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Jury Member Report – Doctor of Philosophy thesis.

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: Professor Yuri Popov
Co-supervisor: Dr. Evgeny Chekhonin

Name of the Reviewer:

I confirm the absence of any conflict of interest, Yes (Alternatively, Reviewer can formulate a possible conflict)	**Date: 27-12-2021**

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

Review of the Ph.D. Thesis "Experimental investigations of thermal properties of unconventional hydrocarbon reservoirs at formation temperatures" by Gabova A.

The Thesis addresses one of the very important scientific and technological areas of current research in applied geophysics and petrophysics (geosciences), namely, experimental study and modeling of the thermal properties (thermal conductivity, heat capacity, linear thermal expansion coefficient, and derived values of thermal diffusivity) of unconventional hydrocarbon reservoir rocks at elevated temperatures (from room temperature to 300 °C). The Thesis includes important information on experimental study and prediction techniques of thermal properties of rocks at elevated temperatures for scientific and technological applications. Therefore, the Thesis is an excellent contribution to the research in the field of thermal properties of unconventional hydrocarbon reservoirs. The Thesis reports very valuable experimental and theoretical information in the field of thermal properties of natural organic-rich rocks at high temperatures. As well-known, reliable thermal properties data of natural oil reservoir is expected to play a key role in heat flow determination, enhanced oil recovery (EOR) methods using thermal method of oil recovery, basin and petroleum system modeling, wellbore stability analysis, designing radioactive waste repositories, *etc*. Thermal conductivity and heat capacity are key thermal properties of natural oil and geothermal reservoir rock materials and useful in a number of applications. For example, to evaluate geothermal energy generation systems, we must predict the amount of heat present and the rate at which it can be extracted. The amount of heat present in a reservoir depends on the heat capacity of the rocks. The heat capacity of the rocks is needed to evaluate energy storage, $Q=(1-\phi)\rho C_P T$, where ϕ is the porosity, ρ is the density, C_P is the heat capacity, and *T* is the temperature. All of the important basic thermal characteristics (C_P, λ, a, and ρ) of rocks are functions of both the temperature and pressure at reservoir conditions. Therefore, the study of the temperature dependency of rock properties is of practical importance. Combined with local thermal gradients, thermal conductivity is used in constraining heat flow estimates as $Q=-\lambda(P,T)\,\mathrm{grad}\,T$, where $\lambda(P,T)$ is the thermal conductivity of the reservoir media as a function of temperature and pressure. The thermal conductivity directly controls the temperature gradient, dT/dz, therefore key variable in thermal modeling. Temperature is one of the most important factors affecting the thermal properties of materials. Temperature exerts a considerable influence on the transmission of heat through materials. For example, the temperature dependence of the thermal-conductivity of porous rock material gives us a clue to the mechanism of heat transfer. In order to model an underground natural oil and geothermal reservoir, a set of differential equations should be solved. For example, the main heat conduction equation which is controlling the heat transfer in reservoirs is

$$\rho C_P \frac{\partial T}{\partial t} + \nabla(-\lambda \nabla T) = Q - \rho C_P u \nabla T\,, \qquad (1)$$

where, Q is the heat source, λ is the thermal-conductivity, C_P is the heat- capacity , and ρ is the density, or $\rho C_P = \frac{\lambda}{a}$, and *a* is the thermal diffusivity of the reservoir rock. As one can see from Eq. (1), in order to numerical modeling of the heat flow processes through a reservoir rock, definitions of the thermal properties (C_P, λ, a, and ρ) of the reservoir media as a function of temperature are required. The solution of the set of differential equations (equations of mass and energy conservation, mathematical simulations of the underground oil reservoir), therefore, predictive capability of the reservoir model depends on the accuracy of the thermal property (ρ, C_P, λ, a) data of the reservoir material as a function of temperature. Solving the set of equations enables the determination the thermal condition (thermodynamic model) of the underground reservoir media. The use of real, precise experimental thermal conductivity and heat-capacity data for oil reservoir material allows improve the accuracy of prediction of temperature profile (reservoir temperature distribution, $T(x,t)$, solution of Eq. 1), i.e., underground oil reservoir modeling. Thus, underground temperature distribution in oil reservoirs is controlling by their thermal properties (ρ, C_P, λ, a). However, as noted in the Thesis, there is very limited experimental thermal property data of unconventional organic-rich reservoir rocks at elevated temperatures and reliable thermal properties predictive techniques. In this point of view the subject of the Thesis and their main objective is a very important for scientific and technological applications. The researches done by the author in the Thesis are a significant contribution to the field of technology of EOR using thermal methods, oil reservoir modeling, improvement of the technique of the thermal properties of oil rocks determination, etc, and considerable improves our understanding of the fundamental bases of the problem of thermal properties of rock materials measurements. Based on vast very high-quality experimental works, the author presents theoretical analyzes and deep interpretations of the results, modeling and prediction of the thermal properties of unconventional reservoir rock samples, detailing each step with powerful arguments. The bibliographic revision of both related experimental results and models used are a comprehensive analysis of the subject, and it can be considered as the perfect complement of the research done before. Consequently, in my opinion the Thesis is a remarkable work that contains very important scientific and technological information which worthy PhD degree. The results of the present experimental study of thermal properties (ρ, C_P, λ) , and new combined technique of the thermal conductivity measurements provides valuable scientific information needs for reservoir modeling and very useful information to deeply understand real thermal properties of reservoir rock at high temperatures. Finally the authors clearly disrobed the gaps in the existing research and the contribution of the present study to fill these gaps.

