SHORT COMMUNICATION

DOI: https://doi.org/10.18599/grs.2019.1.71-76

Research of domanic source rock by pyrolytic gas chromatography-mass spectrometry method

A.E. Chemodanov[1], B.I. Gareev[1], G.A. Batalin[1], R.S. Gerasimov[2]*
[1]Kazan Federal University, Kazan, Russia
[2]Frontier Laboratories Ltd., Koriyama, Japan

Abstract. We applied new novel approach based on pyrolytic gas chromatography-mass spectrometry technology (Py-GCMS) developed by Frontier Lab company (Japan) in order to get the same data as it can be acquired by using conventional core analyzer. Experimental part describes the detailed measurement procedure, temperature program and outcomes acquired by using IFP 160000 as a standard sample. We have managed to demonstrate accuracy and reproducibility of tests for the domanic source rock samples and its kerogen extracted respectively. In results of this analytical challenge we were able to get pyrograms providing the S_1 (free hydrocarbons), S_2 (potential hydrocarbons), T_{max} (temperature at which the maximum rate of hydrocarbon generation is reached) information with level of confidence we usually could see doing conventional core analyzer tests. Some important conclusions regarding petroleum generation and thermal maturity have been made. S_1 and S_2 significantly decrease for kerogen samples with T_{max} growth at the same time. Moreover mass spectra data of core samples pyrolizates can be collected easily to detect certain groups of compounds. Sulfur-containing compounds temperature extracted by Py-GCMS can be measured for example. Py-GCMS technology fully comply with mainstream analytical protocol for whole-rock or kerogen analysis and even more, Py-GCMS has a lot of advantages against conventional approach providing us additional valuable information about a sample.

Keywords: pirolysis, source rock, Py-GCMS, Bulk Rock, thermal maturity

Recommended citation: Chemodanov A.E., Gareev B.I., Batalin G.A., Gerasimov R.S. (2019). Research of domanic source rock by pyrolytic gas chromatography-mass spectrometry method. *Georesursy = Georesources*, 21(1), pp. 71-76. DOI: https://doi.org/10.18599/grs.2019.1.71-76

Introduction

Pyrolysis in geochemistry is one of the very important methods for investigation of reservoir rocks. From the moment of its discovery, pyrolytic investigations have been applying for evaluation of oil-generating potential of source rocks and establishing catagenetic maturity degree of organic matters (Zhao et al., 2018).

The most simple pyrolytic system was composed of combustion chamber and one (or several) detector(s) of evolved gases. In the second half of previous century, Dr. J. Espitalie from the French Institute of Petroleum developed the first Rock Eval type equipment. Even the first equipment could work in two cycles – pyrolysis and oxidation, which has been widely used in geochemistry. At the same time, the similar equipment – «GeoChee-2» pyrolyzer was developed in Russia on the basis of «Svet-100» chromatography (Lopatin, Emets, 1987).

At the end of 90th, Rock Eval 6 VINCI (France) has replaced the Rock Eval 2 pyrolyzer that had been applied for many years and had been working in the helium atmosphere. However, currently the cheapest gas carrier – Nitrogen is used in Rock Eval 6. Today, VINCI Company provides several variations of Rock Eval 6 pyrolyzer. For example, Rock Eval 6 Classic is equipped by one flame ionization detector that allows to determine only S_1, S_2 and T_{max} parameters (Behar et al., 2001).

Apart instrumental differences, there are several options for pyrolytic system itself, the application of which depends on the characteristics of the investigated object. Mainly, the temperature program of the pyrolysis chamber varies, particularly: temperature, speed and the time of heating. Romero-Sarmiento and others showed in their study that application of different temperature regime is rational for various objects (Romero-Sarmiento et al., 2015). Hence, the manufacturer of pyrolyzer usually gives users the opportunity to create an individual temperature program. However, the main fundamental pyrolytic methods (BulkRock, Reservoir, etc.) are installed to the equipment.

In addition to France, other countries also developed and produced various types of pyrolytic systems.

