Skoltech
Skolkovo Institute of Science and Technology

Thesis Changes Log

Name of Candidate: Anastasia Gabova

PhD Program: Petroleum Engineering

Title of Thesis: Experimental investigations of thermal properties of unconventional hydrocarbon reservoirs at formation temperatures

Supervisor: Prof. Yuri Popov

Co-supervisor: Dr. Evgeny Chekhonin

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

Dear Jury Members,

I would like to express my gratitude for your comments and suggestions. I appreciate your participation in the thesis review process that significantly improved the quality of the thesis. I addressed all questions and comments and made corresponding changes in the thesis.

Reviewer: Dr. Andrea Förster

Comment 1:
The DTC-300 data show different thermal conductivity decrease in the temperature range between 30°C and 300°C depending on rock type and degree of organic matter content. The findings are compared to those from other sedimentary rock. In this regard the data are unique. However, the large data set obviously was investigated under dry conditions. It would have been thereby of interest to what degree different porosity would affect the temperature dependence of thermal conductivity.

Response:
Thanks for the interesting comment! The matter is that the topic of the thesis is related to unconventional reservoir rocks that have very low porosity (2-3%). Such a low range of porosity does not let make a qualitative analysis of porosity influence on the temperature dependence of thermal conductivity. However, this topic is still actual and can be provided in future work.

Comment 2:
The thesis could have been improved by citing just full papers and not, in addition, published abstracts. This would strengthen the scientific merit of the thesis. Citation of original literature would be advantageous and would excel over the citation of secondary sources (overview/review papers). This would better show the candidate's detailed knowledge of original sources and a thorough knowledge of the field.

Response:
Thank you for the recommendation! Citing of full papers from journals was added in references.

Comment 3:
Improvements that could be made concern chapter 1 and chapter 2 with respect to content and organization. For example, the content of section 1.1 should have been better brought to the point, which is the link to solutions of problems in oil and gas science. The chapter also should have included the state of the art from international literature on temperature relations of thermal conductivity and volumetric heat capacity for sedimentary rock in general.
Response:
Thanks for the recommendation! The state of the art for temperature relations of thermal conductivity and heat capacity for sedimentary rocks were added to section 1.1.

Comment 4:
Statements on known relations are made late in the thesis (section 4.1.1 and section 4.4.4) and should rather be part of the introduction before they are compared to those from shales/mudstones etc. (this study).
Response:
The statements of relations in sections 4.1.1 and 4.4.4 were made on the basis of experiments made at Skoltech, that's why these relations are included in the part of the experimental study, not in the introduction part.

Comment 5:
The flaws and shortcomings of the different measurement techniques applied to this matter should have been described. This would also concern results from the LFA technique widely used to determine thermal conductivity (as function of temperature) from thermal diffusivity. This is important, as in the thesis work only one specific technique (the DTC-300) was employed for temperature-dependent thermal conductivity measurements.
Response:
Thanks for the reasonable recommendation! The descriptions and shortcomings of different measurements techniques (including LFA) were added to the beginning of section 2.1.

Comment 6:
Unfortunately, in the citations of work by Wang et al. (2018) and Yu et al. (2015) (section 2.1) the candidate claims that these authors have used the Netzsch LFA technique of thermal conductivity measurement. This is misleading as this technique measures the thermal diffusivity of materials.
Response:
Thanks for your remark! To avoid misunderstanding the word "measurement" was changed to "calculation". Parameters that were used for thermal conductivity calculation (thermal diffusivity, density, specific heat capacity) were also mentioned in the text (Section 2.1).

Comment 7:
Table 1 contains "Comparator" as a measurement technique. Some explanation is needed.
Response:
Thanks for the note! The corresponding explanation was added to Section 2.1: "Thermal conductivity was measured using a thermal comparator technique, which compares the ability of the test sample to transport heat with that of reference material to conduct the same amount of heat".

Comment 8:
Figure 8 (section 3.1.1.3) is not mentioned in text. Section 3.1.2 should be renamed to "New measuring methodology for thermal conductivity by combining DTC-300 results with those of TCS". Otherwise one would think of a new machinery for those measurements. Same for section 3.1.3 "Modification of DTC-300 results".

Response:
Thank you! Figure 8 was removed from the text; all information was added to Table 4. The titles of sections 3.1.2 and 3.1.3 were changed according to your recommendations.

Comment 9:
The reference list (page 121) needs editing. References have to be brought into the right order by year. The year of publication shall consistently appear following the name of authors.
Response:
Thanks for the recommendation! References were edited and the year of publications goes after the names of authors now. As for the right order, according to Skoltech's thesis template, all publications should be in the alphabetic order in the reference list.

Comment 10:
Minor grammatical mistakes need to be taken care of.
Response: Thanks for your comment! Minor grammatical mistakes were excluded.

Reviewer: Prof. Sudarshan (Raj) Mehta

Comment 1:
Change number of pages starting with ii,etc. Page 1 should start with Introduction.
Response: Thanks for the comment! The number of pages was changed.

Comment 2:
Put publications and abstracts in the order starting from last years.
Response: Thanks for your remark! The publications and abstracts were put in the order from last years.