The Thesis is organized into 5 chapters. The first Chapter is

Chapter 1. Introduction

In the Introduction the author clearly described why the thermal properties study of unconventional reservoir rocks is important and it connection with the determining heat flow density, designing and optimizing thermal methods of enhanced oil recovery (EOR), basin and oil reservoir modeling, exploitation of geothermal reservoirs and design of radioactive waste disposal problems. Brief description of the current status of the problem of thermal properties measurements of the conventional and unconventional reservoir rocks was provided. Also, brief introductions to two different major thermal conductivity measurement approaches, including contact (divided- bar) and contact-free (optical scanning) techniques were described. In the Introduction part the current status of the previously reported thermal conductivity data of conventional reservoir rocks were detailed and critically analyzed. **Section 1.2** of the Chapter provides the statement of the problem. In this section the author described the problem, motivation and specific objective of the Thesis. Based on comprehensive literature review of the thermal properties technique and their application for various types of reservoir rock samples and identified research gaps the author defined the objectives of the studies and illustrate and motivate the necessity of the present studies.

As well-know, most preliminary studies have been performed the measurements of thermal properties for core samples at reservoir temperatures. However, the experimental thermal conductivity and thermal expansion data as a function of temperature is not representative for unconventional reservoir rocks. Also, detailed literature review of the previous studies revealed that there is no data on heat capacity for unconventional reservoir rocks; no anisotropy analysis for thermal conductivity and thermal expansion coefficients of unconventional reservoir rocks; there is no correlation analysis of the thermal expansion coefficients with other physical properties, there are no measurements of thermal conductivity of non-consolidated rocks at elevated temperatures, and finally, thermal properties of unconventional reservoir rocks at elevated temperatures cannot be estimated analytically due to complex mineral composition and texture. Also, the existing methods of measurement contain systematic uncertainties, no metrological analysis. **Section 1.3** of the Chapter relates to main goals and objectives of the Thesis. The above mentioned problems are motivated the main goal of the Thesis, which are:

Thus, based on comprehensive analyses previous studies the author defined the main goals of the present study as: (1) advantage and disadvantages of the existing methods; (2) develop a new approach to the measurement of rock thermal properties at elevated temperatures for unconventional reservoir rocks and non-consolidated rocks; (3) apply the approach to organic-rich rocks from unconventional reservoirs and improve the quality of thermal conductivity measurements; (4) analyze new correlations between CLTE, thermal conductivity, TOC, and density for unconventional reservoir rocks; (5) analyze temperature behavior of CLTE of unconventional reservoir rocks; and (6) develop a new methodology of VHC measurements and establish new equations which relate VHC to temperature for unconventional reservoir rocks.

Chapter 2. Literature review and the current state of the problem

The Thesis reports a detailed critical analysis of the published researches done before in the filed by other researchers, detailed comprehensive literature review on current problem in this field, technique of the thermal conductivity measurements, the correlation and predictive methods, and problems related with existing approaches. The literature review reveals that very few previous studies used careful metrological analysis, or detailed uncertainty assessments of the thermal conductivity measurements for rock materials, measurement quality analysis. The reason is that shale rocks are very sensitive to mechanical treatment. It is problem to obtain the flatness of the rock (sample preparation), which is required for the divided-bar method, so it is essential to check the degree of uncertainty in the results due to deviation from flatness. Shale rocks are highly anisotropic, so the main axes of thermal conductivity and the anisotropy coefficient of studied rock samples should be defined before high-temperature measurements. It should be taken into account that the point position of the temperature sensors (thermocouples) when the divided-bar method is applied to highly heterogeneous shale causes in a significant measurement uncertainty so that careful control of heterogeneity of the selected rock samples is required.

