

Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Timur Bulatov

PhD Program: Petroleum Engineering

Title of Thesis: Lithological and geochemical study of type I kerogen in the Bazhenov Formation in application to exploration and production of hydrocarbons

Supervisor: Professor Mikhail Spasennykh

Name of the Reviewer: Ksenija Stojanović

I confirm the absence of any conflict of interest ■	Date: 29-09-2022
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The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the report at least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

The summary of issues to be addressed before/during the thesis defense

Please see the Report bellow Table, since I could not insert it into the Table.

Provisional Recommendation

I recommend that the candidate should defend the thesis by means of a formal thesis defense

I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report

The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense



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SKOLKOVO INSTITUTE OF SCIENCE AND TECHNOLOGY Doctoral Program in Petroleum Engineering

Belgrade, September 29, 2022

Dear Colleagues,

First of all I would like to thank you very much to select me as a referee of the work of Timur Bulatov, PhD candidate of highly respectable the Skolkovo Institute of Science and Technology. For me it is a great pleasure and honour.

After reviewing the work of Mr. Bulatov, I submit to the Doctoral School in Petroleum Engineering of the Skolkovo Institute of Science and Technology, the following:

REPORT

A) Preview of the doctoral dissertation content

The doctoral dissertation of the candidate Timur Bulatov is written on 95 pages, A4 (font 12), with 47 figures and 15 tables. The doctoral dissertation is written in English, and contains six chapters. After the first chapter, the *Introduction* (3 pages) there is the second chapter, *Review of the literature data related to origin, characterization and hydrocarbon generation of type I kerogen from different parts of the world and of different age* (14 pages). This is followed by *Materials and methods* (11 pages), divided into three main subchapters, representing *Samples*, *Explanation of performed analyses and Accepted classifications of Bazhenov Formation*. Chapter 4, *Lithological characterization of the alginite-rich layers*, is written on 12 pages and contains 7 subchapters related to microscopical, mineral, inorganic geochemical, morphological and stratigraphic data on studied samples, as well as corresponding *Summary* derived from detailed discussion of above mentioned data. The Chapter 5 comprising *Organic geochemistry, petrography, isotope characterization and depositional environment of the alginite-rich layers* is divided into 10 subchapters that thoroughly elaborate maceral composition, Rock-Eval data, biomarker distributions, isotopic measurements of bulk kerogen, carbon isotopic signatures of individual *n*-alkanes, Pyro-GC×GC-TOF MS/FID results, with 11th subchapter - *Summary*, is written on 22 pages. The Chapter 6 *Modeling of thermal maturation and hydrocarbon generation of the Type I kerogen* is presented on 7 pages. This provides results of artificial maturation in open system and calculation of amount of generated hydrocarbons, followed by corresponding *Summary*. The chapter

Conclusion is given on 3 pages. The last chapter, **References**, contains 82 citations, given on 6 pages. In addition, the doctoral dissertation contains: Acknowledgements; List of tables and figures; Abstract; a Table of contents; List of publications, List of abbreviations and symbols, as well as Declaration of originality.

B) A brief description of the thesis and achieved results

Type I kerogen (sapropelic organic matter) has the greatest petroleum generation potential due to the highest impact of hydrogen-rich organic matter. The majority of sedimentary rocks containing Type I kerogen were formed during lacustrine and marine deposition with a significant accumulation of algal material that had undergone mainly anaerobic bacterial reworking in oxygen-poor conditions. Despite the fact that oil-source deposits containing Type I kerogen are rarely found, they are of interest not only in terms of hydrocarbon exploration but also in order to reconstruct the depositional environment, the processes of diagenesis and catagenesis of sedimentary strata, to solve the problems of rock stratification, and to assess their hydrocarbon generation potential. In the thesis, the comprehensive study of oil prone kerogen type I detected in “alginite-rich layers” of the Bazhenov Formation is performed utilizing wide range of up-to date techniques, including thin section petrography, organic petrography, SEM analysis, Rock-Eval pyrolysis, X-Ray diffraction, X-Ray-fluorescence, inductively coupled plasma - mass spectrometry, kinetics, elemental analysis, Fourier transform infrared spectroscopy, biomarker analysis, isotope analysis of bulk kerogen (C, N, S) and isotopic analysis of individual *n*-alkanes (C) and artificial maturation by GC×GC-TOFMS and Py-GC×GC-TOFMS.

Based on XRD data, thin section petrographical description and SEM analysis, the alginite-rich layers (Type I kerogen) composed mostly of organic matter and quartz grains. Inorganic chemical composition revealed that the alginite-rich layers are characterized by relatively low total REE (9.6-93.4 ppm) compared to the total REE abundance of the host rocks (74.3-186.8 ppm).