Comment 3:
Put a list of symbols and abbreviations after the list of tables.
Response: Thanks for your recommendation! Lists of symbols and abbreviations were added after the list of tables.

Comment 4:
Clarify diameter's change in Figure 10.
Response: Thanks for the note! The correctness for samples diameter's change was provided by the formula (5) (section 3.1.3.2).

Comment 5:
Why is the density of samples in Table 24 so low?
Response: Thanks for the question! Low density values for rock samples from Table 24 (Table 20 in the revised thesis) are related to high total organic content (TOC) in such samples, as density of samples depends on TOC (see Figure 30b). Corresponding clarification was added to the text (section 4.3.2).

Comment 6:
Please, add recommendations on future work in conclusions.
Response: Thanks for the recommendation! Recommendations for future work were added in Section 5.2.

Reviewer: Prof. Ilmutdin Abdulagatov

Comment 1:
In Table 3, where summary of the reported heat capacity data presented, the uncertainties of the method of measurements and data sources (References) are missing, should be provided.
Response: Thanks for the recommendation! References and uncertainties of the method of measurements were added to Table 3.

Comment 2:
Page 36, Lines 5 and 6 from the top " • measurement accuracy (systematic error): from ± 3 to ± 8% (depends on the thermal resistance of studied sample);" I think the best way to write "uncertainty of the measurements is within from (3 to 8) % ..." , but not "measurement accuracy (systematic error, etc.) ....." Otherwise, what mean the "accuracy" is unclear.
Response: Thank you for the remark! The sentence in line 5, page 36 (page 24 in revised manuscript) was changed to "uncertainty of the measurements is within from (3 to 8) %".

Comment 3:
Table 4. "Accuracy of thermal conductivity measurements of standard samples on DTC-300 instrument at room temperature obtained with TCS and DTC-300 instrument measurements". I think title of the Table 4 should be corrected. Actually this is not accuracy, but is comparison of the measured thermal conductivities of the reference samples using contact (divided-bar, DTC-300) and contact-free (TCS) techniques. Also, the Table 4 should include the reference (standard) thermal conductivity values for these samples accepted by NIST (Internationally accepted values of the thermal conductivities for reference materials). Otherwise, both values (TCS and DTC-300 results) may appear to be incorrect. Therefore, comparison with the standard values of thermal conductivity for these samples are required.
Response: Thanks for your comment! Table 4 was corrected, certified values of thermal conductivity including materials accepted by NIST were mentioned with references. Formulas for accuracy and precision of measurements on DTC-300 were added to the text in section 3.1.1.2.

Comment 4:
Too many the same type of Figures, should be some of them combined or some of them deleted, for example, Figs. 1 to 7. Also, the Figs. 1 to 7 captions should be slightly corrected, please do not use word "accuracy" and "precision" or please provide clearly the definition what means "accuracy" or "precision", i.e., the author should clarify the difference between the terminologies "accuracy", "precision" and "uncertainty" used in the Thesis.
Response: Thanks for the recommendation! Figures 2 to 7 were combined in one – Figure 2 (in the revised manuscript). Definitions of accuracy and precision were added to section 3.1.1.2.

Comment 5:
The validation of the reliability, accuracy, and the correct operation of the measuring apparatus should be provided by using the reference material with well-known thermal conductivity (for example, NIST standard).
Response: Thanks for the comment! The validation of accuracy of DTC-300 apparatus was provided by using certified reference standards with literature references (Table 4).

Comment 6:
Eq. (15). According to Eq. (15) , $\rho(T)= \rho_0/(1+\beta T)$, ρ_0 is the density $\rho(T=0)= \rho_0$ at T=0, but not at 25 °C. Should be corrected, may be $\rho(T)= \rho_0/[1+\beta(T-25)]$?
Response: Thanks for your recommendation! Eq.15 was changed to $\rho(T)= \rho_0/[1+\beta(T-25)]$.

***Comment** 7*:

When oil containing reservoir is heated from room to high temperatures, two effects should be considered. The first is the effect of temperature itself, which leads to increased heat capacity to the maximum possible value of 3R/M (high temperature limit, classical value, Dulong and Petit law for all solid materials). Second is the change in composition of the heavy oil in the pores due to chemical reaction (thermal decomposition). Also, at low temperatures around 380 K heat capacity C_P should exhibit some anomaly due to dehydration, i.e., around 373 K the residual pore water evaporation increases the empty space in the pores. At high temperatures, the heavy oil in the pores undergo irreversible changes of components associated with the release of volatile matter (VM), devolatilization. Usually gases (the main constituents of VM are CH_4, C_2H_6, CO, CO_2, H_2, H_2S, and NH_3) released in the experiment during the heating of the oil containing rocks sample at high temperatures. The effect of various physical- chemical processes, such as thermal decomposition of heavy pore oil (chemical reaction), dehydration, and mass variations, occurred in the rock sample during heating in distinct temperature ranges, on the temperature behavior of heat –capacity and thermal conductivity should be considered. These processes occurring in the pores lead to dramatically changes of the heat capacity and other thermophysical properties behavior of the rock sample. In solids in the absence of a phase transition (dry rock sample), the heat- capacity increases smoothly and approaches an asymptote 3R/M as all possible vibrations are excited (Einstein's theory). Any deviation from the smooth behavior of C_P (from a prediction by Einstein's theory) is the result of exothermic or endothermic reactions occurring in the sample under thermal stress. In the Thesis the author considered only mechanical changes (cracks formation) in the rock sample structure and their effect on the thermal conductivity during heating to high temperature. The author should be briefly mentioned about these effects.

