Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Tatiana Bondarenko

Ph.D. 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 Ph.D. defense Jury: Prof. Alexei Buchachenko   ***Email***: *a.buchachenko@skoltech.ru*

Date of Thesis Defense: December 03, 2018

The thesis document includes the following changes in answer to the external review process.

Dear Reviewers,

I would like to thank you for all the comments which were invaluable in improving the thesis. I also consider all the comments in my future research. Below please find the responses.

Yours sincerely,

Tatiana Bondarenko

Reviewer: Prof. Alexei Buchachenko

Comment: *"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."*

Response: The units of activation energies were synchronized. Each value has J/mol unit now. However, activation energies distribution is usually illustrated in kcal/mol in literature for basin modeling, and it is convenient for readers to compare numbers.

Page 67, paragraph 3, line 13-15: I added the reference to the previous study to compare the results obtained. "Notably, the values obtained are consistent with those of *Goncharov et al. (2016)* who analyzed a lot of Bazhenov shale samples from different oil fields."

Nevertheless, I added the most important values in J/mol in parentheses throughout the thesis, for example:

Page 65, paragraph 2, line 10, line 8: 1 kcal/mole (4,184 J/mol)

Page 66, paragraph 2, line 2: 1 kcal/mole (4,184 J/mol)

Page 67, paragraph 1, line 1: 1 kcal/mole (4,184 J/mol)

Page 67, paragraph 2, line 5: 54 kcal/mol (225,936 J/mol)

Also, I added units for frequency factor (1/s).

Page 67, paragraph 4: I added the following the equation for representation of activation energies distribution:

$$Rate = A \cdot (e^{-\frac{E_{a1}}{RT}} \cdot S_1 + e^{-\frac{E_{a2}}{RT}} \cdot S_2 + \cdots + e^{-\frac{E_{an}}{RT}} \cdot S_n)$$

where A – frequency factor ($2 \cdot 10^{14}$ s^{-1}), S_n – relative proportion of each group of reacting species, E_{an} – activation energy for each group of species.

Page 74, paragraph 2, line 1: And added Arrhenius equation for the reference:

$$k_n = A_n \cdot e^{-\frac{E_{an}}{RT}}$$

where k_n is the rate constant of reaction at the nth peak, A_n is the frequency factor for the reaction at the nth peak (1/s), E_{an} is the activation energy for the reaction at the nth peak (J/mol), R is the universal gas constant (8.314 J/(mol·K), T is the absolute temperature (K).

Comment: *"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."*

Response: I agree with this comment. Therefore, I changed this term into just history matching of the experiments. The results presented in this work represent a kinetic model development and tuning. I will more elaborate on that in the response on the next comment.

Comment: *"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. Were 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."*

Response: Thank for this observation. I decided to move this section to the separate Chapter 5 because this topic should be described in more details. And also, the kinetic model does not quite relate to the results of combustion tube test. Kinetic model was developed and tuned based on the results obtained in Chapter 3, namely PDSC and RTO tests results. Validation must be conducted on HPRTO and combustion tube tests using the same core material.

Chapter 5 involves description of aspects of air injection kinetic model development; complex nature of oil shale and oxygen and pyrolysis behavior of its components; choice of pseudo-components and schematic representation of the reactions; results of history matching of conducted experiments and proposed kinetic model. In addition, I added   recommendations   for multistage development and validation of HPAI kinetic model for oil shales, in order to "*draw*

perspectives for what should be done to real validation and improvement of the model." Figure 136 "Proposed schematics of multistage development and validation of HPAI kinetic model for oil shale" was added for illustration.

Figure 130 "Comparison of two DSC curves of isolated kerogen and oil shale sample saturated with oil" and Figure 131 "Comparison of two DSC curves of oil shale samples with different maturity" were added to illustrate the idea behind the selection of pseudo-components.

Comment: *"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."*

Response:

Page 163-165: I added the results of activation energy distributions for samples from different combustion tube zones.

Comment: *"I would attest the density of misprints, improper wording, and formatting inaccuracies as above average."*

Response: I added editorial changes and synchronized formatting throughout the text.

Page xiv, paragraph 2, line 5: added an abbreviation CMG (Computer Modeling Group)

Page xv, paragraph 1, line 13: added an abbreviation TC (thermocouple)

Page 12, Table 1: units of oil density were changed into kg/m^3.

The following wide tables and big figures were Illustrated on pages with a landscape orientation:

Table 1, 10, 18, 23, 34, 35, 36, 37, 38, 49, 50, Figure 100, 136.

Page 66, paragraph 2, line 4: I changed "Table 8**Error! Reference source not found.** lists E_a distributions that were calculated applying two described approaches" into "**Error! Reference source not found.** lists kinetic parameters calculated".

Reviewer: Prof. S.M. Farouq-Ali

Comment: *"The four combustion tube experiments are not quite HPAI. These are really in-situ combustion studies where shale samples are embedded in a porous pack, saturated with oil. It is not clear what was the porous medium nor what was the oil. The temperatures are much higher than those expected in HPAI."*

Response: I agree with this comment. It is not quite what was expected during HPAI. It is known that peak temperatures during HPAI are usually around 300℃, whereas peak temperatures during in-situ combustion are around 500-600℃. We decided to call it HPAI because 1. the reservoir

pressure is higher than 4000 psi, 2. shale oil is very light oil (more than 30°API gravity oil); 3. reservoir temperature is high (around 100℃). Therefore, this process starts like light oil burning, but then resins and asphaltenes and kerogen burning takes place, which causes high temperatures. Oil shale is a hybrid system. I added the schematics from the literature to illustrate the complexity (Figure 28, Section 3.1, page 42). In my view, this method should be called just air injection. And it is still a debate on how to call it.

