kinetics of chemical reactions [9, 10]. To simplify the calculations, it is assumed that kerogen transformation is a series of reactions that occur simultaneously and have the same energy barrier [9, 11]. The energy barrier is the activation energy required to break the chemical bonds of a given set of reactions. The rate of the chemical reaction of OM cracking in laboratory conditions can be described by the first-order Arrhenius equation and extrapolated to geological time [5, 9, 12].

The spectra of OM transformation reactions obtained in the course of kinetic studies represent a set of activation energies and the proportion of total amount of generation products corresponding to each value. The kinetic spectra clearly illustrate the destruction features of kerogen of different genetic types to oil and gas components [5, 13].

Calculation and plotting of kinetic spectra are performed on the basis of studying samples of source rocks applying the method of pyrolysis gas chromatography (or Py-GC) [14-16] which allows dividing the pyrolysis products into groups of HC. Two- (oil and gas) and four-component (methane, gases C₂-C₅, liquid HC C₆-C₁₄ and heavy liquid and solid components C₁₅₊) kinetic schemes are most often applied in basin and petroleum generation modelling [17]. Frequently, due to the lack of data on kinetic constructions on samples of the source rocks of the investigated basin, while modelling, it is necessary to use kinetic spectra from other basins (from the geochemical library of the software package applied). Generation and updating of the database of our own kinetic models for oil and gas source rocks will improve the reliability of oil and gas presence forecast using the basin modelling method [13].

To conduct kinetic studies, it is necessary to be follow by a number of conditions for sampling: the sample should characterize the average OM content for the oil source rocks and their generation potential; the degree of OM maturity should correspond to the beginning of the “oil window” (T_{max} of pyrolysis 420-435 °C, Ro – 0.5-0.7 %), i.e. before the start of generation of the main volumes of HC [6, 18].

The results of kinetic studies of two source rocks highly enriched in marine planktonic OM – Domanik deposits – are presented using core samples from wells of the Volga-Ural and Timan-Pechora oil and gas basins and the Bazhenov formation of the West Siberian oil and gas basin as examples.

Methods. The essence of the pyrolytic chromatography method is heating a weighed quantity of rock in a pyrolytic cell followed by chromatographic separation of kerogen cracking products on a capillary column and registration of the investigated components using a flame ionization detector (FID). A set of devices was applied in the study – a Frontier Lab EGA/PY-3030D pyrolytic cell, an Agilent 7890A gas chromatograph, and a unit for trapping pyrolysis products with liquid nitrogen. One of the main elements of this process flow chart is the PY-3030D pyrolytic cell. This is a multifunctional tool that allows studying samples in both single-stage and multi-stage pyrolysis modes.

For complete separation of gases and their separation from liquid pyrolysis products, a cryogenic trap is installed in the thermostat of the gas chromatograph, into which the initial section of the capillary column is placed. The process of cryogenic focusing of pyrolysis products is fully automated and controlled by the software for operating the pyrolytic cell. Pyrolysis products entering the capillary column are concentrated in its initial section. For separation of light hydrocarbons C₁-C₅, a system of cryotrapping of pyrolysis products with liquid nitrogen in the initial section of the column is applied. This allows achieving complete separation of C₁-C₅ from each other due to the start of the column temperature program from deep-freeze area. A non-polar PONA 50M × 0.2 mm × 0.5 μm column was used in the analysis. The pyrolysis oven temperature was 300-650 °C (with a 25 °C interval); heating time at each stage was 5 min; time of capturing the pyrolysis products with liquid nitrogen 5 min; stable temperature of coolant (liquid nitrogen) –180 °C.



At the same time, rock samples were investigated on a Rock-Eval analyser using the Optkin method to determine the Arrhenius frequency factor characteristic of reactions of a specific kerogen. The investigation of one sample includes a set of six analyses using the Bulk Rock method with different heating rates at the pyrolysis stage – 1; 5; 10; 15; 20; 25 °C/min. Processing of the obtained pyrolysis curves, calculation of kinetic characteristics and plotting of single-component histograms of activation energy distribution are performed using Optkin software.

When solving the Arrhenius equation for each heating stage programmed during the pyro-GC study, a set of activation energies is obtained that describes the reactions of thermal destruction of kerogen in the studied rock samples. The quantities of generated gaseous and liquid HC obtained by stages are normalized to the total yield of generation products during pyrolysis of a specific sample (hydrogen index HI), thus obtaining the ratio of HC-components released during pyrolysis.

All samples were pre-extracted with chloroform until the solvent in the Soxhlet apparatus tube completely ceased to glow in UV light. The chromatogram obtained at heating to 300 °C was not taken into account in the calculations for avoiding the inclusion of sorbed free HC contained in rock.

Discussion of results. A comparative study of oil and gas formation processes in source formations of different ages containing similar types of OM is of scientific interest from the viewpoint of identifying the genetic features and quantitative characteristics of HC generation and migration, which allow to perform a reasonable forecast of oil and gas presence and an estimation of the potential oil and gas resources in prospective areas. The results of geochemical studies of OM in Domanik-type deposits are considered, which include the Domanik (Semilukskii) horizon and the Bazhenov formation in respect of enrichment (over 0.5 % [19]) and the marine type of OM.

Domanik deposits in the Volga-Ural and Timan-Pechora oil and gas basins occur as a broad band along the eastern margin of the East European Platform. Within the Volga-Ural Basin, siliceous-carbonate deposits highly enriched in marine OM occur on slopes of the South and North Tatarskii, Bashkirskii, Zhigulevskii-Pugachevskii, Permskii and Orenburgskii paleodomes and within paleotroughs of the Kamskaya-Kinelskaya system [20-22]. In the Volga-Ural Basin, the Domanik-type deposits are most widespread in the Middle Frasnian Domanik and Upper Frasnian Rechitskii horizons (Devonian). In the Voronezhskii, Evlanovskii and Livenskii horizons of the Upper Frasnian, the occurrence area of Domanik-type deposits narrows. They occur within the axial parts of the Kamskaya-Kinelskaya system of paleotroughs and outer slopes of paleodomes. In the Famennian (Upper Devonian) and Tournaisian (Lower Carboniferous) high-carbon carbonate-siliceous rocks occur only as thin interbeds among the predominantly carbonate sections and are concentrated in axial parts of depressions of the Kamskaya-Kinelskaya system [23].