Response: Thanks for your comment! Corresponding review of physical-chemical processes during heating was added to section 2.5.

Comment 8:

According to the study by Waples and Waples (2004) the great majority of the heat capacities of rocks and minerals at room temperature are between (0.6 to 0.9) $kJ \cdot kg^{-1} \cdot K^{-1}$. The value of $(\rho C)^{-1}$ is defined the slope of thermal diffusivity (a) versus thermal conductivity (λ) plot, $a = (\rho C)^{-1} \lambda$, therefore, very important and physically meaningful parameter (characteristics). Waples and Waples (2004) reported the correlation for thermal capacity of minerals at 293.15 K as $(\rho C)^{-1} = 0.9744\exp(-0.2697\rho)$. The author should use the relation to check and confirm the reliability and accuracy of the measured heat capacity data.

Comment 9:

The heat capacity equation should satisfy the high temperature limit predicted by the theory of solid state, therefore, the general form of temperature- dependence of the heat capacity rocks can be represented as (Berman and Brown, 1985)

$$C_P(T)=3R+\sum k_i T^{-i/2}. \quad (2)$$

Berman and Brown (1985) studied various combinations of the different terms in Eq. (2) and constrains to the sign of the parameters k_i in order to qualitatively correctly reproduce low and high temperature behavior of $C_P(T)$. For example, $k_1<0$ and $k_2<0$ should be negative to correctly represent the high temperature behavior of $C_P(T)$. Whittington et al. (2009) derived the following correlation equation to calculate the heat capacity of rock-forming minerals

$$C_P(T)=C_0+C_1T+C_2T^{-2}$$

with different fitting parameters for various temperature ranges (below and above 846 K). Pertermann et al. (2006, 2008) proposed various semiempirical correlation equations for practical applications for certain temperature ranges.

$$C_P(T)=C_0+C_1T+C_2T^{-1/2}+C_3T^{-2}+C_4T^2$$

The polynomial Maier-Kelley functions was successfully used by Richet et al. (1991, 2001)

$C_P(T)=C_0+C_1T+C_2T^{-2}+C_3T^{-0.5}$,

$C_P(T)=C_0+C_1T^{-1}+C_2T^{-2}$.

$C_P(T)=C_0+C_1 lnT+C_2T^{-1}+C_3T^{-2}+C_4T^{-3}$.

have been applied for heat capacity.

Nabelek et al. (2010) and Miao et al. (2014) proposed another form of the polynomial equation

$C_P(T)=C_0+C_1T+C_2T^2+C_3T^{-1}+C_4T^{-2}$

has been used to describe the temperature dependency of the measured heat capacities of minerals and rocks.

One of the weakness parts of the work is the interpretation of the experimental results on the pure empirical level. The author did not use theoretically based models to represent and interpret the measured thermal conductivity and heat capacity data, for example, well-known DHO (damped harmonic oscillation) model for thermal conductivity, see, for example (Geisting et al. 2002, 2004) and Einstein and Debye's theory of solid-state heat capacity, lattice vibration excitation (lattice vibration spectrum).

$$C_P=3\frac{R}{M}\sum C_i x_i^2 \frac{e^{x_i}}{(1-e^{x_i})^2},$$

where $x_i = \Theta_{Ei}/T$, Θ_{Ei} (i=1, N) are the characteristic Einstein's temperatures corresponding to i-type of vibrating mode, N is number of vibrating modes (N=2 is Merrick's model), C_i are the adjustable parameters which define the contribution of each type of vibrating mode to the total measured heat capacity. The experimentally observed temperature behavior of the thermal-diffusivity and thermal conductivity of rocks and rock forming minerals is in good consistent with the damped DHO model of the phonon gas, although, initially the model was derived for crystalline solids (see Hofmeister et al.). Thus, the author of the Thesis should review available correlation model for temperature dependence of the heat capacity and used theoretically based models. This is important, because theoretically based correlations have a reliable predictive and extrapolation properties than pure empirical correlations.

Response to Comments 8-9: Thanks for your comments and recommendations! Since there are a lot of models for heat capacity of minerals such the comparison with known relations should be done thoroughly and separately. Thesis topic is related to experimental results for organic-rich rocks, firstly it was essential to understand the behaviour of heat capacity for such rocks and if it is different from other sedimentary rocks. Also, behavior of heat capacity for organic matter should be firstly analyzed as it has influence on heat capacity of the whole rock sample. The preparation of samples consisted only of organic matter is enough difficult workflow and requires new methodologies (see section 4.2.2, measurements on kerogen sample). However, such work can be provided in the future. The necessity in comparison of experimental results with modeling was mentioned in recommendations (section 5.2). Thanks!

