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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

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

Date of Thesis Defense: December 03, 2018

Name of the Reviewer:

I confirm the absence of any conflict of interest (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: 26-11-2018**

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

The thesis deals with the investigation of the most complex enhanced oil recovery techniques, the high-pressure air injection in oil shales for in-situ synthetic oil generation, during which oxidation, pyrolysis and hydropyrolysis of oil and organic matter coexist. The expected result of the thesis was evaluating the effectiveness of the promising enhanced oil recovery method. The dissertation include an Introduction (which describes the basics associated with the problem of air injection use, goal and objectives), the Literature Review and three chapters that include the experimental results and discussion. The Literature Review (second chapter) describes the basic of Air injection and mechanisms of air injection, describes methods of in-situ synthetic oil generation from oil shales. It is also contains a summary overview of the laboratory and numerical investigation of processes air injection in oil shales. To summarize review part of this thesis is worth to note that the Author has studied carefully research subject with critical view, and

used appropriate number of bibliography sources.

In the subsequent, third chapter, the author focuses on the author laboratory investigation of oil shale oxidation, pyrolysis, and hydropyrolysis. Firstly, the strategy of investigation described, than the data on thermal analysis and kinetic studies of pyrolysis and oxidation are presented. The next step of the investigation was focused on the results of High-pressure ramped temperature oxidation (HPRTO) experiments. The data were compared with the experiments on High-pressure ramped temperature cracking (HPRTC) without oxygen. Also the results of hydropyrolisis (pyrolysis in the presence of water) were presented. The end of the chapter is dedicated to comparison of three processes: pyrolysis, oxidation, and hydropyrolysis.

The next part of the thesis focused on the results of laboratory investigation of high-pressure air injection in oil shale and development of complex approach of building a formal kinetic modelfor practical application.

In the final section the general conclusions of the work are summarized. The thesis is prepared in good editing standard. The material are carefully prepared and clearly presented. The language errors and inaccuracies are relatively rare.

The study was made using samples from the largest Russian shale formation - Bazhenov Formation. The use of traditional methods of oil recovery for this formation is noneffective and questionable therefore searching a suitable technology is a priority, especially when conventional oil reserves decrease. Also due to the complex chemical structure of kerogen, low permeability of shales of Bazhenov Formation and a limited information about the oxidation processes in this type of formation the air injection has not been extensively used for oil recovery. So evaluation of the effectiveness of the this promising enhanced oil recovery method for oil shale of Bazhenov formation is needed to show advantages and risks associated with air injection in oil shales.

The thesis of Tatyana Bondarenko is devoted to investigations of number of in situ processes in oil shales with gaseous and liquid hydrocarbons formation during air injection in model conditions using complex methodology. Several important issues affecting oxidation in pores of shales, pyrolisys and hydropyrlysis are addressed with the focus on the relationship between the process conditions – kerogene conversion, yield and selectivity of the processes. Thus, this thesis addresses the highly relevant and vital areas of current research in the area of recovery oil from oil shales. The results of this study allow evaluating the a high-pressure air injection potential in generating synthetic oil and point out the necessity of a thorough investigation of right injection regimes for utilize this method.

All experiments are well arranged and measurements techniques and methods are correctly applied. The methods of investigation include experiments on the pyrolysis using differential scanning calorimetry (PDSC), accelerating rate calorimetry (ARC) and ramped temperature oxidation (RTO); Rock-Eval open-system pyrolysis method, High-pressure ramped temperature cracking, on the oxidation pyrolisys study using High-pressure ramped temperature oxidation (HPRTO) of non-extracted core without oil flood. Also the hydropyrolisis in in a high-pressure vessel were performed. So, new experimental methodology for testing HPAI in oil shales based on an investigation of kerogen thermal decomposition, oxidation and hydropyrolysis processes that coexist during air injection in oil shale was designed and tested. In order to assess the potential of high-pressure air injection in the Bazhenov kerogen-bearing rocks, a laboratory experiment was conducted in the combustion tube (hereinafter - CT). Synthetic oil composition and geochemical parameters of oil was studied as standard methods as well as new technic as GCxGC-mass spectrometry. The methods represent accurate studies and lead to plausible and internally consistent

conclusions about the kerogene conversion and products yields. In general, the presented results seem to be reliable and well documented, although, as always in cutting edge research, the interpretation and discussion, especially concerning the chemistry of processes, can be extended and more in-depth. This is, however, the common inherent feature of all the experimental work in the geochemistry and upstream area.

The contribution presented in thesis adds considerable novelty into understanding of regularities of the processes proceed during air injection in oil shale . The following new observations and regularities reported by Author can be highlighted:

due to the oxidation of shale samples, 23.7wt% of organic matter that can be pyrolyzed into hydrocarbons were recovered, while due to the pyrolysis 79.6wt% were collected. Hydropyrolysis treatment of consolidated samples resulted in 31wt% recovery, which might be higher if the time of treatment is decreased and generated hydrocarbons are forced from the sample by pressure-down. Synthetic oil samples from HPRTO (oxidation), HPRTC (pyrolysis) and open-system hydropyrolysis experiments were more mature than extract from the core before the exposure.

-cyclic wet combustion was proposed for optimizing coking process and synthetic oil extraction and lowering air requirement.

However, the are some remarks which occurred to me and need to be explained and concerning chemistry of the processes

- During oxidation experiments in tube the high concentrations of hydrogen sulfide and methane in gas phase were achieved. The explanation f this facts from the chemical point of view is needed.
- Please clarify the differences in the composition of liquid products during the kerogen thermal decomposition, oxidation and hydropyrolysis processes. what the difference in the quantity of naphthenic hydrocarbons and olefins in this processes.
- Why in model in chapter 4 the hydrocarbon gases are not include?

These shortcomings do not substantially affect the quality of the work and do not disqualify it in any way.

To sum up, the dissertation thesis represents high level scientific work. It seems to be an interesting topic for scientists working on oil production. The thesis is very interesting with very high practical value, and is hence in my opinion worth grade. . Unique laboratory experiments eliminated the gaps associated with poor knowledge of the oxidation processes in oil shales and made a significant step forward in Bazhenov Formation development. I would like to emphasize that the studies concern a broad area of research and their main value consists in the detailed description of the obtained results and discussion of advantages and risks associated with air injection in oil shales. The research it describes is of the international standard and the papers published in commonly known and highly ranked scientific journals in petroleum engineering area. This thesis is ready to be defended orally and certainly meets the requirements laid down for the PhD degree in petroleum engineering.

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*