Stratigraphic range of Domanik deposits in the Timan-Pechora oil and gas province coincides with the range of the Volga-Ural Basin. Domanik horizon of the Middle Frasnian is the most OM-enriched part of the Domanik deposits, which also has the greatest areal distribution. The upper boundary of occurrence of Domanik-type rocks gradually changes eastwards – from the Domanik horizon of the Middle Frasnian in Southern Timan to the Tournaisian (Lower Carboniferous) in depressions of the Pre-Ural Trough [24-26].

The Domanik sequence under consideration demonstrates a highly diverse lithological composition of rocks. It comprises limestones, often siliceous, siliceous marls, siliceous mudstones, silicites, and oil shales. The deposits contain a large amount of free silica and have a low clay content [27].

Domanik deposits are considered to be the classic oil source rocks with a high content of marine OM accumulated under conditions of a long-term uncompensated subsidence of large sea basins. The thickness of Domanik-type deposits is small – from a few tens to 100 m. Concentrations of organic carbon (TOC) averaged through the thickness of the Domanik-Famennian complex vary from 0.8 % in zones of paleodomes, where Domanik-type rocks make up only the Domanik and Rechitskii



horizons, to 5-6 % in zones of paleotroughs, where the occurrence range of OM-enriched rocks covers the Middle-Upper Frasnian and the Famennian deposits.

According to the material-petrographic composition [28] the source material of OM in the Domanik deposits, along with planktonic algae, was zooplankton (tentaculites). Zooplankton enriches the OM with humoid components at the expense of transformation products of shell chitin. The specific composition of the source material of OM in the Domanik sequence distinguishes it from other oil source deposits and reduces its initial hydrocarbon generation potential.

In the Volga-Ural Basin, samples of the Semilukskii (Domanik) and Rechitskii horizons were taken from Kutushskaya 264 well on the western slope of the South Tatar Arch. In the Timan-Pechora Region, samples of the Domanik horizon were taken from the shallow Komi 1 well in Southern Timan.

Table 1 shows the results of analysing rock samples by the Rock-Eval method before and after extraction reflecting the content and some data on the composition of OM in rocks of the Domanik and Rechitskii horizons. The selected samples represent three different lithotypes of the studied deposits: oil shales with the highest OM content, siliceous limestones, and silicites [21].

Table 1

Results of investigating samples by Rock-Eval method

Well	Formation	Sampling depth, m	Bit, %	Stage of investigation	S ₁ , mg HC/g of rock	S ₂ , mg HC/g of rock	T _{max} , °C	TOC, %	HI, mg HC/g of TOC	PI
Kutushskaya 264 (siliceous limestone)	D ₃ f ₃ rc	1,958.25	0.42	Before extraction	0.94	20.51	420	3.78	543	0.04
				After extraction	0.20	19.54	420	3.67	532	
Kutushskaya 264 (oil shale)	D ₃ f ₃ rc	1,959.05	2.37	Before extraction	11.24	209.92	406	35.02	599	0.05
				After extraction	2.99	210.05	409	34.87	602	
Kutushskaya 264 (silicite)	D ₃ f ₂ sm	1,972.00	0.23	Before extraction	0.85	15.86	419	2.93	541	0.05
				After extraction	0.66	15.93	421	3.02	527	
Komi 1 (siliceous limestone)	D ₃ f ₂ dm	74.05	0.24	Before extraction	0.47	8.93	415	1.67	536	0.05
				After extraction	0.12	8.84	415	1.62	546	
Komi 1 (oil shale)	D ₃ f ₂ dm	112.85	5.45	Before extraction	24.15	260.65	415	42.09	619	0.08
				After extraction	4.60	208.51	413	35.57	586	
Komi 1 (silicite)	D ₃ f ₂ dm	113.47	3.29	Before extraction	6.72	40.81	415	6.52	626	0.14
				After extraction	0.29	21.63	416	4.11	526	
Verkhnyumskaya 34 (siliceous clay rock from the upper part of formation)	J ₃ -K ₁ bg	2,550.58	1.88	Before extraction	7.22	102.25	425	16.29	628	0.07
				After extraction	0.41	88.96	426	14.56	611	
Verkhnyumskaya 34 (siliceous clay rock from the lower part of formation)	J ₃ -K ₁ bg	2,591.90	0.66	Before extraction	4.58	91.79	426	14.52	632	0.05
				After extraction	0.44	68.86	424	13.73	502	

Notes. Bit – content of chloroform bitumen in rock. Rock-Eval parameters: S₁ – content of thermodesorbed free HC; S₂ – content of HC released during pyrolysis of kerogen and resine-asphaltene fraction; T_{max} – temperature at maximum of S₂ peak; TOC – total content of organic carbon; HI – hydrogen index of kerogen, HI = S₂·100/TOC; PI – productivity index, PI = S₁/(S₁ + S₂).

In accordance with regional Mesozoic stratigraphic charts of Western Siberia, high-carbon deposits of the *Bazhenov horizon* occur in central regions (Bazhenov formation and Nizhnetuleimskaya Subformation) and are surrounded by its less OM-enriched stratigraphic equivalents [29]. According to the OM distribution schemes in the Bazhenov formation and its facies equivalent, the Nizhnetuleimskaya Subformation, TOC content over most of the occurrence area of high-carbon deposits exceeds 5-7 % [30, 31]. At the same time, the most OM-enriched interbeds with TOC content over 10-15 % are mainly confined to the upper part of the formation the thickness of which is 30-50 % of total thickness. The lower part of the Bazhenov formation is less enriched in OM than the upper one.

Taking into account the heterogeneous structure of the Bazhenov formation, samples for kinetic investigations were taken from the two most OM-enriched lithological units from the protocatagenesis zone (Verkhnyumskaya 34 well) (Table 1).



A comparative analysis of Rock-Eval results for a large collection of rock samples showed that the initial characteristics of the Domanik OM differ from OM of the Bazhenov formation. The predominant component of OM in the Bazhenov formation is phytoplankton (peridinium algae, diatoms, coccolithophores, etc.) [32] with a higher proportion of lipids. Before the start of intense HC generation processes, the hydrogen index HI of kerogen in the Bazhenov formation is 700 mg HC/g TOC, and the share of pyrolyzable carbon PC participating in the formation of HC accounts for 60 % of TOC. The remaining share of TOC is non-pyrolyzable RC, i.e. inert carbon. OM of Domanik is characterized by a lower initial HI – 600 mg HC/g TOC and, accordingly, a lower proportion of PC – ~55 % (Fig.1).

Zooplanktonogenic OM in Domanik deposits is characterized by increased initial bituminosity, which is one of the causes of early migration of HC and manifestation of the main phase of oil and gas formation at lower temperatures compared to the Bazhenov formation.