Comment 10:

Chapter 3. Research methods (sound not so good). The title should be changed to, for example, "Experimental".

Response: Thanks for the remark! The title of Chapter 3 was changed to "Experimental".

Comment 11:

Too many subsections, for example, 3.1.1.1 "Characteristics of DTC-300 instrument "or 3.1.1.2 "Thermal conductivity measurements procedure using a DTC-300 instrument". Some sections (for example 4.2.3, or 4.2.4) too short (couple of sentences and Table, very little text without discussion or interpretation of the results). Some of them should be combined or extended.

Response: Thanks for your comment! Subsections 3.1.1.1 was deleted and included in subsection 3.1.1.2. Section 4.2.3 was deleted and included in subsection 4.2.2.

Comment 12:

In the Thesis text I found some incorrect use of the scientific terminologies, for example: "thermal conductivity", I would say "effective thermal conductivity" of rock materials. The terminology "thermal conductivity" cannot be applied for rock materials which are consist of different phases of a material or different materials, i.e., "thermal conductivity" applicable only for single crystalline homogenization materials, according Fourier's law. Moreover, in some cases (some parts of the Thesis) the author uses the "effective thermal conductivity" terminology. Should be explained, although, I think that in the present work we have only "effective thermal conductivity" of rock materials.

Response: Thanks for the recommendation! For rock materials terminology was changed to "effective thermal conductivity".

Comment 13:

I am recommending to change "non-contact" to "contact- free", although the meaning is the same. This is commonly accepted terminology.

Response: Thank you for the recommendation! The terminology "non-contact" was changed to "contact- free".

Comment 14:

The heat capacity should be clarified as isobaric heat capacity and denoted as C_P, but not as "c" or "C= cp". The author in the some part of the Theses using C_P or C to express the same meaning properties. Should be clarified. This sis little bit confusing the readers.

Response: Thanks for the recommendation! The symbol for specific heat capacity was changed to C_p.

Comment 15:

Unfortunately, one thing is missed in the review part of the Thesis, namely, the author did not mentioned in the Thesis some very important and useful publications closely related with the subject of the Thesis. For example, the papers reported by Hofmaister and her research team (see below attached References) were missed. In these publications the authors detailed studied the thermal diffusivity, thermal conductivity, and heat capacity of rocks and rock forming materials and the effect of contact resistance on the measured values of thermal conductivity. Also, in these publications the authors detailed study (experiment and theory) of the temperature dependency of the main thermal properties (thermal diffusivity, thermal conductivity, and heat capacity) of rocks at high temperatures (see Refs.). In particular, Hofmeister et al. (2007) showed that contact resistance with heaters and thermocouples, and possibly among constituent grains, leads to systematic and substantial underestimation of lattice thermal conductivity of 20 %. They also used contact-free technique (Laser Flash Method) to measure of the thermal conductivity at high temperatures (up to 1000 °C).

Response: Thanks for your comment! The matter is that the topic of the thesis is related particularly to unconventional hydrocarbon reservoir rocks. So, the literature review was mainly done for organic-rich rocks and for shales. However, text and reference to the work of Hofmeister et al. (2007) were also added to section 1.1.

Comment 16:

Page 49, right after Eq. (6). "....diffusivity of the material at temperature T correspondingly", should be ".... diffusivity of the material at given temperature of T, respectively". Editing: Grammar needs to be checked carefully.

Response: Thanks for the remark! The sentence was changed to ".... diffusivity of the material at given temperature of T, respectively".

Comment 17:
Too many Figures (around 60), some of them are not informative (can be deleted), other ones are the same type and can be combined. I am strongly recommending to avoid including redundant figures and tables, or using figures and tables where it would be better to just include the information in the text (e.g. where there is not enough data for a table or figure).
Response: Thank you for the recommendation! Figures 1-7 was combined in Figure 2 (see the revised manuscript). Tables 8, 37, 38, 39 were deleted and information from them was added to the text.

Comment 18:
Tables 10, 22, 23,26 should be deleted, this information should be moved to the text, too many small and not informative Tables.
Response: Thanks for the recommendation! Tables 10, 22, 23, 26 were deleted from the text, information was moved to the text.

Comment 19:
Discussion of the experimental results in some cases is very little (for example, sec. 4.2.5), just provided the experimental data without deeply interpretation and discussion. Should be improved the discussion or interpretation of the data or combined with other sections.
Response: Thanks for the recommendation! Deeply interpretation of section 4.2.5 is absent due to small amount of experimental data on the thermal conductivity of kerogen. Only one sample was investigated as the procedure for kerogen sample preparation is rather difficult, which is also mentioned in this section. To avoid misunderstanding, section 4.2.5 was included in 4.2.2.

