ORIGINAL ARTICLE

DOI: https://doi.org/10.18599/grs.2024.4.2

Kinetics of Organic Matter Thermal Transformation in Source Rocks: Overview of Methods and Experimental Results

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The paper is devoted to kinetic studies of thermal decomposition of organic matter in kerogen-rich rocks. Kinetic studies are the consisting part of geochemical investigations of source rocks and petroleum systems. The results are required for petroleum generation prediction and assessment of reservoir hydrocarbons quantity and quality using basin modelling. Kinetic data is also applied for simulation of in-situ kerogen conversion and hydrocarbons generation, which are the main processes of thermal methods of enhanced oil recovery (thermal EOR).

The paper summarizes fundamental concepts and experimental approaches for kinetic studies of organic matter thermal transformation, it provides an overview of modern methods, equipment and experimental procedures for obtaining bulk and compositional activation energy distributions (spectra) in open and closed systems, and discusses the benefits, limitations, and possible applications of the different methods.

The paper presents the scope of experimental procedures, which have been elaborated at Skoltech, and the obtained results: (i) bulk kinetic spectra, which are aimed at prediction of the total yield of mobile hydrocarbons during kerogen transformation; (ii) compositional kinetic spectra, which consider the amount and composition of hydrocarbon products; (iii) kinetic model of organic matter transformation in a closed system, which includes primary kerogen decomposition and secondary reactions of the hydrocarbons. The kinetic spectra were obtained for various organic-rich rocks collected within the Russian Federation.

Keywords: calculation of Ea distribution, kerogen, source rock, pyrolysis, petroleum generation, compositional kinetics, closed-system kinetics

Recommended citation: Spasennykh M., Shirokova V., Ilmenskii A., Kozlova E., Bulatov T., Goncharova A., Leushina E. (2024). Kinetics of Organic Matter Thermal Transformation in Source Rocks: Overview of Methods and Experimental Results. *Georesursy = Georesources*, 26(4), pp. 3–19. https://doi.org/10.18599/grs.2024.4.2

1. Introduction

The kinetics of organic matter (OM) thermal transformations has been studying since the 1980s. The kinetic parameters of kerogen thermal decomposition are controlled by its chemical structure, which in turn predefine mechanisms and products generated under elevated temperatures. Data on the kinetics and mechanisms of OM thermal destruction is commonly applied for investigation of petroleum systems and simulation of oil and gas formation. Kinetic data can be also used for modelling of reservoir treatment through thermal methods of enhanced oil recovery (EOR). In this case, it is utilized for prediction of quantity and composition of hydrocarbons generated during organic matter transformation *in situ*. Thus, the study of kinetics of OM thermal transformation under geological and technological conditions, as well as the application in modelling of reservoir processes of hydrocarbon generation, are the necessary tasks of organic geochemistry studies

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of source rocks. Implementation of kinetic studies into simulators and basin modelling is proved to improve the efficiency and reduce the risks in hydrocarbon exploration and production.

The study of the kinetics of OM thermal transformation is an integral part of geochemical studies of source rocks. The laboratory studies include experiments on kerogen destruction at elevated temperatures, which are conducted under open-, semi-open- or closed-system conditions (Tissot, Welte, 1984), which are discussed in details below. The main outcome of the kinetic experimental studies is the activation energy distribution (activation energy spectrum, kinetic spectrum) describing the main reactions of OM thermal destruction. The obtained kinetic spectra are used for hydrocarbon generation prediction according to the Arrhenius equation, which describes the dependence of reaction rate on temperature and duration of the exposure. Kinetic spectra are used in basin modelling simulators, PetroMod (Schlumberger), TemisFlow (Beicip-Franlab), and others. The kinetics of OM transformation allows one to calculate the amount and composition of HCs at different stages of the basin geological history (Hantschel, Kauerauf, 2009; Peters et al., 2018). Kinetic spectra are also realized in hydrodynamic simulators of thermal EOR, such as CMG Stars and others (Mokheimer et al., 2018). In this case, modelling is aimed at choice of the optimal parameters for the reservoir thermal treatment of the reservoir in order to maximize the production and control the composition of the products. The parameters like temperature, duration of thermal exposure, and composition of the heating agent can be varied. In addition, data on kinetics and products composition can be used for evaluation of the efficiency and geochemical monitoring of thermal EOR methods.

The aim of this study is to provide an overview of existing approaches and methods for kinetic studies of OM thermal transformation, including experimental equipment and procedures, and examples of kinetic spectra for various petroleum source rocks in Russia.

The performed studies, the developed procedures, and the obtained data form the basis for further geochemical studies of OM from source rocks and unconventional reservoirs. Additionally, the presented approaches are valuable for modelling of oil and gas formation in petroleum basins during geological history and for kerogen thermal transformation during reservoir treatment.

2. Review of methods for studying the kinetics of organic matter thermal transformation

Kinetic studies of organic matter are based on experiments on OM thermal transformation in rock of target geological object. Laboratory conditions are not really designed to mimic the geological ones, especially in terms of time. Therefore, laboratory experiments are carried out at higher temperatures and shorter times compared to real ones. Although the research results on organic matter decomposition kinetics are successfully applied to modeling of the reservoir processes, there are doubts regarding the possibility of correct description of geological processes using laboratory kinetics. For example, it was concluded that higher temperatures and lower experiment duration can lead to lower accuracy of forecasts (Peters et al., 2018; Kashapov et al., 2019) of both generated HCs volume and their composition (Behar et al., 2008; Behar et al., 2010). Other conditions of laboratory experiments, such as pressure, system openness (open, semi-open, closed), the presence of water, may also diverge from real ones. These differences could also decrease the accuracy of modeling. The understanding of uncertainties provokes researches to keep improving the methods, as well as to create validation/calibration procedures to obtain more reliable results.

Organic matter of source rocks consists of kerogen, heavy hydrocarbon fractions, liquid oil fractions and hydrocarbon gases. Under thermal stress different chemical bonds (C-C, C-S, S-S, C-O, etc.) in various organic fragments of kerogen structure undergo cracking, and this process is a complex set of simultaneous chemical reactions. To simplify the analysis of OM thermal destruction, kinetic studies are carried out for kerogen separately using rock samples after extraction with organic solvent. However, for a complete description of the OM transformation processes, the experiments on thermal transformation of other components of organic matter should be also performed, as well as the experiments on samples containing the entire hydrocarbons and kerogen. In the case of experimental modeling of in-situ organic matter conversion (thermal EOR), studies can be carried out in the presence of water or another heat carrier.

The fundamentals of kinetic studies of OM thermal decomposition are considered in the works (Tissot, Welte, 1984; Braun, Burnham, 1987; Behar et al., 1997). The model assumes that the decomposition of kerogen into hydrocarbons is a series of parallel first-order reactions, and the rate constant of each reaction follows the Arrhenius equation:

$$k_j = A \cdot \exp\left(-\frac{Ea_j}{RT}\right), \qquad (1)$$

where k_j – rate constant of the j-th reaction; A – frequency factor; Ea_j – activation energy of the j-th reaction; R – universal gas constant; T – temperature.