The rate of OM conversion into HC for the Domanik sequence is lower compared to the Bazhenov deposits. For example, by the maturity level of MK₃-MK₄ ($T_{max} > 455$ °C), the residual generation potential (HI) of Domanik OM is 170 mg HC/g TOC, whereas for OM of the Bazhenov formation it does not exceed 100 mg HC/g TOC, i.e. it is virtually exhausted. According to T.K. Bazhenova, the generation process of liquid HC in Domanik source rocks with algozoogenic OM extends over a larger cata-genetic range compared to the algogenic biocenotic type of OM [33]. This is due to a significant proportion of resinous-asphaltene materials in the products generated by algozoogenic OM which, when subjected to secondary cracking, can be destroyed with release of light liquid HC till the end of apoca-tagenesis.

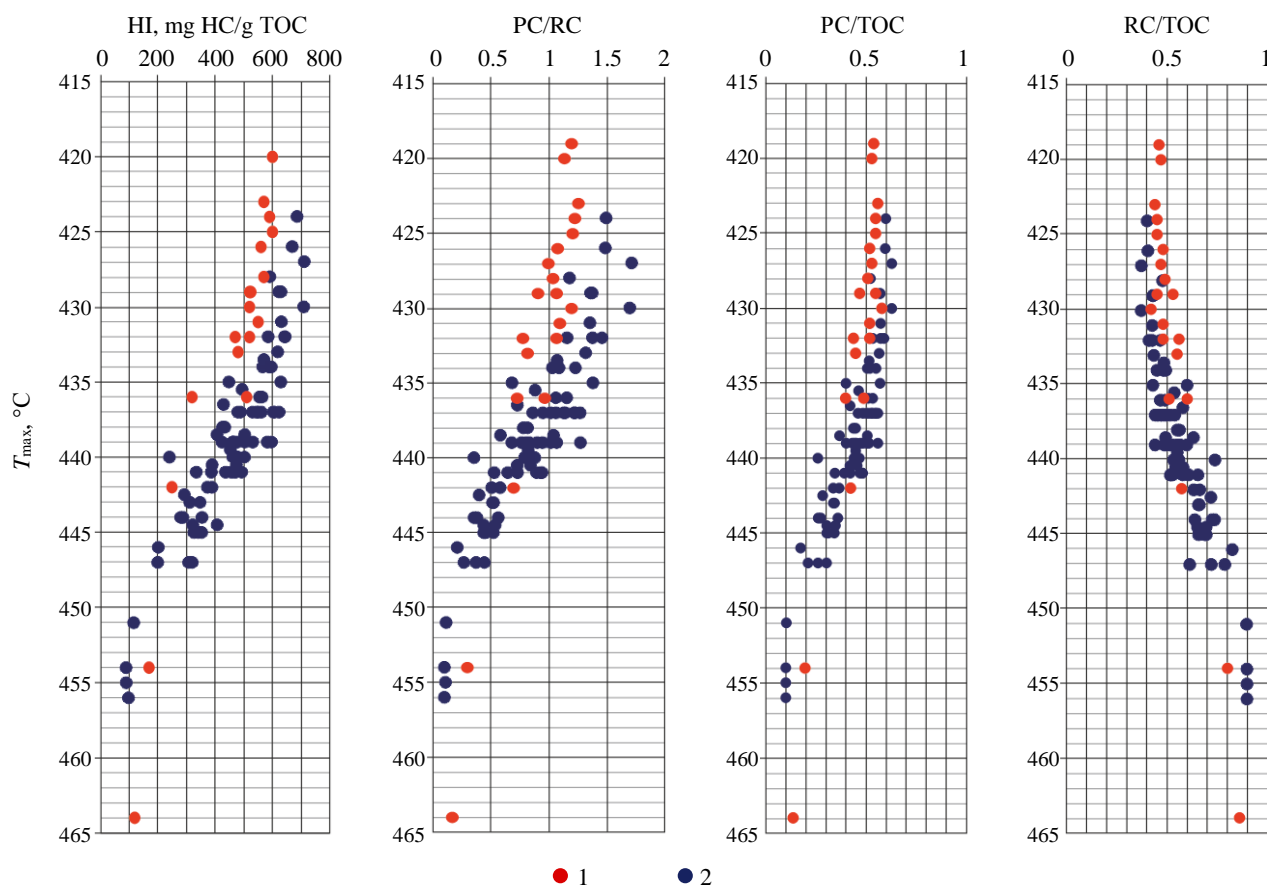


Fig.1. Rock-Eval parameters and their relations with growth of OM catagenesis (T_{max}) in Domanik-type deposits

1 – deposits of Domanik (Semilukskii) and Rechitskii horizons; 2 – deposits of Bazhenov and Nizhnetutleinskaya formations

PC – pyrolyzable organic carbon in rock, %; RC – non-pyrolyzable organic carbon in rock, %.

Values of parameters and ratios are taken as the mean ones for the well section



Modelling of kinetic spectra for samples from *Domanik deposits* showed a similar character of the dynamics of HC generation (Fig.2). An extensive distribution of activation energies E_a in the range of 43-69 kcal/mol, typical of marine planktonic OM, was obtained. More than 80 % of the volume of generated HC are distributed within a narrow range of activation energy – only 4-6 kcal/mol. A pronounced maximum of HC generation is recorded within 52-56 kcal/mol.