The previous studies showed different rates within 5 to 35% of thermal conductivity decrease in the temperature range from 25 to 300 °C for each shale formation. This requires new reliable experimental studies of the problem. Also, the author concluded that no studies of the CLTE anisotropy analysis and standard procedure of sampling core plugs for CLTE studies. The author demonstrates importance of the shale sampling and its significant effect on thermal conductivity measurements. Also, the Chapter reveals the volumetric heat capacity of unconventional reservoir rocks at elevated temperatures is not presented in publications and requires a new approach. Only specific heat capacity values are presented and the number of studied rock samples is not represented (see Table 3). The author found the lack of combined integrated studies of CLTE together with other physical characteristics of shale (density, thermal conductivity, total organic carbon, etc.).

Chapter 3. Research methods

In this Chapter the author presents description of the thermal conductivity measurements in a temperature range of 30-300 °C using the well-known divided-bar (guarded heat flow) method (Popov et al., 2016b) using a DTC-300 instrument. The validation of the accuracy of the method, reliability and correct operation measuring instrument (DTC-300) the test measurements (metrological test) with reference samples such as plexiglass, vespel, technical glass K-8, marble, single-crystal quartz, titanium alloy VT-6 have been performed. This is good confirmation the accuracy and reliability measured data.

Section 3.1.2 is represented how the new measuring technique based on the integration of DTC-300 instrument and Thermal Conductivity Scanner (TCS) can be applied to accurately measure of the thermal conductivity of unconventional reservoir rocks at elevated temperatures.

The author used reliable contact -free method of thermal properties measurement technique since unconventional reservoir rocks are enough fragile due to numerous fractures. For these purposes the author used well-known Thermal Conductivity Scanner (TCS) method previously developed by Popov et al. (2016). This method has been successfully employed before to measure thermal properties rock materials. The combination of TCS with equipment for measurements of thermal properties at elevated temperatures allows solve the problem mentioned above (application the method for unconventional reservoir rocks at elevated temperatures). TCS also can be employed to avoid the anisotropy analysis, i.e. to measure core samples in different directions to the core axis. Finally, it allows to find a new correlation between the thermal conductivity and other properties, for example, with thermal expansion coefficient. Thus, the proposed method allows to estimate the effect of rock sample flatness on the accuracy of the thermal conductivity measurements. Correction for change in the structure (cracks formation) of the rock samples during heating was performed using thermal conductivity data obtained with the TCS after heating (thermal stress). Assuming that thermal conductivity changes are related to the cracks formations after heating the difference between thermal conductivity before and after heating obtained with TCS was included as correction for results obtained with DTC-300 technique.

The Thesis is an experimental and modeling study of a few fundamental scientific problems related with thermal properties measurements of unconventional organic-rich reservoir rocks and improve the quality of thermal conductivity measurements, such as (1) to determine the degree of CLTE anisotropy and range of CLTE values for unconventional reservoir rocks; (2) to compare directions of CLTE anisotropy main axes with the direction of the main axes of thermal conductivity tensor; (3) to analyze new correlations between CLTE, thermal conductivity, TOC, and density for unconventional reservoir rocks; (4) to analyze temperature behavior of CLTE of unconventional reservoir rocks; and (5) to develop a new methodology of VHC measurements and establish new equations which relate VHC to temperature for unconventional reservoir rocks. The results are of considerable scientific and practical importance and value to the field of geosciences.

After carefully reading of the Thesis, I think there are three strong points on this research that I want to emphasize. **Firstly**, divided-bar (contact method) and optical scanning (contact free method) techniques were combined in the thermal conductivity (thermal properties) measurements in order to take into account of thermal anisotropy and heterogeneity of the rocks and improve the quality and reliability of the experimental data. This allowed the author to solve of one of the important problem (long term underlying problem of the contact method), namely, the effect of thermal resistance on the uncertainty measured values of thermal conductivity of rock materials in the contact method (divided-bar). The detailed comprehensive analyses of the problem of thermal conductivity data measurements the author showed that there is still little knowledge about the nature of the contact thermal resistance and its effect on the uncertainty of the measurements.