---

*Corresponding author: Artem E. Chemodanov
E-mail: chemodanov41659@mail.ru

Currently, HAWK (Wildcat Technologies, USA) and SRA (Weatherford Laboratories, USA) are analogues to Rock Eval 6. The given pyrolyzers have the same practical analysis principle as Rock Eval 6, but also have their own advantages and disadvantages. For example, pyrolyzer HAWK starts heating the samples from the room temperature. In this regard, S_0 peak, which characterizes the amount of sorbed light hydrocarbons (C_1-C_7), is added to the pyrolytic parameters (Kozlova et al., 2017).

In Japan, Frontier Lab Company also develops various models of pyrolyzers, which are quite applicable for studying geological materials, particularly source rocks. The aim of this study is evaluation of pyrolytic equipment that was based on the pyrolyzer – EGA/PY-3030D (Frontier Lab, Japan) and review of its applications for various geological objects.

Experimental part

The object of study:

- source rock samples from Bondyuzhskoe area of Domanic deposits of Kamsko-Kinel trench systems of Tatarstan;
- kerogen samples, extracted from source rock according to the methodology provided by some authors in their studies (Vakhin et al., 2016, 2019).

Preparation of samples for pyrolysis involves crushing samples until 0.2-0.25 mm by size and averaging the crushed samples by mixing;

Applied equipment and its software

In this study, we use the pyrolytic system (Fig. 1) that is designed for investigations of geological objects. The pyrolytic system consists of:

- Frontier Lab EGA/PY-3030D pyrolyzer;
- Agilent 7890B gas chromatograph system;
- Agilent 5977B mass selective detector.

The Pyro-GC/MS technology is based on the pyrolysis of a certain weighed sample in inert gas environment with further chromatographic separation (if necessary) of pyrolysis products and their identification by mass-selective detector. The main part of the given technology is pyrolyzer (PY-3030D). It is a multifunctional instrument for implementing several analytical methods with possibility of combining them in one experiment. PY-3030D provides to imitate the work of the system for thermal analysis, to conduct experiments in the modes of thermal desorption, single- and multi-stage pyrolysis. This system provides to carry out the pyrolytic process under high pressure and reactive environment. The specific modification of this equipment turns it into proper reactor.

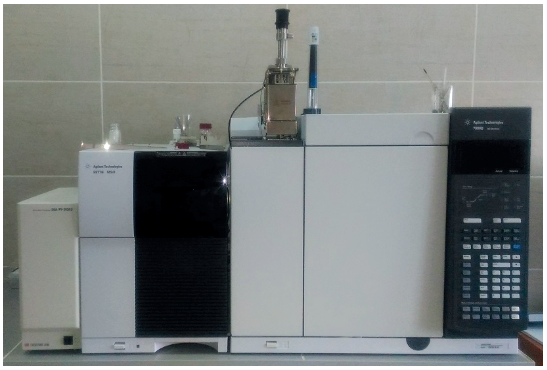

Fig. 1. A pyrolytic system for investigation of geological objects

Aside from geological investigations, the given technology is applied in many other fields such as study of polymer structures, analysis of pigments and modifying agents, monitoring of impurities in plastics, etc.

The main advantages of this equipment – optimum construction (there is no transition lines, interfaces, etc.), expressivity (no need in preparation of samples) in many types of analysis, flexibility (you can work through a variety of modes and analysis options) and clear software interface.

For more detail information about the equipment and Pyro – GC/MS method you can check the website of manufacturer (https://frontier-lab.com/).

Figure 2 demonstrates a general scheme of pyrolysis, applied in this study.