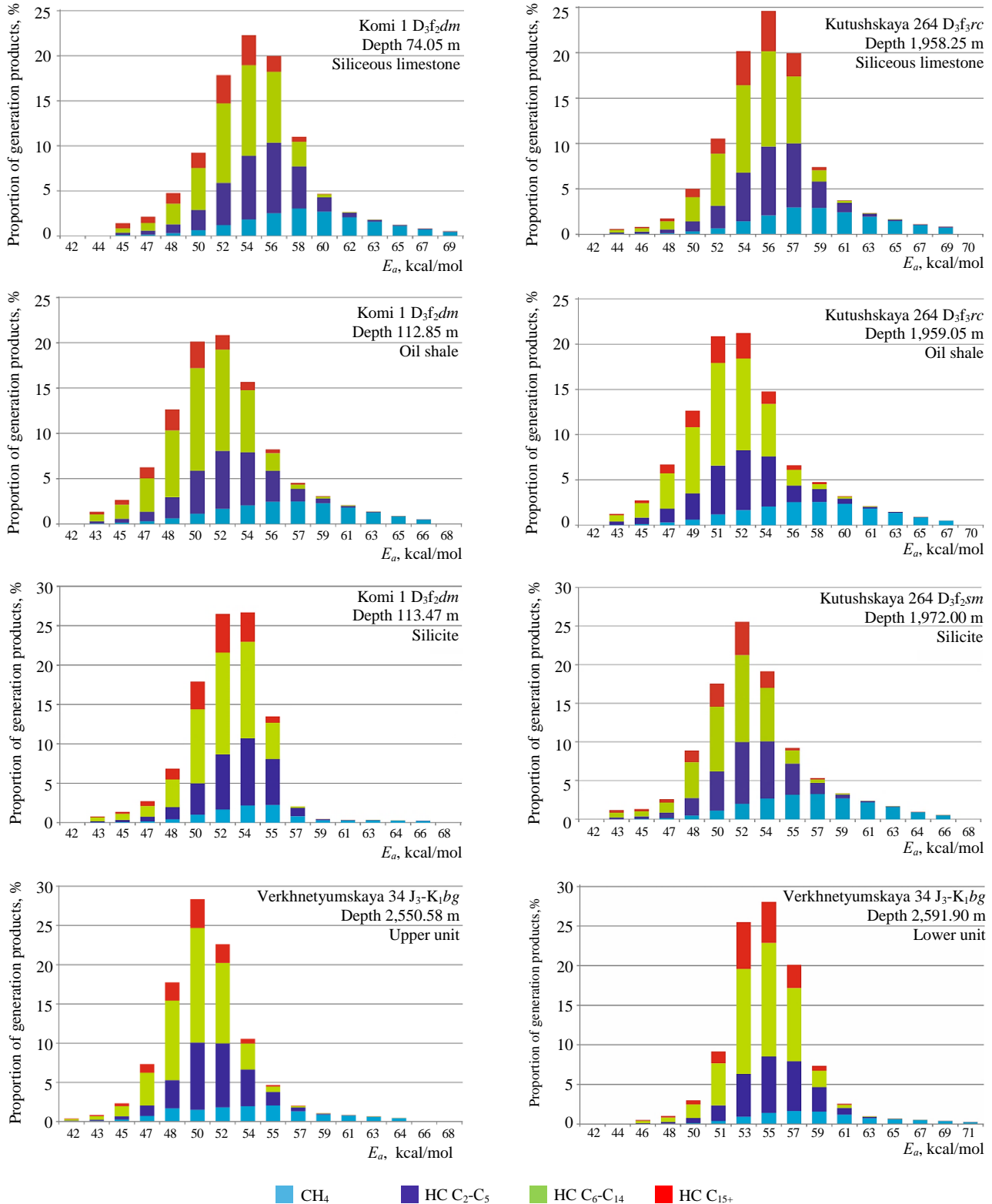


Fig.2. Four-component kinetic distribution spectra of generation potential of kerogen depending on activation energy



At the same time, significant differences in the intensity of HC generation in samples of different lithotypes were recorded. Highly OM-enriched oil shale is characterized by a more symmetrical distribution relative to the maximum – 20-25 % of HC products are generated before the maximum and 30-40 % after the maximum (Table 2). In other samples (more carbonate varieties and silicites), only 11-15 % of total mass of HC pyrolysis products is generated before the maximum and 37-40 % after the maximum.

Table 2

Results of calculating of four-component kinetic spectra of organic matter transformation reactions

Pyrolysis temperature, °C	Activation energy, kcal/mol	Transformation ratio TR, %	Proportion in total volume of generated products, %	HC content, rel. %			
				CH ₄	C ₂ -C ₅	C ₆ -C ₁₄	C ₁₅₊
Kutushskaya 264 well, siliceous limestone, 1,958.25 m, D _{3f3rc} A 58.71E+12 s ⁻¹							
325	44	1.0	0.55	0.12	0.41	0.77	0.74
350	46	2.3	0.75	0.23	0.65	1.02	0.85
375	48	5.3	1.69	0.53	1.35	2.33	2.03
400	50	13.6	4.98	1.61	3.76	6.82	6.53
425	52	29.3	10.51	3.47	8.60	14.68	11.56
450	54	53.5	20.15	7.90	18.60	24.59	26.22
475	56	75.8	24.60	11.60	26.29	26.77	31.32
500	57	90.0	19.93	16.52	24.52	18.78	18.06
525	59	94.6	7.37	16.25	10.06	3.22	2.35
550	61	96.7	3.70	13.59	3.49	0.66	0.28
575	63	98.1	2.30	10.75	1.15	0.16	0.04
600	65	99.0	1.62	8.08	0.51	0.11	0.00
625	67	99.6	1.06	5.46	0.27	0.05	0.00
650	69	100.0	0.80	3.89	0.33	0.05	0.01
Proportion in total HC yield				17.67	28.81	39.30	14.22
Kutushskaya 264 well, oil shale, 1,959.05 m, D _{3f3rc} A 22.02E+12 s ⁻¹							
325	43	2.5	1.26	0.25	1.37	1.61	1.31
350	45	7.7	2.74	0.67	2.63	3.72	2.58
375	47	19.3	6.71	1.73	5.58	9.00	8.67
400	49	37.9	12.67	3.41	10.69	16.80	16.47
425	51	61.3	20.89	6.63	19.83	26.11	26.30
450	52	79.2	21.25	9.24	24.28	23.37	25.10
475	54	89.1	14.78	11.41	20.36	13.37	12.21
500	56	93.0	6.62	14.10	6.73	4.00	4.40
525	58	95.7	4.78	14.21	5.25	1.25	2.10
550	60	97.4	3.23	13.08	2.10	0.47	0.69
575	61	98.5	2.13	10.19	0.71	0.16	0.13
600	63	99.3	1.49	7.63	0.27	0.06	0.03
625	65	99.7	0.92	4.76	0.13	0.04	0.01
650	67	100.0	0.52	2.69	0.08	0.02	0.00
Proportion in total HC yield				18.14	27.20	43.48	11.19
Kutushskaya 264 well, silicite, 1,972.00 m, D _{3f2sm} A 16.06E+12 s ⁻¹							
325	43	2.1	1.19	0.11	0.68	1.78	2.50
350	45	4.5	1.34	0.29	1.06	1.88	2.21
375	47	9.0	2.62	0.70	2.44	3.54	3.61
400	48	22.9	8.91	2.40	7.47	12.84	11.97
425	50	45.7	17.56	5.39	16.75	23.13	23.83
450	52	70.9	25.57	9.60	26.44	31.09	34.30
475	54	85.5	19.17	12.87	24.46	19.08	17.25
500	55	91.5	9.25	15.15	13.34	4.70	2.63
525	57	94.8	5.36	15.57	4.75	1.27	1.50
550	59	96.8	3.37	12.97	1.58	0.42	0.08
575	61	98.2	2.41	10.55	0.52	0.08	0.04
600	63	99.1	1.72	7.64	0.27	0.08	0.03
625	64	99.7	0.98	4.34	0.14	0.06	0.04
650	66	100.0	0.56	2.43	0.11	0.05	0.02
Proportion in total HC yield				21.04	30.19	36.27	12.50