1. Conventional contact methods (divided-bar, needle-probe, hot wire, guarded hot plate, *etc*) include uncertainty due to contact thermal resistance between the heat source (heater) and the measuring sample at interface, and thermocouples. Very important source of error which always present and cannot be removed completely at thermal conductivity measurements is the contact resistance at the sample-equipment interface. For conventional contact methods of ETC measurements the differences between reported data reached up to 20 % and more, even at room temperature. Systematic discrepancy between various data measured with conventional contact methods arise from contact resistance and differential thermal expansion. Surface roughness creates "gap" through which phonons cannot propagate. Differential thermal expansion between thermocouples and sample can create the additional thermal resistance. Most contact areas consists of more than 90 % air voids, which represent a significant resistance to heat transfer since air is not a very effective heat conductor. According to Hofmeister et al. (2007) the contact resistance with heaters and thermocouples, and possibly among constituent grains, leads to systematic and substantial underestimation of lattice thermal conductivity of 20 %. The advantage of the optical scanning or Laser Flash methods is that, it can measure thermal conductivity of the rock sample without having any physical contact of the heat source with the sample (no contact resistance). Also, the other advantages of this contact-free method are: (1) easy sample preparation; (2) fast measurement times; (3) small sample dimensions; and (4) high accuracy. Therefore, the present study allows to overcome systematic uncertainties in previous thermal conductivity measurements of oil shale rock samples using contact method. The author proposed a new technique of the correction of measured data using contact method. This approach allows to correctly estimate the contribution of the thermal contact resistance, non-parallelism (rock sample flatness) of rock samples surfaces, and changes in rock samples structure during heating the samples, i.e., cracks formation due to difference in the thermal expansions of the rock forming materials and anisotropy and heterogeneity.

The second point is that, the linear thermal expansion coefficient (α) of the rock samples was studied with a quartz dilatometer (mechanical properties of rocks). Thermal expansion may have significant effects on the structure of rocks. Because of the multi-mineral composition of rocks, heating causes micro-fracturing due the differential thermal expansion of mineral grains. Differences in thermal expansion characteristics of various minerals in the assemblage of mineral grains can cause structural damage upon heating the rock. Even a given mineral the coefficient of thermal expansion may be different in different crystallographic directions. These differences in thermal expansion results in stress concentrations at grain contact points, when a rock heated, leading to the possibility of fracture of individual mineral grains and disaggregating of the rock. Therefore, the effects of heating rocks are altering their properties. The author found the strong correlations between the thermal expansion coefficient (α, mechanical properties), thermal conductivity (λ, thermal properties), and total organic carbon (TOC). Detailed profiles of thermal expansion coefficient (α) along the wells were obtained for the first time using correlations between the thermal conductivity and thermal expansion coefficient (α). The coefficient of linear thermal expansion of rock samples is the less studied area in the literature, although, the knowledge of the thermal expansion coefficient allows to predict rocks behave under thermal stress and to establish depth intervals with possible borehole wall collapse for prevention of rock drilling equipment damage. Also, the thermal expansion data is related to cap rock integrity assessment for thermal EOR methods. As thermal expansion coefficients are anisotropic and different for rock-forming minerals, it results in stress accumulation at grain boundaries of different minerals. Exceeding breaking points at the contact of mineral grains can lead to rocks disruption (cracks formation) which sufficiently changes thermal properties of the rock. The published data on rock thermal expansion are very restricted and involve a limited range of minerals and rocks and do not provide the necessary quality of CLTE measurements for oil-rich shale. **The third point** is that, the new methodology developed in the Thesis for calculation of the volumetric heat capacity (C_P) at elevated temperatures for unconventional reservoir rocks allows to develop a new equation for temperature dependence of thermal conductivity $\lambda(T)$. Laboratory experiments are very expansive (time and energy consume) and has very limited potentialities. Therefore, the modeling is needed to predict the thermal characteristics of oil-rich reservoir rocks when the potential of the laboratory experiments are limited. A new technique of thermal conductivity measurements at elevated temperatures allows the measurements of unconventional reservoir rocks. It allows to obtain new equations which relate the thermal conductivity of the matrix.

