

PRODUCTS OF THERMAL DECOMPOSITION AND KINETICS FOR IMMATURE AND MATURE KEROGEN FROM THE BAZHENOV SOURCE ROCK FORMATION

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The kinetic study of sedimentary organic matter (kerogen) transformation to gas and liquid hydrocarbons is required for understanding and modeling of geological (petroleum system modeling) and technological (thermal EOR in application to source/oil shale rocks) processes. Kerogen destruction at elevated temperatures is best modeled by Arrhenius law assuming the number of parallel first-order reactions of hypothetical kerogen components decomposition (*Pepper, Corvi, 1995*). Two major kinetic approaches are considered in the literature, including bulk kinetics, representing the total yield of hydrocarbons, and compositional kinetics, describing various products yields (*Hartwig et al., 2012*).

The objective of the study was to obtain bulk and compositional kinetic spectra for the kerogen from the Bazhenov formation. The Bazhenov formation (BF) is one of the largest formations in the world, which covers more than one million square kilometers in the Western Siberia, Russia. The BF deposits contain TOC 10% on average and have high oil generation potential, depending on the amount and maturity of the organic matter (*Spasennykh et al., 2019*). Kinetics of kerogen thermal decomposition has been studied for the samples of different thermal maturity (see examples in Table 1).

Table 1 Pyrolysis parameters for the samples of organic matter from the BF

	Maturation	T max, °C	S2,mg HC/g rock	HI, mg HC/g TOC	TOC, wt. %	GOC/ TOC
BF1	Beginning of the oil window	426	98.8	717	13.8	0.62
BF2	Middle of the oil window	444	69.1	444	15.5	0.38

Geochemical study of the organic matter was performed for whole-rock samples using Rock-Eval pyrolysis (HAWK RW, Wildcat Technologies), and for rock extracts by GC×GC-TOFMS (Pegasus 4D, LECO). Bulk-kinetic studies were carried out using non-isothermal open-system pyrolysis, pyrograms were computed to activation energies spectrum at fixed frequency factor $A = 1 \cdot 10^{14}$ using KINETICS2015 software. The composition of kerogen thermal destruction products was analyzed using pyro-GC with FID and TOF-MS. Hydrocarbon products of kerogen decomposition were divided into four pseudo-components: gas C1÷5, light liquid hydrocarbons C6÷10 and liquid hydrocarbons C11÷15, and hydrocarbons C16+ according to their retention times. Compositional spectrum was calculated from the set of linear equations by the least square method and the gradient descent with the penalty function approach.

It was found that the kinetic spectra of the studied samples depend on maturity. The spectrum of immature kerogen has a shape similar to the normal distribution in the range of activation energies 50-57 kcal/mol with the maximum at 52 kcal/mol. For mature kerogen activation energy spectrum has the maximum at 53 kcal/mol. Compared to immature, it is asymmetrical, and the beginning is eliminated, that indicates that the oil generation has started (Figure 1).

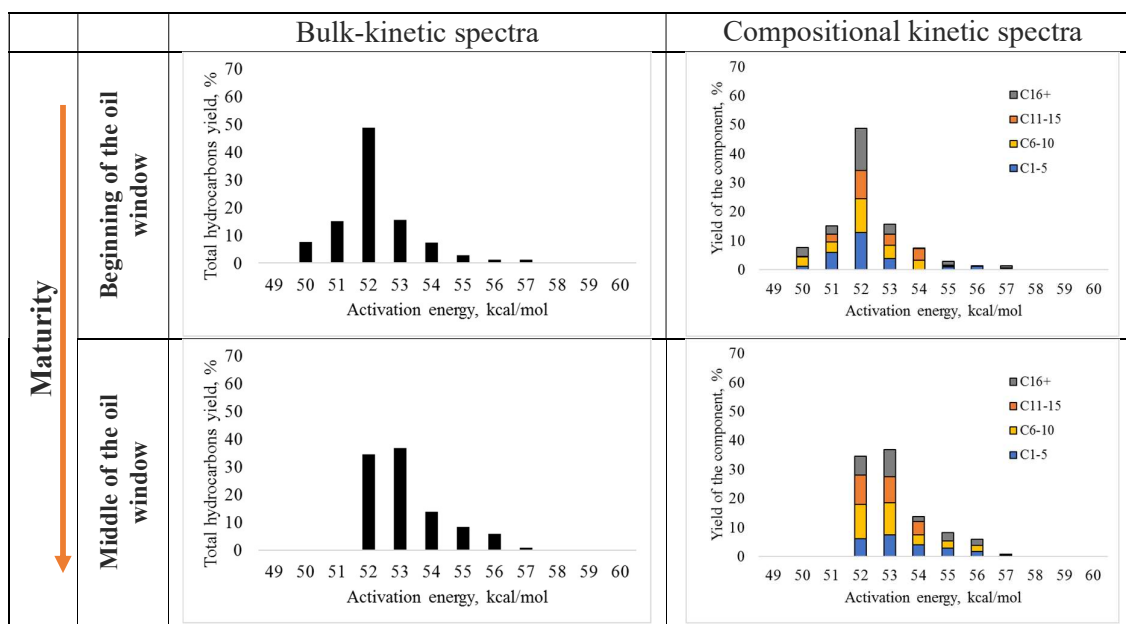


Figure 1 Bulk- and compositional kinetic spectra for the Bazhenov formation kerogen.

The compositional kinetic studies show that lower activation energies are required for generation of early gas and heavy C16+ products. Activation energies in the range 52-53 kcal/mol correspond to generation of liquid hydrocarbons C6-15 (about 50-60 wt.%), gas and C16+, about 25-30 wt.% each. Activation energies higher than 54 kcal/mol are responsible for late gas generation from the residual organic matter.

The observed release of heavy and liquid hydrocarbons at the earlier stages of conversion is in agreement with the hypothesis of predominant destruction of weak heteroatomic bonds in kerogen at elevated temperatures. With the increase of conversion, C-C bond cracking starts, resulting in gases and light oil yield. The analysis of rock extracts supplements the whole scheme of kerogen transformation. Extract from immature sample contains alkanes with chain length more than C15 and alkyl-substituted aromatic compounds (mono-, di-, tri-) which are primary kerogen destruction products, whereas extract from the mature sample has wider alkanes distribution with lower molecular weight compounds.

Results on bulk and compositional kinetics of the Bazhenov kerogen decomposition were obtained for the samples of different maturity. The organic matter maturation influences the composition and the amount of kerogen decomposition products as well as kinetics of the process, closely related to the molecular structure of remained kerogen. We also experimentally proved that at each conversion stage the predominant products of the Bazhenov kerogen decomposition are liquid hydrocarbons.

References

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