Table 2 continued

Pyrolysis temperature, °C	Activation energy, kcal/mol	Transformation ratio TR, %	Proportion in total volume of generated products, %	HC content, rel. %			
				CH ₄	C ₂ -C ₅	C ₆ -C ₁₄	C ₁₅₊
Komi 1 well, siliceous limestone, 74.05 m, D _{3f2dm} A 74,14E+12 s ⁻¹							
325	45	2.5	1.37	0.33	0.83	1.29	4.34
350	47	6.1	2.10	0.65	1.36	2.27	5.36
375	48	13.9	4.74	1.48	3.19	6.01	9.16
400	50	27.6	9.20	3.40	7.26	12.22	12.89
425	52	49.6	17.84	6.46	15.34	23.01	24.17
450	54	71.0	22.28	10.03	23.07	26.21	25.79
475	56	86.2	19.96	13.86	25.54	20.54	13.52
500	58	93.3	10.98	16.76	15.26	7.17	4.15
525	60	96.1	4.64	14.91	5.14	0.87	0.36
550	62	97.6	2.61	11.36	1.68	0.13	0.02
575	63	98.6	1.80	8.64	0.63	0.13	0.08
600	65	99.3	1.21	6.05	0.30	0.07	0.06
625	67	99.7	0.78	3.82	0.22	0.05	0.06
650	69		0.48				
Proportion in total HC yield				2.25	0.19	0.03	0.06
				17.98	30.65	38.42	12.95
Komi 1 well, oil shale, 112.85 m, D _{3f2dm} A 22.02E+12 s ⁻¹							
325	43	2.7	1.32	0.29	0.81	1.72	2.58
350	45	7.8	2.63	0.71	1.64	3.44	4.86
375	47	19.0	6.24	1.73	3.85	8.11	11.69
400	48	37.9	12.63	3.51	8.80	16.19	22.23
425	50	60.9	20.12	6.41	17.85	24.89	28.10
450	52	78.4	20.83	9.50	24.03	24.55	15.39
475	54	88.9	15.67	11.70	21.99	15.04	8.88
500	56	93.6	8.21	14.03	12.76	4.34	3.79
525	57	96.0	4.51	14.18	5.20	1.04	1.71
550	59	97.6	3.05	13.00	1.98	0.41	0.60
575	61	98.7	2.06	10.29	0.69	0.15	0.11
600	63	99.3	1.36	7.24	0.22	0.07	0.02
625	65	99.8	0.87	4.71	0.10	0.03	0.01
650	66	100.0	0.50	2.71	0.06	0.02	0.00
Proportion in total HC yield				17.49	26.57	45.55	10.39
Komi 1 well, silicite, 113.47 m, D _{3f2dm} A 16,24E+12 s ⁻¹							
325	43	1.6	0.79	0.27	0.51	1.10	0.72
350	45	4.3	1.33	0.67	0.90	1.75	1.34
375	47	9.6	2.72	1.61	1.97	3.00	4.01
400	48	21.7	6.85	4.23	5.30	7.73	8.89
425	50	46.8	17.92	10.27	13.61	20.61	23.05
450	52	72.8	26.50	16.85	23.92	28.37	32.09
475	54	91.0	26.71	22.09	29.20	26.85	24.52
500	55	98.2	13.50	22.73	19.97	10.08	5.33
525	57	99.2	2.05	8.26	3.62	0.37	0.03
550	59	99.4	0.45	3.03	0.45	0.04	0.01
575	61	99.6	0.32	2.56	0.20	0.03	0.01
600	63	99.7	0.34	2.82	0.13	0.05	0.00
625	64	99.9	0.28	2.46	0.11	0.01	0.00
650	66	100.0	0.25	2.15	0.12	0.02	0.00
Proportion in total HC yield				9.86	29.26	45.61	15.27
Verkhnyumskaya 34 well, siliceous clay rock of the upper part of formation, 2,550.58 m, J ₃ -K _{1bg} A 9.59E+12 s ⁻¹							
325	42	0.81	0.40	0.40	0.25	0.41	0.78
350	44	2.50	0.84	0.73	0.49	0.95	1.46
375	46	7.00	2.33	1.94	1.37	2.84	3.26
400	48	19.92	7.33	5.11	4.53	9.18	10.06
425	49	44.96	17.75	11.87	12.27	22.36	21.00
450	51	72.96	28.37	10.68	29.11	32.15	33.58
475	53	88.84	22.62	12.80	27.72	22.61	21.70
500	55	94.93	10.56	13.70	15.98	7.30	5.47
525	56	97.42	4.67	14.50	5.90	1.49	1.87
550	58	98.46	2.04	9.31	1.66	0.38	0.54



End of Table 2

Pyrolysis temperature, °C	Activation energy, kcal/mol	Transformation ratio TR, %	Proportion in total volume of generated products, %	HC content, rel. %			
				CH ₄	C ₂ -C ₅	C ₆ -C ₁₄	C ₁₅₊
575	60	99.01	1.08	6.31	0.40	0.13	0.08
600	62	99.43	0.85	5.41	0.15	0.07	0.03
625	64	99.77	0.68	4.30	0.10	0.07	0.12
650	65	100.00	0.47	2.95	0.06	0.05	0.05
Proportion in total HC yield				14.18	29.45	45.38	11.00
Verkhnetyumskaya 34 well, siliceous clay rock of the lower part of formation, 2,591.90 m, J ₃ -K ₁ bg A 1.69E+14 s ⁻¹							
325	46	1.0	0.51	0.16	0.37	0.63	0.57
350	48	2.9	1.00	0.42	0.83	1.20	1.06
375	50	8.5	3.00	1.31	2.39	3.65	3.06
400	51	23.8	9.15	4.02	7.58	11.22	8.68
425	53	56.0	25.49	9.53	20.74	28.06	34.63
450	55	80.2	28.06	14.48	27.46	30.29	30.48
475	57	93.2	20.11	16.81	24.34	19.50	17.24
500	59	97.2	7.32	16.28	11.90	4.37	3.49
525	61	98.6	2.54	12.24	3.25	0.83	0.72
550	63	99.1	0.96	7.53	0.67	0.12	0.04
575	65	99.4	0.68	6.13	0.23	0.05	0.02
600	67	99.7	0.54	5.07	0.12	0.03	0.01
625	69	99.9	0.39	3.71	0.06	0.03	0.00
650	71	100.0	0.25	2.33	0.06	0.03	0.01
Proportion in total HC yield				9.65	25.94	47.40	17.01