Comment 20:
In Figs. 14,15,17,19, 21-23, and 30 meaning of the $\lambda(T_0)$ should be defined in the figure captions. Also, since, most of these figures the same type, then should be combined (see also table 19, the same problem). The values of $\lambda(T_0)$ should be provided, otherwise, it is impossible to reproduce the data using the correlations inserted to the figures.
Response: Thanks for your suggestion! Meanings of the $\lambda(T_0)$ are given in Tables 10-16 (see the revised manuscript). Corresponding clarifications were added to figure captions. The similar equations in Table 19 (Table 17 in the revised manuscript) were combined. The figures are the same type but for different oil fields. To avoid misunderstanding, figures were divided by particular oil fields.

Comment 21:
Figure 47. "The percentage of volumetric heat capacity increasing relatively to initial volumetric heat capacity (T = 25 °C) for Bazhenov formation rocks." Should be corrected. This is not percentage, just ratio of $C_P(T)/C_P(T_0)$, also "T=25 °C" should be changed to "T_0=25 °C".
Response: Thanks for the recommendation! The caption text for Figure 47 (Figure 42 in the revised manuscript) was changed to "The ratio of volumetric heat capacity at elevated temperatures to initial volumetric heat capacity (T_0 = 25 °C) for Bazhenov formation rocks".

Comment 22:
The same equation has been used in different parts of the Theses in different form. For example, eq. (20).
Response: Thank you for the remark! The equations (20)-(22) were deleted from the text as they repeat equations (16)-(18).

Comment 23:
In Fig. 51 presented number of curves of C_P versus of T, what means inserted correlation equation for C_P? Should be clarified. The same problem in Fig. 52.

Response: Correlated equations in Figures 51-52 (Figures 46-47 in the revised thesis) show dependence of average volumetric heat capacity of the matrix overall measured samples on temperature (dashed lines). The corresponding clarification is presented in figures captions.

Comment 24:
Table 39. Please change the numbers presentation, the commas should be changed to dots.
Response: Thanks for your remark! The commas in all tables were changed to dots. Table 39 was deleted from the text and information was moved to the text.

Comment 25:
Page 116. The sentence "Based on the results of comparing the results of determining the dependences of the thermal conductivity of the matrix on temperature (according to the results of measurements on rock cuttings) with the results of determining the dependences of the thermal conductivity of rocks on temperature (according to the results of measurements on standard samples) (Figure), the following conclusions can be drawn: " should be edited, the same word "results" is repeating 5 times. Also please check "(Figure ?)", something is missing.
Response: Thanks for your recommendation! The sentence was changed to: "Based on comparison of the dependences of the thermal conductivity of the matrix on temperature (according to the results of measurements on rock cuttings) with the dependences of the thermal conductivity of rocks on temperature (according to the results of measurements on standard core samples) (Figure 51 in the revised thesis), the following conclusions can be drawn".

Comment 26:
Table 42. Please provide the value of $\lambda(T_0)$, see above. Also, the Title of the Table 42 "The results of determining the dependences of the thermal conductivity of the matrix on temperature from the results of measurements on rock cuttings." Should be edited. For example, "Correlation equations of the temperature dependence of measured thermal conductivities of rock cuttings".
Response: Thanks for the recommendation! The value of $\lambda(T_0)$ is presented in Table 41 (Table 33 in the revised manuscript). The corresponding clarification was added to the title of Table 42 (Table 34 in the revised manuscript). The title of Table 42 (Table 34 in the revised manuscript) was edited to "Correlation equations of the temperature dependence of measured thermal conductivities of rock cuttings".

Comment 27:
Conclusions, first sentence. "The research work has produced new experimental data ..." should be edited, for example, "The present study reports new experimental thermal conductivity data for 39 rock samples from Bazhenov and Abalak formations in the West-Siberian oil basin and Mendym, Domanic, Sargaev, and Timan formations in the Volga-Ural oil basin over the temperature range from (30 to 300 C)."
Response: Thanks for the note! The first sentence of Conclusions was changed to "The present study reports new experimental thermal conductivity data for 39 rock samples from Bazhenov and Abalak formations in the West-Siberian oil basin and Mendym, Domanic, Sargaev, and Timan formations in the Volga-Ural oil basin over the temperature range from 30 to 300 ºC".

Comment 28:
5.2. Conclusions. "After high-temperature measurements (once the samples have cooled down to room temperature)... " , I would say "After thermal stress (or heating and cooling runs.... " Please, throughout the text use "thermal stress" or "cooling run" and "heating run". This is generally accepted terminologies.
Response: Thanks for the recommendation! The terminology in Conclusions was changed to "heating runs".

Comment 29:
5.2. Conclusions. "The average percentage of volumetric heat capacity increase for Bazhenov and Abalak formations rocks is 30%." The best way to express the rate of heat capacity changes with temperature is temperature coefficient of heat capacity or temperature coefficient of thermal conductivity defined as $\beta_T = \frac{1}{C_p}(\frac{\partial C_p}{\partial T}) = (\frac{\partial ln C_p}{\partial T})$ *or for thermal conductivity* $\beta_T = \frac{1}{\lambda}(\frac{\partial \lambda}{\partial T}) = (\frac{\partial ln\lambda}{\partial T})$.
Response: Thanks for the recommendation! The rate of heat capacity changes was presented at percentage since it is the most understandable way of showing the results of heat capacity changes for organic-rich rocks at elevated temperatures in comparison with other sedimentary rocks. Not all publications on heat capacity of rocks have temperature coefficient of heat capacity and it is not easy to compare with them. However, such parameter can be useful for future work.