According to the equation (1), each of the parallel reactions proceeds from a certain fraction of kerogen as a reactant, and has the characteristic activation energy (Ea_j). Thus, organic matter thermal destruction is described by a set of activation energies, and each *Ea* characterizes a certain fraction of pyrolyzable kerogen giving the activation energy distribution or kinetic spectrum. The total HCs yield equals to S_2 after extraction obtained by Rock-Eval method, which describes amount of pyrolyzable kerogen in rock. Such kinetic spectrum is called “bulk”. Frequency factor (A) can be found from experimental data or fixed at a constant value, for example, $1 \cdot 10^{14}$ s^{-1}, for all reactions to compare spectra for different systems and objects (Waples, Nowaczewski, 2013; Waples, 2016).

Bulk spectra are used for calculation of the total yield of hydrocarbons during thermal destruction of kerogen without separation of the products into oil/gas/individual compounds. To determine bulk distribution of activation energies, experimental data on the amount of HCs formed from kerogen during a series of experiments at different temperatures for specified time intervals are required. In practice, it is usually calculated from results of non-isothermal experiments: from pyrograms describing the yields of hydrocarbons during linear heating of a rock sample at different heating rates. The experiment is usually carried out in pyroanalyzers. The sample is heated in a crucible, and the products are transferred from the heating zone to a flame ionization detector (and IR cells optionally) by inert gas flow. The experimental technique was elaborated and described by (Schenk, Horsfield, 1993). Other important works on kinetics of organic matter thermal decomposition and calculation of the spectra are (Sundararaman et al., 1992) and (Pepper, Corvi, 1995). Several issues related to the reliability of spectra calculation methods and possible improvements of the procedure are discussed in (Waples, Nowaczewski, 2013; Peters et al., 2015; Waples, 2016; Chen et al., 2017), the procedures are still being developed.

Bulk kinetic spectra obtained in an open system reflect the composition of the original organic matter and its sedimentation conditions, the kerogen type (Sundararaman et al., 1992; Peters et al., 2006). Spectra define the way OM transforms into HCs at elevated temperatures. The results in the form of characteristic kinetic spectra have been published for different types of kerogen (Behar et al., 1997; Peters et al., 2006) and for objects in the Russian Federation (Galushkin, 2007; Astahov, 2016). The main area of application is HC generation prediction using basin modelling.

Kinetic model obtained in an open system and resulting bulk kinetic spectra allow one to assess the total yield of HCs, but not the yields of individual HC components or groups of components (pseudo-components). This is the main limitation of this approach. To evaluate pseudo-components yields, one need to obtain compositional kinetic spectra. The fundamental concepts for compositional model are the same as for bulk model, and the same assumptions are used. The experimental procedure is aimed at study of the composition of the generated hydrocarbon products. Calculation of kinetic characteristics is made for each of the component separately: methane, hydrocarbon gas, oil, oil fractions or individual hydrocarbon compounds. Procedure and data processing for determining the compositional activation energy spectra in an open system were first considered in the works (Ungerer, 1990; Braun, Burnham, 1992), and are still being developed. To determine compositional kinetic spectra in an open system, the most commonly used methods are pyrolysis with determination of the amount and composition of products (pyrolytic mass spectrometry, pyrolytic gas chromatography), as well as thermogravimetric analysis (TGA) in combination with various detection systems (Espitalié et al., 1988; Ungerer, 1990; Braun, Burnham, 1992; Hartwig et al., 2012; Chen et al., 2017; Dubille et al., 2020; Cedeño et al., 2021; Leushina et al., 2021; You, Lee, 2022, Mozhegova et al., 2024) .

It is generally accepted that the activation energy distributions of kerogen thermal destruction obtained in an open system reliably describe natural oil generation processes in basin modelling. Its adaptation to geological conditions through calibration of the model to vitrinite reflectance is a fairly simple procedure. As a result, implementation of kinetic data into basin models helps to enhance the accuracy of the predictions of the time and amounts of generated oil and gas for the selected geological object (Morozov et al., 2016; Peters et al., 2018; Sannikova et al., 2019; Deshin, Yazikova, 2021). Moreover, composition of HCs estimated from compositional model controls the properties of the reservoir fluids: gas to oil ratio (GOR), PVT properties, etc. (di Primio, Horsfield, 2006; Hartwig et al., 2012; Baur, 2019; Dubille et al., 2020).

Despite the apparent benefits of compositional kinetics obtained in an open system, this approach has a number of limitations. The model considers primary kerogen cracking only, since products are removed from heating zone during the experiment. While in real conditions the products can be retained in the heating zone and undergo secondary transformations. In particular, compositional kinetic spectra obtained in an open system do not describe the secondary cracking of heavy oil fractions, which are an additional source of HCs during reservoir thermal treatment. Moreover, the studies of pressure and media influence on the rate of OM transformation are not available in open-system experiments.

The influence of the mineral matrix of rocks on the properties of syngenetic organic matter and the rates of its decomposition are discussed in a number of papers (Horsfield, Douglas, 1980; Espitalié at al., 1984, and others). For example, there is sorption of organic components by mixed-layer (clay) minerals, this effect is ceased after the complete transformation of smectite into illite (Sen-Zhermes et al., 2000; Velde, Espitalié, 1989; Rahman et al., 2018; Green et al., 2020; Paez-Reyes et al., 2024). Heating of OM in a presence of clay minerals such as kaolinite and montmorillonite promotes the decomposition of hydrocarbons into products with lower molecular weight (Aizenshtat et al., 1984; Tannenbaum, Kaplan, 1985; Huizinga et al., 1987; Li et al., 1998). Carbonate minerals could also alter the composition of kerogen pyrolysis products (Xinmin et al., 2022; Labus et al., 2023). A number of studies have shown that iron sulfates and sulfides (especially pyrite) can significantly accelerate petroleum generation (Huizinga et al., 1987; Ma et al., 2016), however, opposite observations have also been published (Galukhin et al., 2017). The influence of the mineral matrix on the kinetics of kerogen transformation is a controversial topic, since it often influences not the rate of kerogen destruction itself, but related processes of the hydrocarbons retention in the rock and/or their secondary chemical transformations, which take place simultaneously during source rock heating. The influence of the mineral matrix on OM decomposition kinetics is often accounted for in the experimental methodology, when extracted rock is used instead of pure kerogen obtained by acid treatment.

The secondary transformations of HCs generated from kerogen, influence of elevated pressure and reaction media (water, HCs, CO_2, etc.) can be studied in closed-system experiments. In this case, the process of organic matter transformation is more complex than in an open system, and the conditions are closer to the reservoir ones. For laboratory experiments, different reactor designs may be used, including gold ampoules, micro-scale sealed vessels (MSSV) and other quartz reactors, steel reactors, and autoclaves (Zumberge et al., 1988; Behar et al., 1992; Schenk, Horsfield, 1993; Landais et al., 1994; Behar et al., 1997; Vandenbroucke et al., 1999; Lewan, Ruble, 2002; Behar et al., 2008; Berwick et al., 2010; Hartwig et al., 2012). The reactors are designed to meet the following requirements: to perform the transformation of the OM; to investigate products composition; to establish a mass balance. The data then used to formulate model chemical reactions and calculate their kinetic parameters. The results of kinetic studies in a closed system consist of model reactions of primary kerogen destruction with the formation of hydrocarbon and non-hydrocarbon products (hydrogen, carbon dioxide, etc.), as well as secondary transformations of oil fractions and interactions of hydrocarbons with other components of the reaction system. Reconstruction of the kinetic model of OM transformation in a closed system is more complicated task, compared to modelling of open system pyrolysis (Burnham, 2017). In a closed system the process of OM transformation is described by kinetic spectrum of kerogen decomposition and a few spectra representing the reactions of decomposition products, including heavy oil fractions and liquid HCs. In most of published studies the calculation algorithms are presented in general terms, and software for reconstruction of the spectra is not publicly available.

