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Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: Tatiana Bondarenko

PhD Program: Petroleum Engineering

Title of Thesis: EVALUATION OF HIGH-PRESSURE AIR INJECTION POTENTIAL FOR IN-SITU SYNTHETIC OIL GENERATION FROM OIL SHALE: BAZHENOV FORMATION

Supervisor: Prof. Alexey Cheremisin

Co-advisor:

Chair of PhD defense Jury: Prof. Alexei Buchachenko ***Email:*** *a.buchachenko@skoltech.ru*

Date of Thesis Defense: 03 December 2018

Name of the Reviewer: Prof. Alexei Buchachenko

X I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: Nov 21, 2018**

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

The Thesis submitted by Tatiana Bondarenko seeks for understanding and evaluation of the high-pressure air injection (HPAI) method application to the shales of Bazhenov formation. Overall, it is extremely intricate and elaborate problem with potentially very valuable solution. The main difficulties and challenges I see on the route towards the solution are (i) very complex chemical composition; (ii) complex structure of the rock matrix; (iii) lack of well-established standard methodology for laboratory testing; (iv) upscaling of laboratory tests to pilot projects. The work presented by Tatiana certainly makes significant contribution to three former issues and hints the way to address the latter. Diversity of these challenges combines chemical and physical properties of the shale, their thermal and chemical transformation upon HPAI conjugated to propagation of the multicomponent front in inhomogeneous matrix, dynamical changes of phase and viscosity, transformation of the matrix itself. The strong point of the whole research is the focus on chemistry as the core aspect. To my understanding, chemical transformation kinetics is indeed the cornerstone of the problem. Describing it properly, one can proceed step by step with remaining aspects building and verifying concepts and numerical models toward pilot project simulations. In addition, writing a good, logical and self-contained report on the topic in the form of PhD Thesis is by no less challenging task. I think Tatiana did her best here as well. I like the way of proving all the results by tables and illustration, and, especially, intermediate conclusions for each Section/Subsection that greatly facilitate the comprehension of diverse Thesis material.

Introductory Chapter 1 provides concise and transparent statement of the problem with logical formulation of the research goal and objectives. It may look a bit broad for PhD research, but concluding Chapter 5 convinces that each objective was at least tackled and discussed in the work.

Literature review presented in Chapter 2 exposes the current state of the art at multiple levels of complexity, from brief overview of in-situ retorting oil shale methods and the corresponding pilot projects implemented, to specific aspects of HPAI implementation and to relevant methods and results of laboratory studies and modeling.

Chapter 3, constituting the major part of the Thesis, describes the variety of laboratory tests performed on shale samples. Selection of the tests and methods is rationalized by the chemical focus: reacting components and products of the processes occurring during pyrolysis, oxidation and hydropyrolysis at relevant temperature and pressure ranges are the subjects. The reader gains a lot from introductory explanations of the purposes to undertake each test performed, as well as summarizing remarks. Not being a specialist in the petrochemical and oil sample testing, I nevertheless must admit the great variety of characterization methods used and novelty of many of them. I assume that some of the approaches developed in the work may rise in future to standard tests for Bazhenov-like formations.

In Chapter 4, the complex laboratory study of HPAI is performed using combustion tube experiment, the first one ever performed for Bazhenov formation samples. This part is essential step towards specific HPAI modeling as providing unique and invaluable information on the front propagation, temperature profile, gas composition and structural changes of the matrix

induced by various physico-chemical processes. In the same Chapter, new chemical kinetic model is suggested for chemical transformation of oil and kerogen matrix relevant to HPAI approach.

Concluding remarks constitute Chapter 5. All conclusions made looks qualitative, but one can trace out their quantitative aspects back through "partial" conclusions to each Chapter. All statements are justified well enough.

List of publications where the Thesis materials were presented is impressive and features all essential results of the thesis research. Three papers are published in the top Q1 title of the research field, J. Petrol. Sci. Eng.

Despite the efforts invested in logical presentation of the diverse and novel methodologies, great body of complimentary results and conjectures, the Thesis is not above the criticism. I would attest the density of *misprints, improper wordings and formatting inaccuracies* as above average. My main criticism is, however, related to chemical kinetic part, as one close to my own expertise.

First, it would be appropriate to *reproduce Arrhenius form of the rate constant temperature dependence for clarity and synchronize the units of activation energies (kcal/mol, kJ/mol, J/mol). So-called frequency factor is presented without units.*

Second, *the term "validation" used in Section 4.2 is too rigorous for the tests performed. Normally, "validation" refers to the tests performed for the few different, sometimes certified, datasets. "Assessment" better suits the results presented.*

Third, the *description of the "complex approach to building a kinetic model" is very brief.* The data used to develop the model are taken form laboratory tests presented in Chapter 3, while the description is combined with the comprehensive combustion tube experiment. Was the results of the latter used? *More clear explanations are required.* Also, it can be instructive *to draw perspectives for what should be done to real validation and improvement of the model.*

Fourth, the model, as it presented in section 4.2, lacks important connection with the previous materials. No comparison is made with the model by Shchekoldin presented in the literature review. Connections with the effective rate constants extracted by the author for pyrolysis, oxidation, and hydropyrolysis remain hidden. Why the latter process was not considered at all? *These points are worthy to be addressed*, as the model proposed is essential and valuable result of the thesis research.

These comments are not crucial for my very positive assessment of the Thesis as presenting original, novel and impactful methodology and results. PhD qualification of Tatiana herself is out of question.

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* ***(highlighted in italic for clarity)***
☐ *The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*