Comment 30:
The subsection "1.4 Outline of the Thesis" should be moved to right before Chapter 1.
Response: The subsection "1.4 Outline of the Thesis" was formulated after the review of current problems related to the topic of the thesis, so subsection 1.4 is logically followed after it.

Comment 31:
I am recommending to present (graphically or Tables) and discussion of the temperature dependence of the derived values of thermal diffusivity a(T). This is extremely important for theory and in order to test correctness and consistence of the measured temperature dependency of both thermal conductivity and heat capacity.
Response: Thanks for the suggestion! The temperature dependence of thermal diffusivity will not be correct in this case as thermal conductivity and volumetric heat capacity at elevated temperatures were determined on different rock samples. For correct values of thermal diffusivity at elevated temperatures, it is necessary to provide experiments on the same rock sample (or on rock samples with similar physical properties). This work can be provided in the future with the preparation of a particular set of rock samples.

Comment 32:
Also, Chapter 2 should be combined with Chapter 1. Too many small subsections in the Thesis.
Response: Thanks for the suggestion! Chapter 1 and Chapter 2 provide different information, so the combination of them can be rather misunderstanding. Chapter 1 presents the actuality of the topic in oil&gas industry and current problems related to it. Chapter 2 presents literature review on investigated thermal properties of rocks. To avoid misunderstanding, some subsections were excluded, for example, subsection 1.3 was included in subsection 1.2.

Reviewer: **Dr. Irina Bayuk**

Comment 1:
Page 19. The authors writes that the thermal conductivity is influenced by different factors including anisotropy. However, anisotropy is also a result (of rock composition and fabric) and not a reason.
Response:
Thanks for the note! Anisotropy factor was mentioned to show that it can change during heating. However, it was mentioned in experimental results and to avoid misunderstanding anisotropy was excluded from the factors that influence thermal conductivity in introduction part.

Comment 2:
It would be helpful to show formulas for calculating the precision and accuracy of thermal conductivity measurements on standard materials (section 3.1.1.3).

Response:
Thanks for the recommendation! Formulas for calculating the precision and accuracy of thermal conductivity measurements on standard materials were added to section 3.1.1.3.

Comment 3:
Page 44. I guess that the gradual correcting of thermal conductivity based on the results of optical scanning and divided-bar methods should be described in more details (page 44), step 6 of the algorithm.
Response: The percent of thermal conductivity decreasing after heating (measured with Thermal Conductivity Scanner) was equally spread at all temperature intervals. The description was added in the text (step 6, section 3.1.2).

Comment 4:
Page 50. Many different rock-physics approaches can be used to invert the cuttings' thermal conductivity from the thermal conductivity of mixtures, not only the two Licktenecker-based approaches that are commonly used just due to their simplicity. Some of the rock-physics method operate with the aspect ratio of particles (that have a clear physical meaning and could be experimentally estimated) instead of correction factors used in Licktenecker-based formulas.
Response: Thanks for your comment! The Licktenecker-based approaches were used as an example of inverting the cuttings' thermal conductivity from the thermal conductivity of mixtures. The main addition to early observed experiments was measurements of thermal conductivity of rock cuttings at elevated temperatures. However, references to other methods were also added to the text (section 3.2.2).

Comment 5:
Page 52. The problem of determination of thermal conductivity of cuttings is non-unique since this is an inverse problem. I suggest to analyze a non-uniqueness of the inverted thermal conductivity of cuttings when applying the described procedure. By now, this is a recommendation for future work. However, this should be at least mentioned in the thesis.
Response: Thank you for the recommendation! The fact that determination of thermal conductivity of cuttings is an inverse problem was added to the text (section 3.2.2).

Comment 6:
Data shown in Figure 15 are not clear. A disagreement with figure description in the text exists.
Response: Thanks for your comment! Figure 15 (Figure 10 in the revised thesis) shows curves that relate the average percentage of thermal conductivity decrease (relatively to initial thermal conductivity at room temperature) to temperature for the Bazhenov and Abalak samples in the 30-300 ºC temperature range. Corresponding changes were added to the figure description in the text and to the figure caption.

Comment 7:
Is the TOC provided by HAWK pyrolysis given in weight percent? Or this is in the volume percent?
Response: Thank you for the question! TOC provided by HAWK pyrolysis is given in weight percent.

Comment 8:
Figure 33. Please, clarify blue lines and numbers in the left figures.
Response: Blue lines and numbers in the left figures 33 (Figures 28 in the revised manuscript) show main axes directions and CLTE values that were provided by the application of ellipse with unknown semiaxes and determination of unknown values by the least square method (the result of solving the optimization problem by the ellipse parameters method). The corresponding explanation was added to the text (section 4.3.3).

Comment 9:
In the derived correlation dependences the units for all variables should be given.
Response: Thank you for your remark! The units for variables in correlations were added to Figures 29-30 (see the revised thesis).