There are uncertainties in the results of kinetic studies in a closed system, as well as discrepancies are present between the results of different studies. In particular, there is no single point of view on the effect of water on OM thermal destruction process. For example, the authors of (Tumanyan et al., 2015; Vasiliev et al., 2020; Zakieva et al., 2020; Liu et al., 2023) came to conclusion that water can act both as a reactant and a solvent for polar fractions, a hydrogen donor and/or an acid, depending on the conditions. Significant differences were noted between the kinetics of OM destruction for the same sample in an open system and in a closed system in the presence of water (Lewan, 1997; Lewan, Ruble, 2002). At the same time, the following works (Landais et al., 1994; Behar et al., 2010) show the absence of a significant effect of water on the transformation of OM. The influence of pressure on kerogen transformation rate is also debatable. The vast majority of studies show that pressure does not have a significant effect on the processes of oil formation from kerogen in a closed system (Freund et al., 1993; Schenk, Horsfield, 1993; Behar et al., 2010). However, there are exceptions, for example, the researchers observed decrease in the yield of hydrocarbons with increase in the confining pressure (up to 300–1300 bar) (Landais et al., 1994). The above-mentioned contradictions indicate the need for further research in this area. In general, the study of the kinetics of OM thermal transformations under various conditions is important and of high demand for industry.

Present research is devoted to review of current methods and summary of the obtained results of kinetic studies for geological objects of the Russian Federation.

3. Research methods and examples of kinetic spectra

Bulk kinetics in an open system

In this work, bulk kinetic studies was carried out using HAWK RW pyrolyzer (Wildcat Technologies, USA). This instrument is a close analogue of the Rock-Eval device (Vinci Technologies, France), which was the first for the method elaboration (Espitalie, Bordenave, 1993).

For determination of the bulk kinetic spectrum of kerogen decomposition in an open system, the kerogen rich rocks were used. The samples were crushed, homogenized and extracted with chloroform to remove liquid hydrocarbons. The sample weight was 30–50 mg, the fraction was 200 mesh.

The analyses were carried out using the common kinetic program: a series of one to five experiments with heating of the sample in a crucible in a helium flow (50 ml/min) at different heating rates and detection of the released HCs using flame ionization detector (FID) (Braun, Burnham, 2015b). For our experiments, we used the temperature range from 300 to 650 °C and three heating rates of 3, 10 and 30 °C/min. The Green River shale standard was used to calibrate the temperature, standard sample was studied under the same conditions before and after a series of experiments.

The results of each experiment contain three pyrograms, which are the profiles of HCs yield vs. temperature. Each pyrogram includes 600 points by default. The pyrograms were processed to calculate the bulk kinetic spectrum using the Kinetics2015 software (Braun, Burnham, 2015a). Before processing, the pyrograms were smoothed and normalized to 1.

The Kinetics2015 algorithm is based on equation, which relates the conversion/yield of hydrocarbons to the kinetic parameters of the first-order reactions under non-isothermal conditions:

$$\alpha = 1 - \sum_j \exp\left[-\frac{A}{Hr}\int_{T_0}^{T} e^{-\frac{Ea_j}{R\tau}} d\tau\right] \cdot a_j, \qquad (2)$$

where α – pyrolyzable kerogen conversion; $A = 1\cdot10^{14}$– frequency factor (1/s); *Hr*– heating rate (K/s); T_0 – initial temperature (K); *T* – temperature required to reach the conversion α (K); R = 1.897– universal gas constant (cal/mol/K); Ea_j – *j*-th activation energy (cal/mol); a_j – contribution (fraction) of pyrolyzable kerogen with characteristic *j*-th activation energy of the destruction.

The search for the contributions (fractions) of kerogen (a_j) with a specified activation energy of the destruction is carried out using optimization procedure. The nonlinear least squares method with constraints on the non-negativity of the fractions ($a_j \geq 0$) and their sum ($\sum_j a_j = 1$) is applied. In particular, the Levenberg-Marquardt algorithm (Burnham, 2017) is used in the Kinetics2015 software.

Correct reproducible results can be obtained only for the samples with a sufficient proportion of pyrolyzable kerogen. The basic criterion is a well-defined peak S_2 during standard Rock-Eval pyrolysis of the sample (S_2 not lower than 2 mg HC/g of rock). It is worth noted that immature or low maturity samples must be investigated for further application of the spectra in basin modeling (T_{max} lower than 430–435 °C, vitrinite reflectance index VRo less than 0.5–0.6%). When more mature samples are studied, the results describe the residual generation potential, and their spectra need to be recalculated to the initial state.

The experimental bulk kinetic spectra of source rocks from West Siberian, Yenisei-Khatanga and Lena-Tunguska petroleum basins located on the territory of the Russian Federation are presented in the following sections. As examples, we provide the results for the samples containing different types of OM (samples 1, 2, 3, 6, 7). For the Bazhenov Formation, three samples at different maturity stages were selected (samples 3, 4, 5), ranging from the beginning to the middle of oil window, they illustrate the dynamics of oil generation. Geological and lithological data are given in Table 1, Rock-Eval pyrolysis data are given in Table 2 (Espitalie, Bordenave, 1993). Low-mature samples containing various kerogen types were selected, which is derived from T_{max}. For the Bazhenov Formation samples, maturity stage was estimated from not only T_{max}, but also hydrogen index HI, productivity index PI and K_{GOC} = GOC/TOC×100, reflecting the degree of realization of petroleum generation potential, which was recently suggested for characterization of the Bazhenov Formation rocks (Spasennykh et al., 2021).

Sample ID	Petroleum Basin	Age	Formation	Lithology	OM type	Maturity
1	Lena-Tunguska	R	Iremeken	Argillite (mudstone)	I	Early mature
2	West Siberia	J_3-K_1	Bazhenov	Clayey -siliceous rock	IIS	Early mature
3	West Siberia	J_3-K_1	Bazhenov	Clayey -siliceous rock	II	Early mature
4	West Siberia	J_3-K_1	Bazhenov	Clayey -siliceous rock	II	Mature
5	West Siberia	J_3-K_1	Bazhenov	Clayey -siliceous rock	II	Mature
6	West Siberia	J_2	Tyumen	Coaley argillite (mudstone)	II-III	Early mature
7	Yenisei-Khatanga	K_1	Shuratovsk	Argillite (mudstone)	III	Early mature

Table 1. Lithological-geochemical data for the samples from petroleum basins of the RF selected for kinetic studies of organic matter thermal decomposition

Sample ID	S_2, mg HC /g rock	TOC, wt.%	T_{max}, °C	HI S_2/TOC×100, mg HC /g TOC	OI S_3/TOC×100, mg CO_2 /g TOC	$CaCO_3$, wt.%	GOC, wt.%	K_{GOC}, %
1	135.57	17.3	437	784	7	2.0	11.7	68
2	79.42	12.5	425	637	2	1.5	6.9	55
3	82.85	13.4	434	621	4	3.2	7.1	53
4	39.53	10.0	435	397	6	1.4	3.5	35
5	12.84	5.2	444	248	8	2.1	1.2	22
6	167.50	66.7	438	251	8	0.0	15.3	23
7	1.99	1.9	429	104	61	4.1	0.2	13

Table 2. Rock-Eval pyrolysis data for the samples from petroleum basins of the RF selected for kinetic studies of organic matter thermal decomposition. Calculation and interpretation of the parameters are available in (Espitalie, Bordenave, 1993; Spasennykh et al., 2021)

Fig. 1 shows bulk kinetic spectra of kerogen types I, II, II-III and III of similar maturity at the beginning of oil window. For easier comparison, all the spectra were calculated at fixed frequency factor $A = 1 \cdot 10^{14}$ s^{-1}.