The increased volume of HC for the generation of which low reaction energy is required is associated with high initial bituminosity of Domanik deposits. Carbonate-siliceous rocks of Domanik deposits have a high sorption capacity due to both a relatively high silica content [34], and a significant concentration of OM – to 30-35 % TOC. Despite a long-term extraction with chloroform, parautochthonous bitumen partially remained in rocks. According to Rock-Eval results, the content of free HC (S₁) in these samples after extraction was determined at the level of 2-3 mg HC/g of rock, which is about 25 % of S₁ value before extraction. Although the S₁ peak is not taken into account in the calculations of kinetic models, pyrolysis decomposition of resinous-asphaltene components could make a small contribution to the S₂ peak exactly in the region of low temperatures. It is very difficult to quantitatively assess such a contribution to the volume of generated products.

The greatest differences are recorded between shales and carbonate rocks. In highly OM-enriched shales, an abrupt jump in generation is recorded at pyrolysis temperature of 400 °C, which corresponds to the activation energy of 49-50 kcal/mol. Before this jump, C₆₊ HC prevail among the generation products; after the jump, HC of C₂-C₅, C₆-C₁₄ and C₁₅₊ groups are generated in approximately equal volumes. Starting from the temperature of 500 °C ($E_a = 56-58$ kcal/mol), the extent of generation decreases, and, at the same time, the proportion of methane increases significantly reaching 90-95% in the composition of the generated products at temperatures above 550 °C.

In limestones and silicites, an increase in the volume of generated HC is recorded up to a higher temperature of 425-475 °C ($E_a = 50-54$ kcal/mol) compared to shales; a decrease in generation begins from 525 °C ($E_a = 59$ kcal/mol). The patterns of change in the ratios of different HC groups in the generation products remain the same as those observed in shales: C₆₊ HC predominate up to the generation maximum, after which methane generation increases. Thus, at the same temperature, the difference between the volumes of generated HC in rocks of the above lithotypes reaches 20-30 %. This is especially noticeable during generation of groups of gaseous HC of C₂-C₅ and liquid C₆-C₁₄, and C₁₅₊ HC. The generation of large volumes of methane begins at higher temperatures compared to liquid HC, and by this stage the differences in the intensity of its formation between lithotypes become less noticeable. All other things being equal, the extent of HC generation in different rock lithotypes can differ 3-5-fold. In the presence of interbeds of different lithological composition in the source



rock formation, which is especially characteristic of Domanik deposits, it is necessary to calculate weighted average kinetic models depending on the ratios of different lithotypes in the composition of formation.

In all the investigated samples of Domanik deposits, the proportion of liquid C_{6+} HC in total volume of generated products is 50-55 %, and the share of gaseous C_1-C_5 HC is 45-50 %.

Thermal transformation of kerogen of the Bazhenov formation is also divided into several stages for each of which certain patterns are recorded.

The first stage is characterized by a significant prevalence of liquid HC (C_6-C_{14} and C_{15+}) in the composition of generation products. Thus, in all analysed samples of the Bazhenov formation, the prevalence of liquid HC (60-70 %) is recorded to the temperature of 475 °C. E_a value corresponding to this temperature is somewhat higher compared to the Domanik samples – 53-55 kcal/mol (Fig.2).

At the second stage (500-550 °C, $E_a = 53-58$ kcal/mol), a gradual decrease in the proportion of liquid HC and an increase of gaseous HC in the composition of kerogen pyrolysis products is recorded. At the same time, a significant decrease in the content of relatively heavy hydrocarbon components (C_{15+}) is noted in the composition of liquid HC, and a gradual increase in the proportion of methane in the composition of gases.

The third stage of OM transformation in the Bazhenov formation is distinguished by a significant increase in the proportion of methane (over 80 %) in the composition of the generation products, which is recorded at heating above 575 °C, which corresponds to $E_a = 60-65$ kcal/mol. At this stage, there is an almost complete cessation of the generation of liquid HC, especially heavy C_{15+} , which indicates the manifestation of processes characteristic of the main gas formation zone.

Based on results of thermal transformation of kerogen from different oil and gas source rocks obtained in laboratory experiments, modelling of HC generation was performed, which takes into account both the heterogeneous chemical structure (OM type) and the change in geological conditions (geothermal gradient and subsidence rate). For a correct comparison, the calculation of kinetic models was carried out for the same averaged geological conditions of deposit subsidence: subsidence rate of 50 m/Ma with a constant geothermal gradient of 25 °C/km.

OM of the Domanik deposits begins to generate HC at lower temperatures compared with OM of the Bazhenov formation (Table 2). Early generation of HC by the Domanik deposits was noted by many scientists [28, 35]. According to the results obtained, the generation of HC by the beginning of the main phase of oil formation (vitrinite reflectivity $R_o = 0.5$ %) in Domanik reaches 15-20 % of the initial generation potential, and in the Bazhenov formation it is less than 5% (Fig.3). A probable cause of early generation of HC in Domanik is an increased bituminosity of the source OM [28]. The specificity of thermal transformation of Domanik OM, along with a more intense geothermal regime

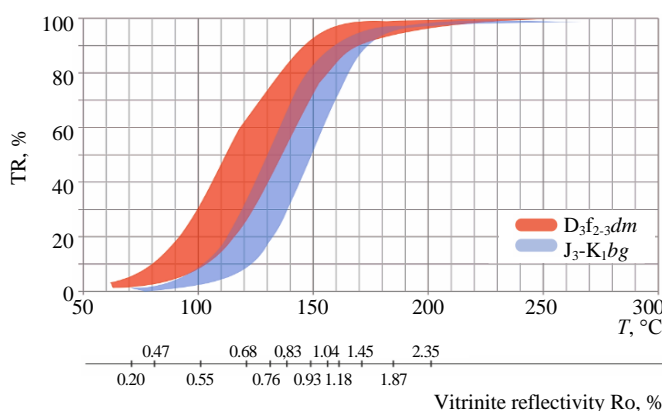


Fig.3. Comparison of results of kinetic modelling of HC generation by different source formations. Modelling of HC generation is performed for averaged values of subsidence rate 50 m/Ma, geothermal gradient 5 °C/km

in the past characteristic of Paleozoic basins contributes to a decrease in the manifestation depth of oil and gas formation phases. The Timan-Pechora and Volga-Ural basins are characterized by reduced depth zonation of OM catagenesis [24].