The temperature program of pyrolyzer (Fig. 3):

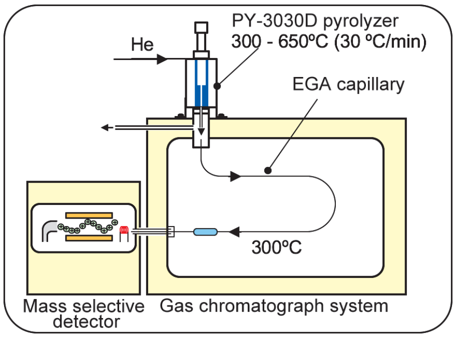

Fig. 2. A scheme of pyro – chromatography complex in the mode of Evolved Gas Analyzer – Mass Spectrometer (EGA – MS)

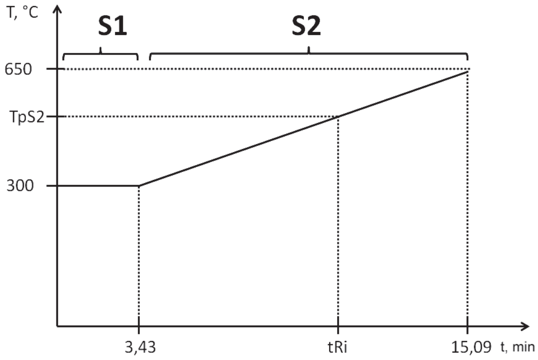

Fig. 3. The temperature program of pyrolyzer. The time intervals of S_1 and S_2 peaks are also shown. TpS2 – temperature of maximum peak (S_2), tRi – time of maximum peak (S2).

I stage – isotherm at 300°C in 3.43 min

II stage – linear increase in temperature from 300 to 650°C with a speed of 30°C/min in 15,09 min.

The provided temperature program is applied during measurments in Rock-Eval 6 in the mode of Bulk Rock. However, the pyrolyzer allows adjusting all temperature regimes with infinitive number of step. The maximum temperature limit is 1050°C. This means that equipment is allowed to conduct not only classical pyrolysis methods such as Bulk Rock, Reservoir, Shale Play, Pure Organic Matter, etc. (Romero-Sarmient et al., 2015), but also to create its own regimes.

The first step is extraction of free hydrocarbons from the porous rock sample. Their amount is determined by mass-spectrometry detector Agilent 5977B and symbolized by S_1 (mg HC/gr rock samples).

The second step is to define the hydrocarbon amount that can be generated if the source rock potential is fully realized. This amount is appeared as S_2 and it reflects the remain of generating potential of rocks – the part that was unable to turn into oil and gas during its natural evolution. Besides, the T_{max} (the temperature of maximum hydrocarbon yield during kerogen cracking) is determined in second step. T_{max} is a function of maximum peak (S_2) temperature.

In pyrolytic system, a metallic capillary installed in thermostat instead of chromatography column. The capillary eliminates the separation of both free and bounded hydrocarbons into particular compounds, which allows obtaining clear and symmetric peaks of S_1 and S_2.

The results of pyrolysis investigations are processed by Agilent Mass Hunter software. The standard source rock sample – «IFP 160000» is used as a reference to calibrate the equipment and control the accuracy of measurements. The main pyrolysis characteristics of IFP 160000 are provided in Table 1. Figure 4 demonstrates the typical program for IFP 160000 standard sample.

The pyrolysis technique for the given equipment is certified in accordance with the requirements of GOST P 8.563-2009 – «State system for ensuring the uniformity of measurements. Procedures of measurements». The certificate was issued by All-Russian Research Institute of Metrological Service (Moscow). The main metrological characteristics of technique are given in Table 2.

Parameter	**Value, mg HC/g of rock**	**Deviation, mg HC/g of rock**
S_1	0,14	+/- 0,07
S_2	12,43	+/- 0,50
T_{max}	416	+/- 2

Table 1. Pyrolysis characteristics of IFP 160000 standard sample

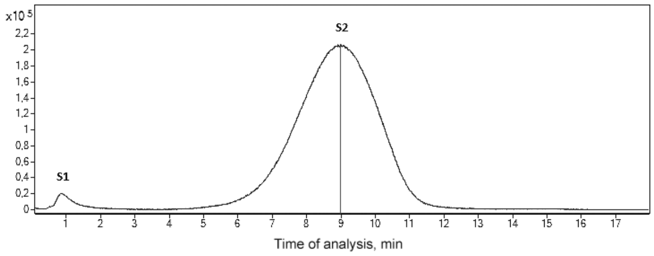

Fig. 4. Pyrogram of IFP 160000 standard sample

The boundaries of relative error are provided in Table 2 as an accuracy value. The repeatability and reproducibility are described by relative standard deviation. The metrological indicators S_1 and S_2 are presented as a range of values, rather than specific numbers due to the very wide range of measurements to which they correspond. It is worth noting that relatively high error in determination of S_1 peak is due to wide range of deviations in certified S_1 value of IFP 160000 standard – 0.14+/-0.07 mg/g (Table 1).