As it follows from Fig.1, the width of kinetic spectra of different types of kerogen differ significantly, and the width of distribution increases from type I to type III. This correlates with the differences in the composition of organic matter, in particular, with content of aliphatic, aromatic, as well as heteroatom-containing fragments (Tissot, Welte, 1984; Tegelaar, Noble, 1994).

Calculation of the spectra at constant fixed frequency factor, as it is done above, is not generally accepted approach; the influence of this parameter on the predictions of hydrocarbon generation is discussed in the literature (Waples, Nowaczewski, 2013; Peters et al., 2018). In this paper, we use fixed A value in order to compare the activation energy distributions for different types of kerogen and to track the changes in its shape during maturation of OM. Change of frequency factor leads to a shift and change in the distribution of activation energies. For example, kinetic spectrum of type I kerogen (Fig. 1a) does not show a single activation energy, as expected based on previous studies (Peters et al., 2006). It can be shown that distribution comprising two values of E_a could be recalculated to give a single E_a by choosing another frequency factor.

The kinetic spectra can significantly vary within one kerogen type for different geological objects due to differences in accumulation conditions and transformation processes of organic matter. The composition of organic matter and the resulting activation energy distribution are controlled by the initial organic matter composition, sedimentation conditions, diagenetic and catagenetic transformations of rocks. Even the rocks with similar pyrolytic characteristics show significant differences in the kinetic spectra. Therefore, the kinetic studies for each geological object are strongly recommended.

Fig. 2 shows the kinetic spectra of kerogen type II and IIS for the samples with comparable degree of thermal maturity (beginning of the oil window). The rocks show close values of TOC and hydrogen index HI, as well as residual generation potential K_{GOC}, whereas there are dramatic differences in the value of T_{max} and the maximum of the kinetic spectra.

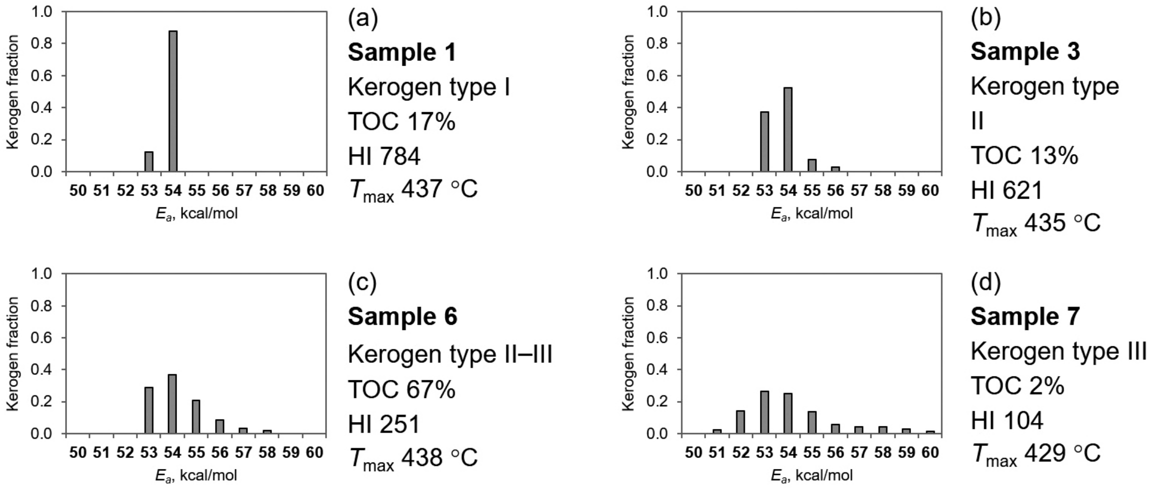


Fig. 1. Examples of bulk kinetic spectra for different kerogen types at early mature stage, $A = 1 \cdot 10^{14}$ s^{-1} (sample data are in Table 1)

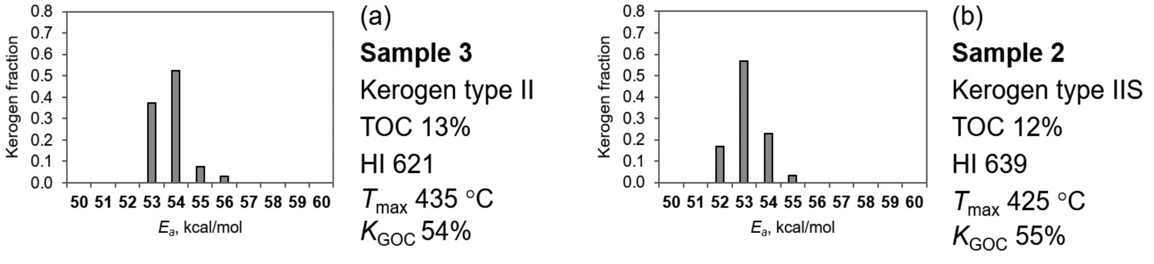


Fig. 2. Examples of bulk kinetic spectra for kerogen types II (a) u IIS (b) at $A = 1 \cdot 10^{14}$ s^{-1} (sample data are in Table 1)

The maximum of the distribution for kerogen IIS (Fig. 2b) is 1 kcal/mol lower compared to that for type II kerogen (Fig. 2a), which leads to a shift in the generation of HCs by kerogen to the region of lower temperatures. This is explained in the literature by higher sulfur content in type IIS kerogen (Reynolds et al., 1995; Rosenberg, Reznik, 2021).

Figure 3 shows the kinetic spectra for samples containing type II kerogen in a range of thermal maturities: from the beginning to the maximum of the oil window. There is an obvious shift of kinetic spectrum to higher activation energies during maturation. At the beginning of the oil window the spectrum is nearly symmetrical, at higher maturity, the contribution of lower E_a decreases, which leads to asymmetry of the spectrum. This is explained by the faster consumption of OM with lower E_a according to the Arrhenius equation, whereas OM with higher E_a at the same conditions converts into hydrocarbons at lower rates (Jarvie, Lundell, 2001; Leushina et al., 2021).

Thus, kinetic studies in an open system are an express method for quantitative assessment of OM petroleum generation potential in geological history and under any thermal exposure. Moreover, kinetic spectra reflect the features of the kerogen chemical structure, the shape of the distributions are controlled by OM type and maturity. These observations are helpful for comprehensive geochemical studies of organic matter.