Quantitative assessment of realization of oil and gas source potential of the Domanik and Bazhenov formations showed that the differences in the ratio of different groups of HC (CH_4 , C_2-C_5 , C_6-C_{14} and C_{15+}) in total generation are insignificant (Fig.4). The predominance of “light” oil (HC C_6-C_{14}) in the generation products is characteristic of all the studied oil source rocks. OM of the Domanik formation



is distinguished by a slightly higher proportion of methane in the composition of the generated HC. This is due to a significant contribution of the transformation products of chitinous parts of zooplankton, which belong to humoid components and enrich OM with cyclic structures [28], which distinguishes it from OM of the Mesozoic formation.

The kinetic studies of two highly OM-enriched oil source rocks in sedimentary basins in the Russian Federation (Bazhenov formation and Domanik deposits) demonstrated specific features of catagenetic transformation of OM in each of them. Multicomponent kinetic models of HC generation calculated for oil source rocks increase the reliability of basin modelling results.

Conclusion. One of the main target of modelling oil and gas generation and accumulation systems of sedimentary basins consists in identification of oil source deposits and their generation characteristics, which, along with OM-enrichment of rocks, comprise the kinetics of its thermal transformation. Therefore, generation and updating of libraries (databank) of kinetic spectra of oil and gas source rocks in sedimentary basins with new multicomponent models is a relevant challenge. The article presents the results of determining the kinetic parameters of source formations of three main oil-and-gas bearing basins in the Russian Federation.

Comparative analysis of the results of kinetic studies of high-carbon source deposits of the Domanik and Bazhenov horizons containing similar types of OM showed significant differences in the time-temperature dynamics of HC generation. OM of the Domanik deposits begins to generate HC at lower temperatures compared to OM of the Bazhenov formation. Generation products of both source rocks are dominated by “light” oil (C₆-C₁₄ HC – 40-45 %). OM of the Domanik formation is noted for a slightly higher proportion of methane in the composition of the generated HC.

The use of experimentally obtained kinetic spectra enables geologists to make more reliable forecasts of the generation time and relative quantities of oil and gas in computer modelling of HC formation process in the history of geological evolution of the basin.

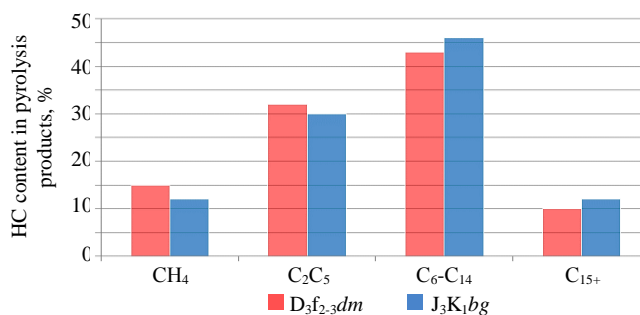


Fig. 4. Ratio of different HC groups in total volume of generation products in oil-gas source rocks of different age

REFERENCES

1. Vassoevich N.B. The theory of sedimentary-migrational origin of oil (Historical review and present state). Selected works. *Geochemistry of Organic Matter and Origin of Petroleum*. Moscow: Nauka, 1986, p. 149-174 (in Russian).
2. Killops S.D., Killops V.J. Introduction to Organic Geochemistry. Blackwell Publishing, 2005, p. 405.
3. Vandenbroucke M., Largeau C. Kerogen origin, evolution and structure. *Organic Geochemistry*. 2007. Vol. 38. Iss. 5, p. 719-833. DOI: [10.1016/j.orggeochem.2007.01.001](https://doi.org/10.1016/j.orggeochem.2007.01.001)
4. Peters K.E., Moldowan J.M. The Biomarker Guide. Interpreting Molecular Fossils in Petroleum and Ancient Sediments. New Jersey: Prentice-Hall, 1993, p. 363.
5. Tissot B.P., Welte D.H. Petroleum formation and occurrence. Moscow: Mir, 1981, p. 501.
6. Espitalie J., Drouet S., Marquis F. Petroleum evaluation by using the petroleum evaluation workstation (a Rock-Eval connected with computer). *Oil and gas geology*. 1994. N 1 (in Russian).
7. Peters K.E. Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis. *The American Association of Petroleum Geologists Bulletin*. 1986. Vol. 70. N 3, p. 318-329. DOI: [10.1306/94885688-1704-11D7-8645000102C1865D](https://doi.org/10.1306/94885688-1704-11D7-8645000102C1865D)
8. Lafargue E., Marquis F., Pillot D. Rock-Eval 6 Applications in Hydrocarbon Exploration, Production, and Soil Contamination Studies. *Revue de l'Institut Français du Pétrole*. 1998. Vol. 53. N 4, p. 421-437. DOI: [10.2516/ogst:1998036](https://doi.org/10.2516/ogst:1998036)
9. Ungerer P., Pelet R. Extrapolation of the kinetics of oil and gas formation from laboratory experiments to sedimentary basins. *Nature*. 1987. Vol. 327. N 7, p. 52-54. DOI: [10.1038/327052a0](https://doi.org/10.1038/327052a0)
10. Ungerer P. State of the art of research in kinetic modelling of oil formation and expulsion. *Organic Geochemistry*. 1990. Vol. 16. Iss. 1-3, p. 1-25. DOI: [10.1016/0146-6380\(90\)90022-R](https://doi.org/10.1016/0146-6380(90)90022-R)
11. Astakhov S.M. Georeactor. Algorithms of oil and gas generation. Rostov-na-Donu: Kontiki, 2015, p. 256 (in Russian).
12. Peters K.E., Burnham A.K., Walters C.C., Schenk O. Guidelines for kinetic input to petroleum system models from open-system pyrolysis. *Marine and Petroleum Geology*. 2018. Vol. 92, p. 979-986. DOI: [10.1016/j.marpetgeo.2017.11.024](https://doi.org/10.1016/j.marpetgeo.2017.11.024)