The S_1 and S_2 values determine the oil generation potential of source rocks. However, T_{max} stands for catagenetic maturation of organic matters.

Results and discussions

The result of pyrolytic analysis is a pyrogram – dependency of output signal intensity from the time of analysis. In our case, it is not correct to use a term «component retention time», because there is no separation into individual components occurs. It is known that area under chromatographic peak of any compound (or group of compounds) is directly proportional to its mass content. Once the numerical values of S_1 and S_2

Measured values	Measuring range, unit.	Accuracy (boundaries of relative error), ±δ, % at P=0.95	Repeatability (relative standard deviation of repeatability), σ_r, %	Reproducibility (relative standard deviation of reproducibility), σ_R, %
Mass fraction of total free hydrocarbons (S_1), mg/g	0,05 – 20	30-60	5-13	10-25
Mass fraction of total insoluble organic matters (S_2) , mg/g	1,0 -200	15-20	2-3	7-9
Cracking temperature of OM (T_{max}), ^{0}C	400 – 500	4	1	2

Table 2. Metrological characteristics of certified pyrolysis technique

parameters for standard sample IFP 160000 are known, the given parameters can be found for the unknown rock samples if the condition is the same. However, the situation is complicated with Tmax value. As it was mentioned before, T_{max} is a temperature of maximum hydrocarbon yield during cracking. Only analysis time (which is equal to the maximum extremum of S_2 peak) can be determined from the pyrogram. However, if the temperature program of pyrolyzer is known, which has a linear behavior in the range of 300-650, the temperature of maximum peak – S_2 can be determined. Thus, in its turn the Tmax can be evaluated from S_2 curve. Some pyrograms of source rock samples from Bondyuzhskoe area of Domanic deposits (Kamsko-Kinel trench systems of Tatarstan) are illustrated in Figure 5 (Vakhin et al., 2018). The given samples were extracted from the same well, but from different interval depths.

From the figure, it is seen that S_2 peak shifts to the right side as the catagenetic transformation degree of rocks increases. This shift is due to the fact that more mature organic matter requires more severe conditions for thermal decomposition. The area under S_2 is significantly decreasing that indicates to the decrease of oil-generating potential of organic matter and increase of its thermal maturity. In addition to pyrogram, the described pyrolytic method provides to measure the mass-specters of produced compounds by mass-spectrometry detectors. The registration of mass-specters is performed in the range of 45-300 a.m.u. The initial range is determined by the need to eliminate the effect of CO_2 to overall hydrocarbon signals.

The composition of pyrolysis products can be different depending on the heating temperature. The lower part shows the mass spectra at the vertices of the S_1 and S_2 peaks. It can be seen that saturated hydrocarbons (alkanes and isoalkanes) with specific mass numbers of 57, 71, 85, etc. dominate in the products of low-temperature pyrolysis of samples. For S_2 peak, there is a noticeable increase in compounds with mass numbers of 55, 69, 83, etc., which correspond to naphthenic hydrocarbons.