Compositional kinetics in an open system

Bulk kinetic spectra are used for estimation of bulk HC yield from OM at elevated temperatures. In turn, compositional kinetic spectra are used for calculation of the yields of individual components or groups of components (pseudo-components) at specified time and temperature. To determine the compositional activation energy distribution, experimental data on the amount and composition of products are required, and a series of experiments of kerogen thermal decomposition at different temperatures over different time intervals is usually performed.

The compositional kinetic studies technique is described below. It was developed at Skoltech Center for Petroleum Science and Engineering; the first version of this technique was published earlier (Leushina et al., 2021), the updates are presented below.

Compositional kinetic spectra of kerogen decomposition in an open system were calculated on the basis of bulk spectra and data on composition of pyrolysis products obtained in a series of isothermal pyrolysis – gas-chromatography experiments (pyro-GC×GC-TOFMS/FID) on a Pegasus 4D

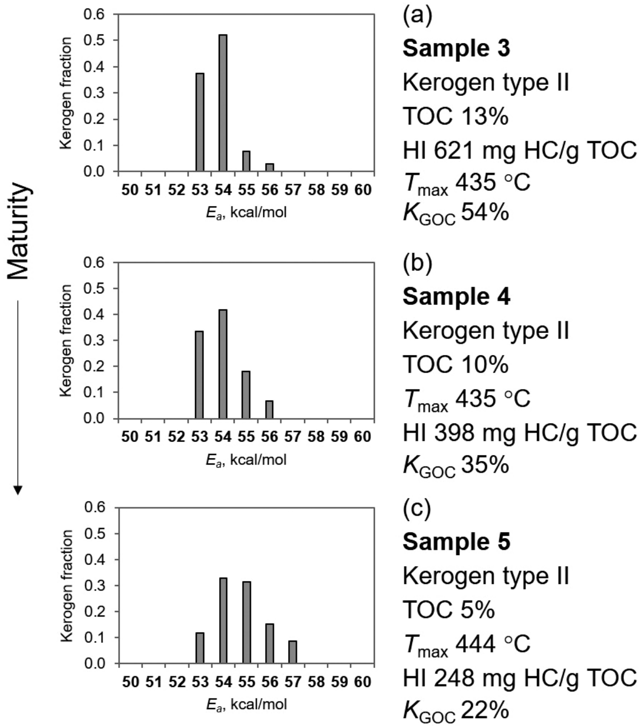


Fig. 3. Examples of bulk kinetic spectra for the samples of kerogen type II from immature (a) to mature (c) at $A = 1 \cdot 10^{14}$ s^{-1} (sample data are in Table 1)

instrument (LECO, USA) with an injection unit for thermal desorption TDU2 and pyrolysis option PYRO (Gerstel GmbH & Co. KG, Germany). The first step was bulk kinetic studies of an extracted rock sample according to the procedure discussed above. The second step was a series of isothermal experiments for 1–10 mg of rock in the temperature range of 350–600 °C and the exposure time of 10–60 seconds, T–t conditions were chosen to reach different kerogen conversions. In the instrument, pyrolysis products were transferred from pyrolysis unit to chromatograph by a constant flow of carrier gas (helium), and collected on the top of the column held at 50 °C. After chromatographic separation, the products were detected using time-of-flight mass spectrometer (TOFMS) and flame ionization detector (FID) simultaneously. Individual compounds were identified based on retention time and comparison of obtained mass spectra with the ones from NIST database.

For compositional kinetic model, the number of pseudo-components can be as high as the number of individual compounds or could be reduced according to the objectives of the study and the capabilities of the simulators. In the present case, individual organic compounds identified in the products of kerogen decomposition were combined into pseudo-components based on their physical and chemical properties: hydrocarbon gas (C_1–C_5), light saturated and aromatic hydrocarbons (C_6–C_{15}), saturated and aromatic hydrocarbons (C_{15}–C_{35}), and heavy oil fractions (C_{35+}). Methane C_1 is combined with other hydrocarbon gases C_2–C_5 due to the limitations of chromatographic separation of products, although in most applications it should be considered separately. Additional analyses are required to find out the proportion of methane. Further calculations of each component contribution to bulk kinetic spectrum (fractions) were based on evaluation of kerogen conversion in pyro-GC isothermal experiments from bulk kinetic spectrum and analysis of the mass fractions of the pseudo-components in total HCs for each conversion.

The equation (3) was applied for calculation of the yield for each pseudo-component based on the model of the first-order reaction of kerogen decomposition under isothermal conditions:

$$x_{k,i} = 1 - \sum_j \exp\left[-A \cdot t_i \cdot e^{-\frac{Ea_j}{R \cdot T_i}}\right] \cdot a_{k,j}, \qquad (3)$$

where $x_{k,i}$ – the yield of k-th product in i-th pyrolysis isothermal experiment; t_i – time of the i-th experiment (s); T_i – temperature of the i-th experiment (K); $a_{k,i}$ – the proportion of kerogen that produce the k-th product at the j-th E_a during pyrolysis.

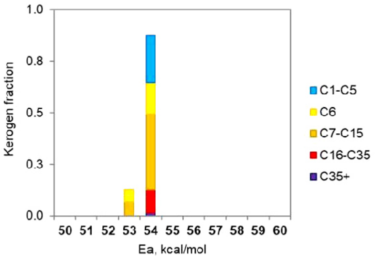
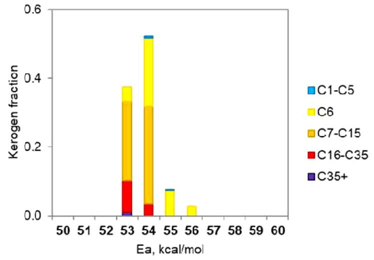
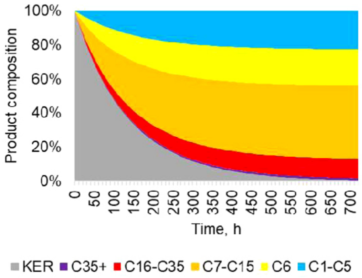
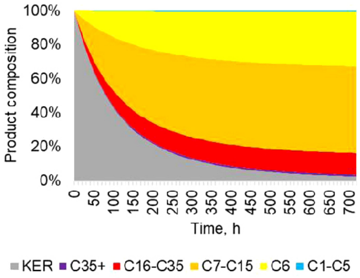
The search for kerogen fractions ($a_{k,j}$) that contributed to generation of each of the pseudo-components at a certain activation energy was carried out using the linear least squares method with restrictions on the non-negativity of fractions ($a_{k,j} \geq 0$) and on their sum ($\sum_k a_{k,j} = a_j$). In particular, we used the projected gradient descent algorithm (PGD).

The compositional spectra obtained for the source rocks represent three petroleum basins, there are 4 samples containing different types of OM (Table 1, Fig. 1). The obtained compositional spectra of kerogen thermal transformation, the composition of the pyrolysis products and the predicted HCs yields during isothermal heating at 350 °C are presented in Table 3.

The data show that the formation of gaseous HCs (C_1–C_5) proceeds at higher activation energies of 54–65 kcal/mol, while the formation of heavier fractions (C_{16}–C_{35}, C_{35+}) has lower E_a 52–53 kcal/mol. Thus, one can conclude that heavy oil (bitumen) releases at the early stages of kerogen maturation, and gas forms at the later stages. This observation correlates well with the data presented in the literature (Tissot and Welte, 1984; Behar et al., 1997).