Comment 10:
Figures 40 – 42. Please, indicate the sample direction.
Response: Thanks for the note! The sample direction was added to figures captions.

Comment 11:
Page 116. It would be helpful to discuss the difference in the dependences obtained for the whole rock samples and cuttings prepared from the samples.
Response: The main difference in dependences obtained for the whole rock samples and cuttings is that for the whole rock sample effective thermal conductivity is determined, for cuttings – the thermal conductivity of matrix is determined. So, also rock samples and tablets prepared from rock cuttings have different porosity and degree of fracturing. The corresponding discussion was added to the text (section 4.5).

Reviewer: Prof. Sergey Stanchits

Comment 1:
The rock in reservoirs exists under elevated temperature and elevated stresses, and DTC-300 instrument is able to apply only a very small compressive load of 7 kPa to the sample, which is not enough to close all the cracks. How significant is the influence of stresses in comparison with the influence of the temperature on the thermal properties of the rock studied in Ph.D. thesis?
Response: Thank you for the question! Nowadays, the problem of simultaneous measurements of thermal conductivity at elevated temperatures and pressures exist and only few devices are suitable for such measurements (for example, Abdulagatova, Z.Z., Abdulagatov, I.M., Emirov, V.N., 2009. Effect of temperature and pressure on the thermal conductivity of sandstone. Int. J. Rock Mech. Min. Sci. 46: 1055–1071). The main problem in the reliability of such experimental results is that it is rather difficult to obtain an appropriate base of metrological standards and tests. In the thesis, the problem of pressure absence and cracks appearance was solved by applying a new measurement methodology that combined Thermal Conductivity Scanner (TCS) and divided-bar technique (DTC-300). Considering that thermal conductivity changes are related to the appearance of cracks after heating the difference between thermal conductivity before and after heating obtained with TCS was included as correction for results (obtained with DTC-300 at elevated temperatures). The correction steps are described in section 3.1.2).

Comment 2:
I expect some cracking of rock samples to occur during the coring procedure, as well as during the lifting of the core samples from depth to surface. Is it possible to estimate how significant the influence of these artificially created cracks will be on the coefficients of linear thermal expansion and thermal conductivity measured under laboratory conditions?
Response: Thanks for the question! Taking into account my practical experience, the artificial or induced rock micro-fracturing that highly affects both thermal conductivity and linear thermal expansion coefficient is usually observed for layered and heterogeneous rock types. Thus, I see several options to estimate the effect of these cracks on thermal conductivity and linear thermal expansion coefficient. First approach relies on experimental investigations. To estimate the effect of microfractures, we need to conduct several measurements of rock thermal conductivity and thermal conductivity and linear thermal expansion coefficient under increasing loading pressure on a representative core sample. The relative changes in the understudy properties will be an approximate estimate of the micro-cracking effect. I underline the “approximate” since we

understand that pressing core samples does not guarantee that the investigating core sample will have the same structure (that is crucial both for thermal conductivity and linear thermal expansion coefficient) as it was at in situ conditions. The second approach relies on numerical modeling of the process of recovering a core sample, drilling out the core plugs, and the process of core aging.

Comment 3:
I think it is worth mentioning in the thesis how the results measured under laboratory conditions can be extrapolated to the reservoir conditions?
Response: Thanks for your recommendation! In reservoir conditions, temperature, pressure, and fluid influence the thermal conductivity of rocks. According to previous studies (Abdulagatov, I., Emirov, S., Abdulagatova, Z., Askerov, S., 2006. Effect of pressure and temperature on the thermal conductivity of rocks. *J Chem Eng Data* 51:22–33) pressure increases thermal conductivity values up to 5% for the rocks with low porosity at the pressure of 150 MPa. The rate of pressure increase is less than that of temperature. Therefore, the effect of pressure can be neglected in correction. In-situ temperature of studied samples can be calculated using temperature gradient. Temperature at a certain depth can be formulated as: $T = T_0 + h \cdot gradT$, where T is a temperature at a certain depth, T_0 is land surface temperature, h is depth, and gradT is geothermal gradient. Using experimental data on thermal conductivity of studied rocks at elevated temperatures it is possible to make corrections for thermal conductivity values for certain depths and in-situ temperatures. Corresponding clarification was added to section 4.2.2.

Comment 4:
In the "Conclusions" section, I would recommend Anastasia to specify – where can the results of her Ph.D. study be applied in Industry?
Response: Thank you for the remark! The results of this work were used in industrial projects (jointly with Lukoil-Engineering, Rosneft, VNIINeft, Zarubezneft, Gazpromneft, Novatek) on the investigation of thermophysical properties on cores. Experimental data on thermal properties (thermal conductivity, CLTE, VHC) of rocks at elevated temperatures were used for heat flow density determination, basin, and petroleum system modeling. The corresponding clarification was added to the "Conclusions" section.

Reviewer: Prof. Alexey Cheremisin

Comment 1:
Page 3. "Nowadays, there is a lack of experimental data on thermal properties of organic-rich rocks at elevated temperatures and reliability of results is not provided". "Not provided" does not mean that reliability was not measured. Change: the data is not reliable (with proper references).
Response: Thanks for the recommendation! The sentence was changed, proper references are provided in sections 2.1, 2.2, 2.3.