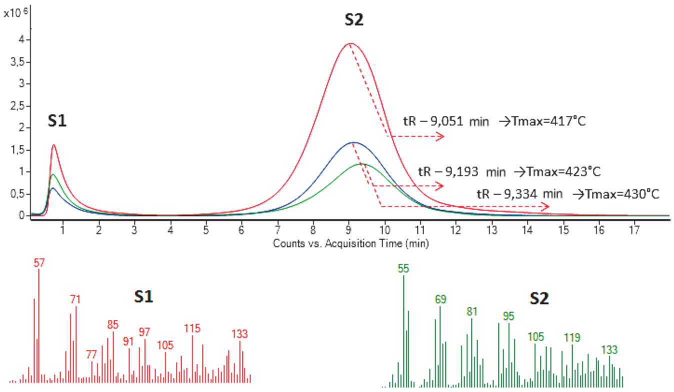

Fig. 5. Mass-Spectra of S_1 and S_2 peaks for investigated samples

Below the data are provided on the pyrolysis of kerogen extracted from a sample of the Domanic deposits of the Bondyuzhskaya area of the Tatarstan. The kerogen was extracted according to the technique described by Vakhin and his group (Vakhin et al., 2019), but without extracting pyrite that was a part of mineral composition. In this case, the pyrite (its presence was confirmed by X-ray phase analysis) influences the composition of both low-temperature and high-temperature pyrolysis products.

On the chromatogram (Fig. 6), additional peaks appear in the first and nineteenth minutes with maximum vertices at temperatures of 230 and 560°C, respectively. The mass detector registers several intensive ions with the m/z of 48, 60, 64 and 76. These ions indicate the presence of SO_2 (m/z 48 и 60), COS (m/z 60) and CS_2 (m/z 76) compounds in the products of low-temperature and high-temperature pyrolysis. However, carbon oxide/sulfide and carbon disulfide appear only at high-temperature pyrolysis, while sulfur oxide in both cases. Their relative content in evolved gases can be easily measured by applying the external standard method in SIM mode.

Moreover, during creating chromatography method one can exclude recording of ions that allows obtaining more specific and clear picture of pyrolysis. Hence, the content of sulfur-containing minerals in reservoir rocks can significantly influence the results of pyrolytic investigations. The pyrograms of Domanic rock sample and the kerogen extracted from it are illustrated in Figure 7.