There are differences in the composition of the products generated by different types of OM. In the line I–II–III, a significant decrease in the mass fraction of light oil (C_6–C_{15}) and an increase in the proportion of gas components (C_1–C_5) are noticeable, which will significantly affect the volume of generated hydrocarbons, since gas has low density. Moreover, type II–III is distinguished by a significant amount of medium-boiling and heavy oil components (> 20%), which is associated with higher aromaticity and the presence of heteroatoms in kerogen structure.

The results of a series of pyro-GC analyses of kerogen destruction and quantitative compositional kinetic models of organic matter transformation allows direct calculation of the composition of products at any stage of kerogen conversion.

Sample ID		1	3
Kerogen type		I	II
E_a distribution			
Product composition, wt.%	C_1–C_5	23	1
	C_6–C_{15}	65	85
	C_{16}–C_{35}	11	13
	C_{35+}	1	1
Product generation profiles at 325 °C			

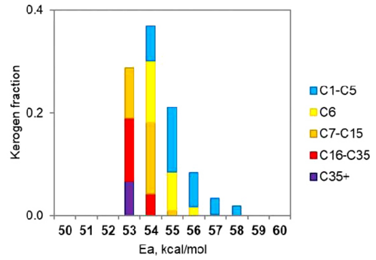
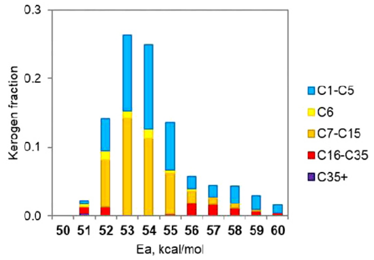
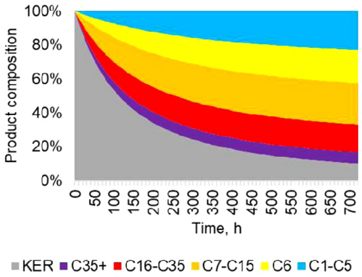
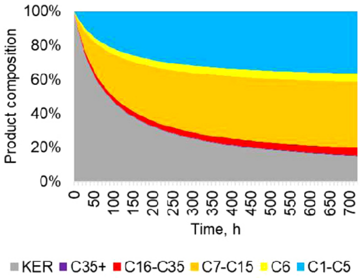
Sample ID		6	7
Kerogen type		II–III	III
E_a distribution			
Product composition, wt.%	C_1–C_5	31	44
	C_6–C_{15}	46	47
	C_{16}–C_{35}	16	8
	C_{35+}	7	1
Product generation profiles at 325 °C			

Table 3. Examples of compositional kinetic spectra for different kerogen types at early mature stage obtained in an open system, $A = 1 \cdot 10^{14}\ s^{-1}$ (sample data are in Table 1), hydrocarbons composition at full conversion and their generation profiles at 325 °C

In turn, the composition of HCs determines oil/gas/gas condensate potential of the studied source rocks, which is essential for basin modeling and forecast of the properties of reservoir fluids, i.e. petroleum volume, oil/gas ratio, PVT properties of fluid, etc. Another application of compositional kinetic models is calculation of pseudo-components yields at specified time and temperature conditions, which are necessary for optimization of the reservoir stimulation conditions for in-situ OM conversion and thermal EOR.

It has been confirmed that the forecasts obtained in basin modeling with compositional kinetic spectra reliably describe the volume of hydrocarbons in reservoirs and the composition of reservoir fluids for the Bazhenov Formation (Morozov et al., 2016; Sannikova et al., 2019). The further efforts in this research area are aimed at creating a reliable spectra database for basin modeling software libraries.

Compositional kinetics in a closed system

Compositional kinetic models in a closed system not only consider primary kerogen cracking, but also secondary cracking of the products. Moreover, there is possibility to study the effect of pressure and media. The conditions of experiments in a closed system (pressure, media, temperature range, etc.) are not universal from case to case, they are to be chosen based on the problem being solved and the object of the study. The common thing is to review the results of the kinetic studies in an open system and literature data prior to experiments. Experimental conditions (temperature, time) are selected in such a way as to study the composition of the products in the range of conversion of OM from a few percents to 100%, and different extent of secondary transformations. A series of at least 10–15 experiments is recommended to get reliable product generation profiles and to check reproducibility of the results.

In this work, a setup based on a 50 ml stainless steel reactor was used. The temperature allowed was up to 500 °C, pressure up to 100 atm, inert media (helium, nitrogen) or heat carrier (water, CO_2) can be used. Rock-Eval pyrolysis, bulk and compositional kinetic spectra in an open system were studied prior to experiments. For each experiment, 50 g of extracted rock sample was loaded into the reactor, evacuated, and then the free volume was measured. During the experiment, the pressure around 10 atm in the reactor was created by helium. The temperature was increased by an external electric tube heater. The pressure and temperature were monitored throughout the experiment. Upon completion of the experiment, the system was cooled by a compressed air flow for 5–10 minutes. After cooling, gaseous products quantity was determined by the pressure increase and their composition was analyzed by GC. Liquid products were collected by washing of the reactor and ASE extraction of the rock sample with chloroform. Liquid products were analyzed using GC and GC-TOFMS. Rock samples after the experiment were analyzed by pyrolysis twice: before extraction to study saturated rock and after extraction to determine the degree of kerogen conversion.

Depending on the task, the set of analytical methods for analysis of rock, gaseous and liquid components before and after the experiment could be expanded. In particular, one could apply analysis of rock mineral part; elemental and isotopic composition analyses of rocks; SARA, elemental and isotopic composition of fluids; isotopic composition of gases and others. The results of additional analyses are not directly related to the calculation of kinetic spectra, but they help to determine the mechanisms of OM and rocks transformation at elevated temperatures.

The kinetic model of organic matter transformation in a closed system was based on the model chemical reactions. The following components were considered in the kinetic model: kerogen (KER) and its destruction products, i.e. heavy oil fractions (HO, C_{15+}), medium-boiling and light fractions (LO, C_6–C_{15}), hydrocarbon gas (HCG, C_1–C_5):

$$\begin{cases} \mathrm{KER} \overset{k_1}{\rightarrow} a_1\mathrm{HCG} + b_1\mathrm{LO} + c_1\mathrm{HO}, \\ \mathrm{HO} \overset{k_2}{\rightarrow} a_2\mathrm{HCG} + b_2\mathrm{LO}, \\ \mathrm{LO} \overset{k_3}{\rightarrow} a_3\mathrm{HCG}, \end{cases} \tag{4}$$

where KER – kerogen; HO – heavy oil; LO – light oil; HCG – hydrocarbon gas; a_1, a_2, a_3, b_1, b_2, c_1 – stoichiometric coefficients of reaction products; k_1, k_2, k_3 – reaction rate constants.

The calculation of the discrete bulk kinetic spectrum of kerogen decomposition in closed-system experiments was carried out using the activation energy distribution method (Braun, Burnham, 1987) in accordance with the equation:

$$\alpha_i = 1 - \sum_j \exp\left[-A \cdot t_i \cdot e^{-\frac{Ea_j}{R \cdot T_i}}\right] \cdot a_j, \tag{5}$$

where α_i – kerogen conversion in i-th isothermal experiment; α_j – the proportion of kerogen that has the j-th E_a of decomposition.