Comment: "*The results of the experiments (these and those mentioned previously) would depend on the on the grain size resulting from the crushed shale. There should be a discussion of these limitations.*"

Response: I agree with this comment. It would depend. In this work, HPRTO and combustion tube experiments were conducted on 0.1-1 mm grain size to create lower permeability. For surface retorting, researchers point to some numbers of the critical size for oil shale samples for heating, such as 15 mm. One of the reasons for this is to prevent coking of generated synthetic oil on the way out from the sample and, thus, to maximize the extraction.

Comment: "*The question of whether it is possible to carry out HPAI in virgin shale with a permeability well below 1 mD remain unaddressed. If air injection can be achieved at a high enough rate, then the next question is what is the range of temperatures and whether these are high enough to generate synthetic oil, as seen in the basic studies (TGA, RTO, etc.)*".

Response: Thank you for your comment. In the literature review, I describe field pilots conducted by RITEK oil company, where they inject air in permeable part of virgin shale. It can be seen from the coring analysis from the observation well and gas analysis from the production well that burning occurred. But the question of vertical sweep efficiency remains unclear. Pyrolysis of kerogen starts at 300°C. Therefore, we tend to reach these temperatures by air injection.

Comment: "*…in several cases, second-hand papers are referred to instead of the original works. One of the key oil shale researchers (Kyung Jae Lee) is not mentioned at all.*"

Response: Thank you for the reference. I studied her impactful thesis and added a reference to her recent paper in SPE journal. The author works on the development of a simulator that models oil shale in-situ upgrading processes. The simulator was validated through matching production data from Shell ICP field pilot (Green River Formation). The kinetic model she used was Shell ICP pyrolysis kinetic model. In one of her papers, she studied the effect of fracture network permeability on liquid hydrocarbons production. It was shown that low permeability of the fracture caused the higher amount of cracked synthetic oil. Great work! This result confirms the ideas how important to produce generated synthetic oil before the cracking process causes gas and coke production.

I added the reference: Page 30, paragraph 2, line 1-6.

Reviewer: Prof. Anton Maximov

Comment: "*During oxidation experiments in tube the high concentrations hydrogen sulfide and methane in gas phase were achieved. The explanation of these facts from the chemical point of view is needed.*"

Response: High concentrations of methane and hydrogen sulfide were observed. It is known that methane is the product of oil cracking, kerogen pyrolysis and secondary cracking of generated products. Hydrogen sulfide is also a product of oil cracking and kerogen pyrolysis. The existence of these gases in evolved gases composition indicates kerogen conversion ahead of the front. Pyrite may also contribute to the hydrogen sulfide generation. Core elemental analysis results revealed sulfur content decrease, which explains the high concentration of H_2S. This explanation was added in gas analysis section 4.5 after Figure 105.

Comment: "*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?*"

Response: It should be noted that samples analyzed by GC×GC-MS are different in terms of preparation. Due to the production of hard-to-break emulsion and a small amount of fluids in HPRTO test, oil sample was obtained by mixing emulsion with chloroform. Therefore, extract of oil sample obtained in HPRTO was analyzed. In HPRTC and SCW extraction tests oil samples were analyzed, which makes it very difficult to compare results from different tests (extracts and oil samples). However, if we compare pyrolysis and hydropyrolysis results, we notice higher olefins and naphthenes content in pyrolysis products. It can be explained that olefins reacted with water.

Comment: "*Why in chapter 4 the hydrocarbon gases are not included?*"

Response: I must accept this fact that the absence of hydrocarbon gases in the proposed reactions scheme is a noticeable limitation. It was my first attempt to develop reactions. While proposing pseudo-components, one must keep in mind that calculation time in numerical simulation grows with the addition of new components. Therefore, it is essential to find the optimal number that can truly represent oxidation and pyrolysis behavior of oil shale. The reason of omitting hydrocarbon gases as a pseudo-component is just simplification of the model.

Reviewer: Prof. Yuri Popov

Comment: "*Unfortunately, statistical processing of the experimental cannot be estimated as comprehensive on some cases that influence on the reliability of few conclusions.*"

Response: Unfortunately, detailed statistical processing of the porosity and permeability changes due to organic content conversion requires conducting of series of high-pressure and high-temperature experiments. I plotted permeability, porosity and thermal properties changes against temperature/mass loss without trend lines at Figure 128 (page 170), Figure 127 (page 169) and Figure 126 (page 167), the raw data illustration remained as it. I am about to continue this research

in the future, which, I hope, helps me to see the trends we cannot see now. Also, these illustrations make it convenient for other researchers to analyze the results.

Minor revisions recommended during formal thesis defense:

- Thesis text was corrected according to comments and marks in a printed version by Prof. Farouq-Ali.

- Thesis text was corrected according to comments and marks in a printed version by Prof. Mehta.

- Contribution to knowledge paragraph was added in Chapter 6, Section 6.3 (p. 197).

- Conclusions were added in Chapter 6, Section 6.2 (p.196).

- Recommendations to the further investigation were added in Chapter 6, Section 6.4 (p.198).

- Acknowledgments section was expanded. The supervisor is identified by full name.

- Spelling and formatting mistakes (Table of contents, page numbers, etc.) were corrected.