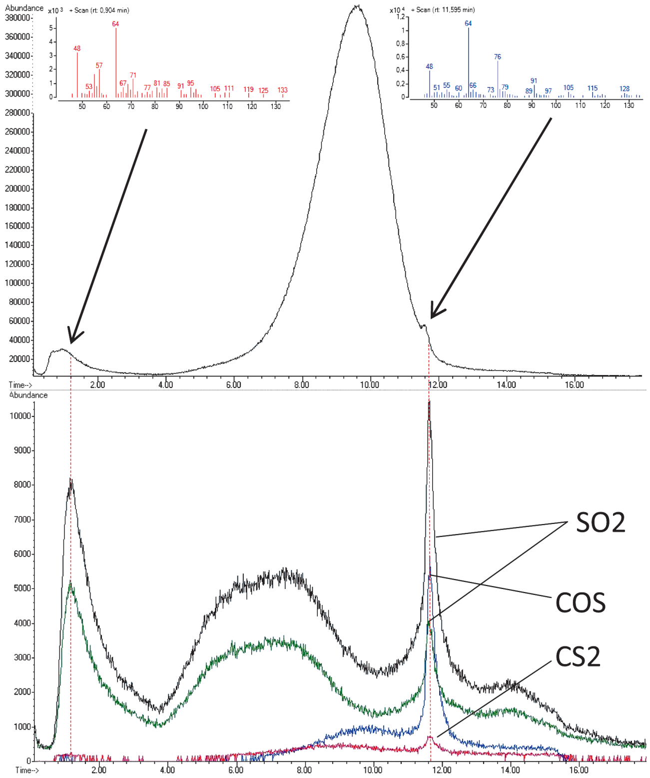

Fig. 6. The chromatogram of sulfur containing compounds

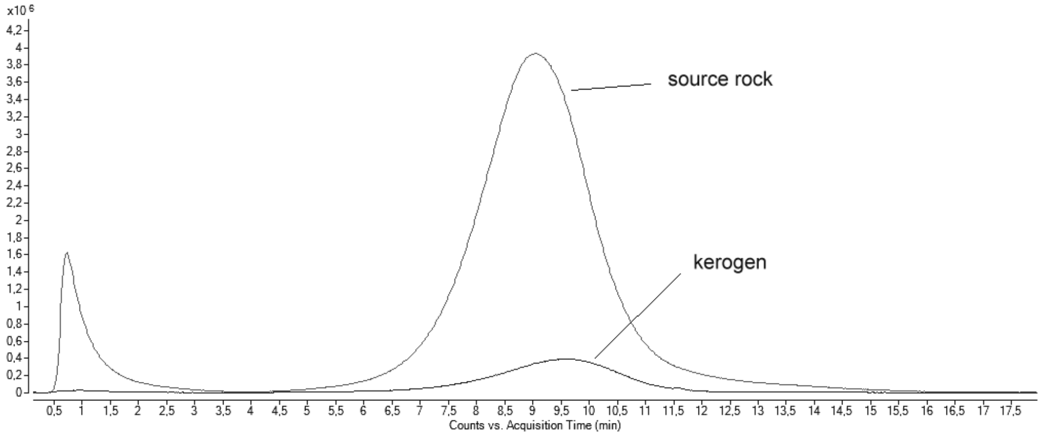

Fig. 7. Pyrograms of source rock and kerogen samples

From the pyrogram it is seen that S_1 peak is totally escaped, where S_2 peak value is significantly decreased. In addition, the vertex of S_2 peak shifts to the left. The pyrolytic characteristics of investigated samples are provided in Table 3.

Decreasing S_1 and S_2 parameters in kerogen sample are due to loss of source rock hydrocarbon during one of the steps of extracting kerogen from the rock. A small increase in T_{max} parameter is probably due to increasing the share of insoluble part of organic matter in bonded hydrocarbons.

It was mentioned that S_1 and S_2 define the generation potential of source rock, and Tmax stands for the catagenetic maturity of organic matter. The relations between these parameters and the generating potential are provided in Table 4 and 5 (Tisso, Velte, 1981).

Sample	S_1, mg HC/g rock	S_2, mg HC/g rock	T_{max}, °C
Source rock	15,39	173,04	416
Kerogen	0,36	17,31	435

Table 3. The pyrolytic investigation of samples

Generating potential of source rock	Pyrolytic parameters, mg HC/g rock	
	S_1	S_2
Poor	<0,5	<2,5
Satisfactory	0,5-1,0	2,5-5
Good	1-2	5-10
Very good	2-4	10-20
Excellent	>4	>20

Table 4. The generating potential of rocks as a function of S1 and S2

Based on the data provided in Table 3, 4 and 5 one may conclude that generating potential of Domanic rock samples are excellent as per S_1 and S_2 parameters. Surely, in order to achieve more precise correlations it is necessary to involve the content of total organic carbon as well. The upper described equipment allows measuring this parameter, but the gas scheme of pyrolyzer has to be changed prior to each group of samples. Hence, it is appropriate to measure the C_{org} content on an elemental CHN-analyzer after preliminary removal of carbonates from samples. In any case, C_{org} parameter is directly related with S_1 and S_2 parameters.

Thus, the main advantages of application of described pyrolytic system are as follows. Firstly, the simultaneous results of pyrolytic parameters (S_1, S_2 and T_{max}) with mass-spectra of evolved gases (pyrolysis products) with the possibility of group component or distinct compound identification. Secondly, the construction of the given equipment allows replacing the metallic capillary with chromatography column. This provides decomposition of S_1 and S_2 peaks into components with further identification of compounds. Thirdly, it is possible to study the kinetics of chemical reactions during organic matter conversion by determining the composition of pyrolysis products depending on temperature and time. Overall, these advantages allow applying the given equipment to solve the wide range of scientific tasks of geochemical laboratories.

Maturity of organic matter		Tmax, °C	Characteristics of generation products
Immatured		<435	Heavy oil
Matured	early maturity	435-445	oil
	peak of oil generation	445-450	oil
	late maturity	450-470	Light oil
Super-matured		>470	gas

Table 5. The maturity of organic matter as a function of Tmax

Acknowledgements

The authors are grateful to the Doctor of Chemical Sciences, Professor Galina P. Kayukova for help in preparing and writing an article.

The studies were carried out using the funds of subsidies allocated to Kazan Federal University as part of the State Program to improve the competitiveness of the Kazan Federal University among the world's leading research and education centers.