The experimental values of kerogen conversion were calculated from S_2 peak from Rock-Eval pyrolysis before and after the experiment according to the equation:

$$\alpha_{\mathrm{ker},i} = 1 - \frac{S_{2i}}{S_{20}}, \tag{6}$$

where $\alpha_{\mathrm{ker},i}$ – kerogen conversion in i-th experiment; S_{2i} – S_2 value after the i-th experiment; S_{20} – initial S_2 value.

The search for kerogen fractions (a_j) pyrolyzed at a given activation energy was carried out using the linear least squares method with restrictions on the non-negativity of the fractions ($a_j \geq 0$) and their sum ($\sum_j a_j = 1$). In particular, the projected gradient descent (PGD) algorithm was used. In this case, the optimal range of activation energies corresponding to the smallest sum of square errors was iteratively selected.

The calculation of the kinetic parameters of secondary reactions of heavy and light oils, as well as kerogen fractions for each of the pseudo-component (compositional kinetics of kerogen decomposition), was carried out by solving the system of kinetic equations corresponding to the model reactions:

$$\begin{cases} \dfrac{dM_{\mathrm{KER}}}{dt} = -k_1, \\ \dfrac{dM_{\mathrm{HO}}}{dt} = f_1^{\mathrm{HO}} k_1 - k_2, \\ \dfrac{dM_{\mathrm{LO}}}{dt} = f_1^{\mathrm{LO}} k_1 + f_2^{\mathrm{LO}} k_2 - k_3, \\ \dfrac{dM_{\mathrm{HCG}}}{dt} = f_1^{\mathrm{HCG}} k_1 + f_2^{\mathrm{HCG}} k_2 + f_3^{\mathrm{HCG}} k_3, \end{cases} \tag{7}$$

where M_{KER}, M_{HO}, M_{LO}, M_{HCG} – mass fractions of kerogen, heavy oil, light oil and HC gas in the system; f_1^{HO}, f_1^{LO}, f_1^{HCG} – mass fractions of heavy oil, light oil and HC gas, which were formed from kerogen (primary cracking); f_2^{LO}, f_2^{HCG} – mass fractions of light oil and HC gas, which were formed from heavy oil (secondary cracking); f_3^{HCG} – mass fraction of HC gas, which was formed from light oil (secondary cracking).

The search for the optimal range of activation energies for secondary cracking reactions was performed iteratively. The calculation of the proportions of kerogen, heavy and light oil, pyrolyzed into a specific product, was carried out using the nonlinear least squares method with constraints on the non-negativity of the proportions and their sum ($\Sigma_k f_i^k = 1$, k is a pseudo-component, i is the ordinal number of the reaction). This method was implemented using the trust region reflective algorithm (dogbox).

The resulting compositional kinetic model is then presented as a series of parallel first-order reactions. The stoichiometric coefficients for the chemical reactions were calculated using molecular weights of HC pseudo-components which were experimentally measured and the one for kerogen from (Lee et al., 2020).

As an example, we provide compositional kinetic model of aqueous pyrolysis of OM in a closed system, obtained for mature kerogen-rich rock of the Bazhenov Formation (Table 4).

The experiments were carried with extracted rock sample, the temperature range was 250–450 °C, duration 5 h, distilled water was added. The obtained results of mass balance for the entire experiment and organic matter, the composition of gas, liquid hydrocarbons were transformed to model reactions (4). As the result, kinetic model was calculated at a fixed frequency factor $A = 1{\cdot}10^{14}\ \mathrm{s}^{-1}$. The obtained kinetic spectra of thermal transformations of kerogen, heavy and light fractions of oil are shown in Fig. 4.

The main products of kerogen pyrolysis are light oil (49 wt.%) and hydrocarbon gas (42 wt.%), heavy oil presents in low quantity (9 wt.%). The maximum yield of heavy oil from kerogen occurs in the range of 335–340 °C (5 h), this is the result of heavy oil cracking with the formation of light oil (39 wt.%)

	S_0, mg HC/g rock	S_1, mg HC/g rock	S_2, mg HC/g rock	S_3, mg CO_2/g rock	TOC, wt.%	*Tmax*, °C	K_{GOC}, %
Before extraction	1.87	2.52	44.19	0.66	10.31	441	41
After extraction	0.02	0.18	35.43	0.40	10.16	436	30

Table 4. Rock-Eval pyrolysis data for the Bazhenov Formation sample used for kinetic studies of organic matter decomposition in a closed system. Calculation and interpretation of the parameters are available in (Espitalie, Bordenave, 1993; Spasennykh et al., 2021)

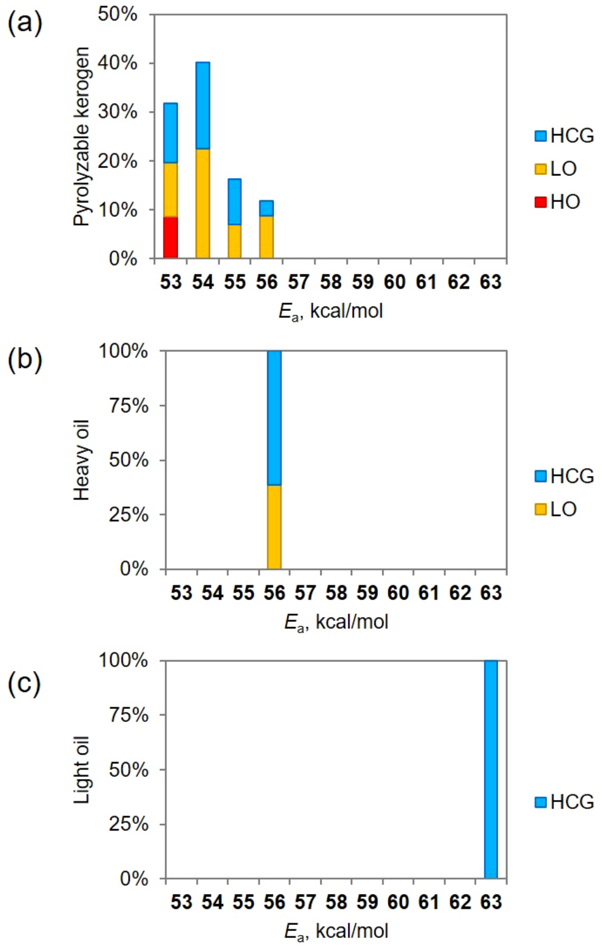


Fig. 4. Compositional kinetic spectra obtained for the Bazhenov Formation sample in a closed system (sample info in Table 4): a) kerogen decomposition spectrum (KER); b) heavy oil decomposition spectrum (HO); c) light oil decomposition spectrum (LO) with formation of HC gas (HCG)

and significant amounts of HC gas (61 wt.%). The experiments also showed the decomposition of light oil (the peak generation at 400–405 °C) with the formation of HC gas. The obtained kinetic parameters for heavy and light oil cracking are in good agreement with the literature data on thermal cracking of individual petroleum HCs (Al Darouich et al., 2006). In addition, Waples reported that the average E_a of thermal conversion of oil into gas under geological conditions is 59 kcal/mol at the same frequency factor ($A = 1\cdot10^{14}$ s^{-1}) (Waples, 2000), this value is consistent with both the experimental data and theoretical models of OM thermal destruction.