According to Rock-Eval pyrolysis and elemental analysis, the alginite-rich layers are characterized by exceptionally high initial hydrogen index (HI_0 up to 1100 mg HC/g TOC) and H/C ratio (up to 1.88) typical for Type I kerogen. The high K_{goc} (up to 90 %) and T_{max} (higher by 6–14 °C) also distinguish the alginite-rich layers from host rocks, containing Type II kerogen. The high hydrogen concentrations are in good accordance with FTIR spectroscopy data indicating the highly aliphatic structure of the kerogen. Type I kerogen of the alginite-rich layers shows narrow energies distribution with dominant E_a of 53 kcal/mol, according to kinetic analysis. Pyrolysis products suggest generation of light crude oils with predominance of normal alkanes C_7 - C_{15} . The $\delta^{15}N$ values (5.9–25.7‰) and C/N ratio (76.8–193.4) of the alginite-rich layers are exceptionally high compared to the host rocks. The obtained results indicate that alginite-rich layers were deposited in anoxic conditions but they were more oxidizing compared to the host rocks. During the deposition, the lipid-rich organic matter had undergone extensive bacterial reworking in a reducing environment according to high $\delta^{15}N$ values and low nitrogen content.

The enrichment of deposits with Type I kerogen is due to the high bioproductivity of the basins. The formation of such sediments occurred in various territories and under various sedimentary facies conditions, including marine basins, large lakes and swamps, under certain conditions due to the accumulation of lipid, hydrogen enriched organic matter. An important condition for the formation of such sediments is the additional supply of a large number of nutrients to the sedimentation basin from various sources (episodic removal of desert material into the basin by sandstorms, activity of paleovolcanoes, marine transgression).

The observed alginite-rich layers and tuff interlayers are isochronous and have good correlation through the Bazhenov sequence within the central part of Western Siberia. Therefore it is proposed that they can be chosen as the possible Jurassic-Cretaceous boundary.

For comparison 34 samples of the surrounding host rocks, containing Type II kerogen were analyzed using all techniques applied on alginite rich samples. This allows identifying notable differences between Type I and Type II kerogen, regarding to sources and depositional environment of organic matter, kinetics and hydrocarbon potential including the amount of generated hydrocarbons.

Answers to the specific questions:

- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation

In my opinion, the scientific research presented in this dissertation is in line with modern trends in Geosciences and represents a scientific contribution to the field.

The thesis is well organized, written and illustrated. The interpretation is documented by data. It is clear and well done. Discussion is consistent and supported by numerous citations. The technical quality of thesis is good. Numerous up to date relevant laboratory techniques were applied and interpretation have been done on relative large sample set.

All objectives defined in current research project were achieved. However, the candidate, in the manner of experienced scientist, recognized certain new questions that arise from the obtained results, and made good guidelines for future research.

C) Significance of the candidate's results (The scientific significance of the results obtained and their compliance with the international level and current state of the art)

A total of 26 scientific publications have resulted from this research. Three of them are published as the original scientific papers in international journal, Geosciences, one in the national journal, Moscow University Geology Bulletin (that is reasonable, since main objective of the study was the Bazhenov Formation), and there is also 22 contributions to scientific conferences. Furthermore, candidate is coauthor of three side topic manuscripts published in Russian Oil and Gas Geology (two) and Nedropolzovanie (one).

D) Conclusion and recommendation

Based on all previous statements, it can be concluded that in the submitted dissertation entitled "LITHOLOGICAL AND GEOCHEMICAL STUDY OF TYPE I KEROGEN IN THE BAZHENOV FORMATION IN APPLICATION TO EXPLORATION AND PRODUCTION OF HYDROCARBONS", the candidate TIMUR BULATOV, successfully answered to all tasks defined in current research project.

I suggest very few technical corrections:

1. Abstract, fifth line from the top:

The sentence "The majority of petroleum source rocks for oil fields." should be deleted.

2. Title of sub-chapter 2.1.:

Replace source by sources.

3. Page 56, fourth line from the top:

Replace oh by of.

4. Page 72, the second paragraph:

The last sentence in this paragraph “The carbon isotope composition for the alginite-rich layers varies in the range from -31.1 to -31.9% , while for the host rocks $\delta^{13}\text{C}_{\text{org}}$ it varies from -30.5 to -31.9% .” should be deleted since it represents repetition of the previous sentence.

In my opinion, the scientific research presented in this dissertation is in line with modern trends in Geosciences and represents a scientific contribution to the field.

In this regard, with a great pleasure, I propose to the Thesis Committee to issue the authorization for the defense of the doctoral dissertation.

Kind regards,
Sincerely,

Ksenija Stojanović, PhD
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University of Belgrade
Faculty of Chemistry
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Serbia