Comment 2:
Provide full references in Publications.
Response: Thank you for the remark! Full references of Publications were added to the text.

Comment 3:
Section 2.5. Rephrase the first sentence.
Response: Thanks for the recommendation! The sentence was rephrased to: "As can be seen from the overview of previous publications, careful metrological analysis or measurement quality and levels of uncertainty in the results were provided only in few publications".

Comment 4:

Section 3.1.1.1. "Thermal conductivity measurements in a temperature range of 30-300 C were carried out with the well-known divided-bar method (Popov et al., 2016b)". Refer to original work + your group.

Response: Thanks for the recommendation! Refer to original work was added to the text.

Comment 5:

Section 3.1.1.1. "The thermal conductivity measurements are based on the guarded heat flow meter method (Popov et al., 2016b)". If it is ASTM method? Why you refer to Prof. Popov group?

Response: Thanks for your note! The reference to Prof. Popov's group was added because of the detailed explanation of this method in this reference. To avoid misunderstanding, only reference to ASTM method was left in the text.

Comment 5:

Section 3.1.1.3. Why you decided to measure accuracy of DTC based on TCS? Why TCS is measuring "true" thermal conductivity vs DTC? Provide accuracy of both devices.

Response: Thanks for your remark! Accuracy of DTC-300 instrument measurements was calculated with certified reference standards (NIST and literature references, see Table 4 in the revised manuscript). The accuracy of TCS was provided in section 3.1.2. All changes were added to the text and Table 4.

Comment 6:

Table 4. Are you sure that you calculate accuracy (systematic error)? What is precision?

Response: Thanks for the question! To avoid misunderstanding, formulas of accuracy and precision were added to section 3.1.1.2.

Comment 7:

Figure 2. Why precision depends on temperature? How did you measure true values for glass, marble and etc.?

Response: Thanks for your question! For precision calculations it is necessary to know root mean square deviation, number of measurements, averaged measured value, and Student's coefficient (see the formula for precision in section 3.1.1.2). So, precision for DTC-300 measurements was calculated by several thermal conductivity measurements on standard reference samples at all studied temperature points (30-300 ºC). Certified values are necessary only for accuracy calculation. Accuracy was estimated at room temperature; certified values were taken from NIST and literature references (see Table 4).

Comment 8:

Figure 9. How you can prove that TCS measurements are "true" values? Different rock thickness or flatness?

Response: Thanks for your question! TCS measurements are more accurate than measurements on DTC-300 (see section 3.1.2), that's why for correction influence of rock's flatness on thermal conductivity values, TCS measurements were used. To avoid misunderstanding, the terminology "rock thickness" was changed to "rock flatness".

Comment 9:

Figure 10. Did you make corrections in Thermal Conductivity for the sample D during measurements at DTC-300?

Response: Thanks for your question! The correction in thermal conductivity values were made during measurements at DTC-300 instrument (see formula 5) if diameter of measured rock sample was less than 50 mm (for example, in case of measurements on tablets with rock cuttings).

Comment 10:
Section 3.2.1. Methods are repeated in the section, rewrite the section.
Response: Thanks for your recommendation! Section 3.2.1 was rewritten.

Comment 11:
Section 3.3.1. "The basic requirements of the ASTM standard (Popov et al., 2012; ASTM D4535-85, 2000) were accounted for during CLTE measurements". Is the method is standard, ASTM reference only. If the method is modified, then refer to ASTM and modification.
Response: Thanks for your recommendation! Only reference to ASTM was left in the text.

Comment 12:
Section 4.2.2. The section is main results of you study: detailed explanation of the achieved trends is required. Compare b/w oil fields, wells and etc. Try to explain different trends with available data (porosity, lithology, heterogeneity, fluid saturation and etc.)
Response: Thanks for the recommendation! Explanations of achieved results on thermal properties at elevated temperatures are presented in sections 4.2.4, 4.3.5, 4.4.4.

Comment 13:
Figure 32. Try to explain the sharp change in thermal conductivity after 180 deg. C. Please add accuracy + precision bars to all graphs.
Response: Thanks for the recommendation! The sharp change in thermal conductivity after 180 ºC is mostly related to fracture propagations during heating of the tablet. Precision bars were added to figures with CLTE measurements. Precision for thermal conductivity measurements was properly discussed in section 3.1.1.2.

Comment 14:
Figure 36. Very difficult to analyze, use moving average to smooth TCS data.
Response: Thanks for the recommendation! In figure 36 detailed profile of CLTE is presented. Moving average can lead to misunderstanding and cannot show the possibility of getting such detailed CLTE profile (from TCS profile and correlation CLTE&λ).

Comment 15:
Section 5.2. I suggest to add how the methods and the obtained results will improve basin modelling, heat flow prediction., EOR and etc.
Response: Thanks for the recommendation! The corresponding clarifications of uncertainties in modeling was added to Conclusions.

Comment 16:
English proof is required.
Response: Thank you for the recommendation! I performed several proofreadings and essentially enhanced the language quality.