13. Astakhov S.M. Chemical kinetics of organic matter transformation of petroleum source rocks. *Neftegazovaya geologiya. Teoriya i praktika*. 2016. Vol. 11. N 1, p. 28 (in Russian). DOI: [10.17353/2070-5379/5_2016](https://doi.org/10.17353/2070-5379/5_2016)
14. Burnham A.K. Global Chemical Kinetics of Fossil Fuels. How to Model Maturation and Pyrolysis. Cham: Springer, 2017, p. 315. DOI: [10.1007/978-3-319-49634-4](https://doi.org/10.1007/978-3-319-49634-4)
15. Behar F., Vandenbroucke M., Tang Y. et al. Thermal cracking of kerogen in open and closed systems: determination of kinetic parameters and stoichiometric coefficients for oil and gas generation. *Organic Geochemistry*. 1997. Vol. 26. Iss. 5-6, p. 321-339. DOI: [10.1016/S0146-6380\(97\)00014-4](https://doi.org/10.1016/S0146-6380(97)00014-4)
16. Leushina E., Mikhaylova P., Kozlova E. et al. The effect of organic matter maturity on kinetics and product distribution during kerogen thermal decomposition: the Bazhenov formation case study. *Journal of Petroleum Science and Engineering*. 2021. Vol. 204. N 108751. DOI: [10.1016/j.petrol.2021.108751](https://doi.org/10.1016/j.petrol.2021.108751)
17. Hantschel T., Kauerauf A.I. Fundamentals of Basin and Petroleum Systems Modeling. Berlin: Springer, 2009, p. 476. DOI: [10.1007/978-3-540-72318-9](https://doi.org/10.1007/978-3-540-72318-9)
18. Kashapov R.S., Oblasov N.V., Goncharov I.V. et al. Determination of source rocks kinetic parameters using the destruction pyrolysis method. *Neftegazovaya geologiya. Teoriya i praktika*. 2019. Vol. 14. N 1, p. 20 (in Russian). DOI: [10.17353/2070-5379/6_2019](https://doi.org/10.17353/2070-5379/6_2019)
19. Varlamov A.I., Petersile V.I., Poroskun V.I. et al. Temporary guidelines for calculating oil reserves in Domanik plays. *Nedropolzovanie XXI vek*. 2017. N 4 (67), p. 102-115 (in Russian).
20. Varlamov A.I., Melnikov P.N., Poroskun V.I. et al. Unconventional oil reservoirs in high-carbon carbonate-siliceous Domanik formations, Volga-Urals Province: results of studies and future development trends. *Russian Oil and Gas Geology*. 2020. N 6, p. 33-52 (in Russian). DOI: [10.31087/0016-7894-2020-6-33-52](https://doi.org/10.31087/0016-7894-2020-6-33-52)
21. Aflyatunov R.R., Bachkov A.P., Vedenina N.G. et al. High-carbon carbonate-siliceous domanik-type deposits: object of hydrocarbon resource base development in central part of South Tatarsky Arch. *Russian Oil and Gas Geology*. 2022. N 6, p. 67-83 (in Russian). DOI: [10.31087/0016-7894-2022-6-67-83](https://doi.org/10.31087/0016-7894-2022-6-67-83)
22. Stoupakova A.V., Kalmykov G.A., Korobova N.I. Domanic deposits of the Volga-Ural basin – types of section, formation conditions and prospects of oil and gas potential. *Georesources*. 2017. Special Issue. Part 1, p. 112-124 (in Russian). DOI: [10.18599/grs.19.12](https://doi.org/10.18599/grs.19.12)
23. Fortunatova N.K., Zaitseva E.L., Bushueva M.A. et al. Unified Upper Devonian subregional stratigraphic chart in Volga-Ural Subregion. Moscow: All-Russian Research Geological Oil Institute, 2018, p. 64 (in Russian).
24. Bazhenova T.K., Shimansky V.K., Vasilieva V.F. et al. Organic geochemistry of the Timan-Pechora basin. Saint Petersburg: VNIGRI, 2008, p. 164 (in Russian).
25. Kiryukhina T.A., Bolshakova M.A., Stoupakova A.V. et al. lithological and geochemical characteristics of domanic deposits of Timan-Pechora basin. *Georesources*. 2015. N 2 (61), p. 87-100 (in Russian).
26. Prishchepa O.M., Sinitisa N.V., Ibatullin A.K. Assessment of the influence of lithofacies conditions on the distribution of organic carbon in the Upper Devonian “Domanik” deposits of the Timan-Pechora Province. *Journal of Mining Institute*. 2024. Vol. 268, p. 535-551.
27. Zavyalova A.P., Chupakhina V.V., Stoupakova A.V. et al. Comparison of the Domanic Outcrops in the Volga-Ural and Timan-Pechora basins. *Moscow University Geology Bulletin*. 2018. Vol. 74. N 1, p. 56-72. DOI: [10.3103/S0145875219010149](https://doi.org/10.3103/S0145875219010149)
28. Neruchev S.G., Rogozina E.A., Zelichenko I.A. et al. Oil and gas generation in Domanik-type deposits. Leningrad: Nedra, 1986, p. 247 (in Russian).
29. Braduchan Yu.V., Gurari F.G., Zakharov V.A. et al. Bazhenov Horizon of Western Siberia (stratigraphy, paleogeography, ecosystem, oil saturation). Novosibirsk: Nauka, 1986, p. 216 (in Russian).
30. Kontorovich A.E., Nesterov I.I., Salmanov F.K. et al. Geology of oil and gas in Western Siberia. Moscow: Nedra, 1975, p. 680 (in Russian).
31. Skvortsov M.B., Dakhnova M.V., Mozhegova S.V. et al. Geochemical methods for prediction and assessment of shale oil resources (case study of the Bazhenov formation). *Russian Geology and Geophysics*. 2017. Vol. 58. N 3-4, p. 403-409. DOI: [10.1016/j.rgg.2016.09.015](https://doi.org/10.1016/j.rgg.2016.09.015)
32. Rovnina L.V., Konyshva R.A., Sadovnikova T.K. On material composition of Bazhenov formation in Western Siberia. Neftenosnost bazhenovskoi svity Zapadnoi Sibiri. Moscow: Institut geologii i razrabotki goryuchikh iskopaemykh, 1980, p. 148-175 (in Russian).
33. Neruchev S.G., Bazhenova T.K., Smirnov S.V. et al. Assessment of potential hydrocarbon resources on the basis of modeling their generation, migration, and accumulation processes. St. Petersburg: Nedra, 2006, p. 364 (in Russian).
34. Burlin Yu.K., Plyusnina I.I. Phase transitions of silica in oil-bearing rocks. *Vestnik Moskovskogo universiteta. Seriya 4. Geologiya*. 2008. N 3, p. 24-31 (in Russian).
35. Larskaya E.S. Diagnostics and methods of studying oil and gas source rocks. Moscow: Nedra, 1983, p. 196 (in Russian).

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