References

Behar F., Beaumont V., Penteado H.L. De B. (2001). Rock-Eval 6 Technology: Performances and Developments. *Oil & Gas Science and Technology,* 56(2), pp. 111-134. DOI: http://doi.org/10.2516/ogst:2001013

Kozlova, E.V., Spasennykh M.Yu., Kalmykov G.A., Gutman I.S., Potemkin G.N., Alekseev A.D. (2017). Balance of the Petroleum Hydrocarbon Compounds in Pyrolyzed Organic Matter of the Bazhenov Formation. *Neftyanoe Khozyaystvo = Oil Industry,* 3, pp. 18-21. DOI: http://doi.org/10.24887/0028-2448-2017-3-18-21 (In Russ.)

Lopatin, N.V., Emets T.P. (1987). Piroliz v neftegazovoy geokhimii [Pyrolysis in oil and gas geochemistry]. Moscow: Nauka, 144 p. (In Russ.)

Romero-Sarmiento M.-F., Pillot D., Letort G., Lamoureux-Var V., Beaumont V., Huc A.Y., Garcia B. (2015). New Rock-Eval Method for Characterization of Unconventional Shale Resource Systems. *Oil and Gas Science and Technology,* 71(37), pp. 1-9. http://doi.org/10.2516/ogst/2015007

Tisso, B. Velte D. (1981). Obrazovanie i rasprostranenie nefti [The formation and distribution of oil]. Moscow: Mir, 501 p. (In Russ.)

Vakhin A.V., Mukhamatdinov I.I., Aliev F.A., Kudryashov S.I., Afanasiev I.S., Petrashov O.V., Sitnov S.A., Chemodanov A.E., Varfolomeev M.A., Nurgaliev D.K. (2018). Aquathermolysis of Heavy Oil in Reservoir Conditions with the Use of Oil-Soluble Catalysts: Part II – Changes in Composition of Aromatic Hydrocarbons. *Petroleum Science and Technology,* 36(22), pp. 1850-1856. DOI: http://doi.org/10.1080/10916466.2018.1514412

Vakhin, A.V., Onishchenko Y.V., Chemodanov A.E., Sitdikova L.M., Nurgaliev D. K. (2016). Thermal Transformation of Bitumoid of Domanic Formations of Tatarstan. *Neftyanoe Khozyaystvo = Oil Industry,* 10, pp. 32-34. (In Russ.)

Vakhin A.V., Onishchenko Y.V., Chemodanov A.E., Sitnov S.A., Mukhamatdinov I.I., Nazimov N.A., Sharifullin A.V. (2019). The Composition of Aromatic Destruction Products of Domanic Shale Kerogen after Aquathermolysis. *Petroleum Science and Technology,* 37(4), pp. 390-395. DOI: http://doi.org/10.1080/10916466.2018.1547760

Zhao X., Zhou L., Pu X., Jiang W., Jin F., Xiao D., Han W., Zhang W., Shi Z., Li Y. (2018). Hydrocarbon-Generating Potential of the Upper Paleozoic Section of the Huanghua Depression, Bohai Bay Basin, China. *Energy & Fuels,* 32(12), pp. 12351-12364. DOI: http://doi.org/10.1021/acs.energyfuels.8b03159

About the Authors

Artem E. Chemodanov – Chief Project Engineer, R&D Center «GeoLab», Kazan Federal University

4/5, Kremlevskaya st., Kazan, 420008, Russian Federation

Bulat I. Gareev – Chief Project Engineer, R&D Center «GeoLab», Kazan Federal University

4/5, Kremlevskaya st., Kazan, 420008, Russian Federation

Georgy A. Batalin – Design Engineer, R&D Center «GeoLab», Kazan Federal University

4/5, Kremlevskaya st., Kazan, 420008, Russian Federation

Roman S. Gerasimov – Product Manager
Frontier Laboratories Ltd.
4-16-20, Saikon, Koriyama, Fukushima, 963-8862, Japan

Manuscript received 17 February 2018;
Accepted 07 March 2019;
Published 30 March 2019