Hydrocarbon generation profiles from kerogen rich rocks under elevated temperatures can be easily calculated using kinetic parameters from the obtained kinetic model and Arrhenius equation. The primary kerogen decomposition and secondary reactions in the presence of water are all included and take place simultaneously. Fig. 5 shows the estimated products generation curves during thermal treatment of rock at temperatures of 300 °C, 325 °C and 350 °C for 30 days (the conditions mimic one flooding cycle). One can see that with increasing temperature not only the degree of transformation of the OM increases, but also the composition of the products changes. This illustrates that compositional kinetics of organic matter transformations is helpful for selection of the optimal temperature for thermal treatment of the reservoirs.

4. Conclusion

The paper summarizes the recent achievements in the kinetic studies of organic matter thermal transformation. The benefits, the limitations, and the applications of different techniques are provided together with the overview of the equipment and experimental procedures for obtaining bulk and compositional kinetic spectra of kerogen decomposition in open- and closed-system conditions.

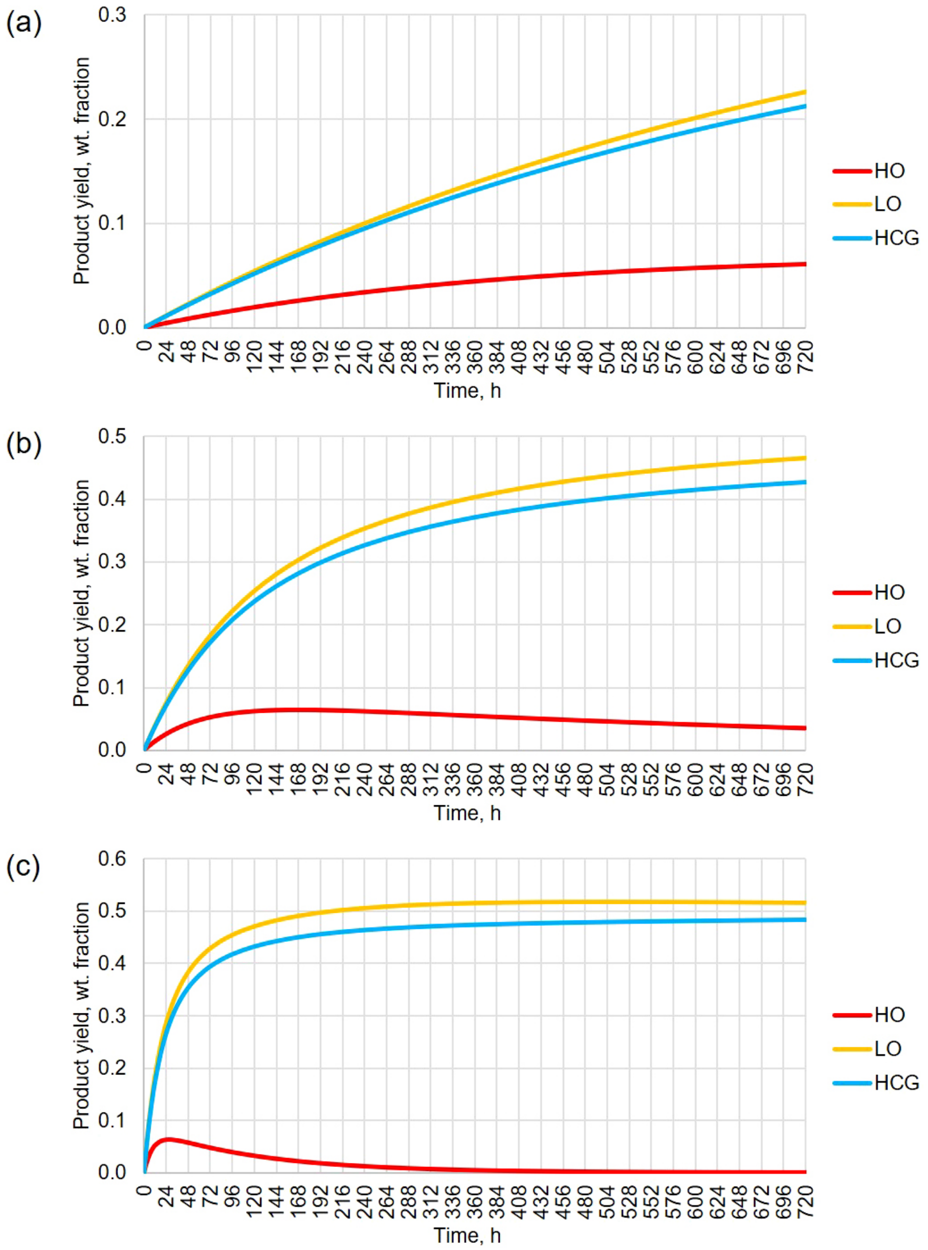


Fig. 5. Hydrocarbon generation profiles predicted using kinetic model obtained in a closed system for the Bazhenov Formation sample under isothermal heat exposure for 30 days at a) 300 °C; b) 325°C and c) 350°C

The following experimental methods are described in details: (i) bulk kinetic studies of hydrocarbons generation during kerogen thermal decomposition in an open system – quantitative analysis; (ii) compositional kinetic studies in an open system aimed at the analysis of hydrocarbons composition during kerogen cracking – both qualitative and quantitative analysis; (iii) kinetic modelling of organic matter transformation in a closed system, which includes kerogen decomposition and secondary cracking reactions of hydrocarbons.

Several bulk and compositional kinetic spectra obtained in an open system for source rocks and organic-rich rocks from various geological objects of the Russian Federation are presented: the Bazhenov and Tyumen formations of the West Siberian basin, the Iremeken formation of the Lena-Tunguska basin and the Shuratovsk formation of the Yenisei-Khatanga basin. The closed-system kinetics of kerogen transformation during aqueous pyrolysis was studied for the Bazhenov formation sample.

The obtained spectra could be implemented in basin modeling for prediction of the amount and composition of oil and gas generated during organic matter maturation and to estimate the composition of the petroleum in reservoirs.

Hydrodynamic simulators and models supplemented with kinetic parameters of kerogen transformation and thermal cracking of oil and bitumen can be used to select optimal conditions for the field technologies of in-situ kerogen extraction and thermal EOR. Without the use of simulators, the proposed model reactions and their kinetic parameters allow one to predict hydrocarbons generation from organic-rich rocks under elevated temperatures under geological or technological operations conditions.

Acknowledgements

The work was supported by the Ministry of Science and Higher Education of the Russian Federation under agreement No. 075-10-2022-011 from 20.04.2022 within the framework of the WLSC development program.

The authors express their gratitude to N. Morozov, D. Kalacheva (Gazpromneft – STC) and K. Prochukhan, A. Gavrilov (Gazpromneft - Technological Partnership) for support of kinetic studies and participation in the work, V. Polyakov, E. Popov, E. Mukhina and Skoltech CPSE laboratory staff for participation in experimental studies.

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*Manuscript received 24 September 2024;
Accepted 14 October 2024; Published 20 December 2024*