114 rock samples from 7 oil fields have been studied in the Thesis with the techniques developed and enhanced to establish the behavior of the thermal properties at elevated temperatures over the temperature range from 25 to 300 °C. The approaches proposed in the Thesis allow to test the thermodynamic consistence of the independent measured values of thermal properties (heat capacity C_P, thermal conductivity λ, thermal diffusivity a, and density ρ) using the well-known theoretical relation $\lambda = \rho a C_P$. This is one of the very strong point of the Thesis. The temperature behavior of the thermal conductivity (λ) of the rock sample is the result of the complexity of the temperature behaviors of a, C_P, and ρ, *i.e.*, is the superposition of various temperature behaviors of a, C_P, and ρ, and reflects the temperature behavior of the thermal diffusivity or heat –capacity behavior in the distinct temperature ranges. Although the importance of thermal properties measurements for unconventional reservoir performance has been well-documented, very few laboratory studies over the world have been conducted.

Thus, the present Thesis provided comprehensive (experiment and modeling) studies of the problem of main thermal properties of unconventional oil reservoir rocks as a function of temperature from room to 300 C. This is very important contribution in further improvement of the reliable methods of thermal property measurements of rocks. For these purposes the author studied the new combined techniques of thermal conductivity measurements based on contact and contact –free methods.

Chapter 5. Conclusion. Chapter 5 presents the main conclusions drawn from the experimental and modeling studies of the temperature effect on the thermal properties of unconventional oil reservoir rocks. The conclusion provides what this work contributes to its field. Based on the vast and very high quality experimental works, the author deal with the theoretical analyzes, interpretations, and modeling of the key thermal properties (thermal conductivity, heat capacity, thermal diffusivity, and density) of unconventional reservoir oil rocks at high temperatures. Based on the detailed analysis of the research done in the Thesis the following conclusion can be made. The author highly understands the problem considering in the work and current status of the problems, advantages and disadvantages various approaches to solve the problems. The author proposed a new approach to measurement of the unconventional oil-rich rock thermal conductivity at elevated temperatures which considerable improves the quality of thermal conductivity measurement. For example, DTC-300 thermal conductivity results caused by non-parallelism of studied rock samples can be improve the uncertainty up to 20%, and systematic decrease up to 12% in thermal conductivity caused by rock sample fracturing was corrected. This is very strong results. The proposed approaches were experimentally and theoretically tested and provided strong verification their reliability.

Thesis reports valuable experimental and theoretical results in the field of geophysics and petrophysics. The Thesis is the excellent contribution of previous researches on the field of experimental study and modeling of the thermophysical properties of unconventional oil reservoir rocks. The detailed analysis of the research results conducted in the Thesis showed that the author derived new results which are making an important and valuable contribution in the field, namely, comprehensive experimental and modeling study of the fundamental thermal properties (thermal conductivity, heat capacity, thermal diffusivity, and density) of reservoir rock samples, which is extremely important for enhanced oil recovery and energy security. The Thesis will help researchers to deeply understand and used for own research and for practical applications of main results. The Thesis is clear and logical structure, good and logically organized. The scientific merits of the work are very high. The quality of the experimental results is also very high. The presentation of the results is very good, understandable, and easy to read. The level of the theoretical interpretation and analyze of the experimental results is very high. The main idea and results of the Thesis were published in the high impact factor (Q1) and prestige International journals.

The results of the researches conducted by the author in the Thesis are very useful for the researchers in the field and can be recommended for future used for scientific and practical applications. The experimental work and modeling of the thermal property data of reservoir rocks and interpretation of the results performed by the author are very high quality. The Thesis is significant value to all engineers and scientist who are working in field of thermal properties of reservoir rock materials, EOR technologies, oil reservoir modeling, oil industry professionals, earth science engineers, petroleum engineers, for senior undergraduate and graduate PhD students, etc. Methods presented in the Thesis are expected to be of value to develop new techniques of the thermal property measurements or improve the existing ones. The author provided comprehensive study (experiment and modeling) of the problem and the effect of various factors on the uncertainty of measured thermal conductivity data. The author illustrates deeply understanding of the problem in this field and provides the theoretical interpretation of the experimental results. Consequently, in my opinion the Thesis is a remarkable work that contains very important scientific and technological information, **therefore, the author deserves awarding the degree of Doctor of Philosophy.**

Nevertheless, I have some comments and suggestions to improve the quality of presentation of the results.

Comments:

(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.

(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.

(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.

(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.

(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).

(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 $\rho(T)= \rho_0/[1+\beta(T-25)]$?

(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.

(7) 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·kg^{-1}·K^{-1}. The value of $(\rho C_P)^{-1}$ is defined the slope of thermal diffusivity (a) versus thermal conductivity (λ) plot, $a = (\rho C_P)^{-1}\lambda$, 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

$$(\rho C_P)^{-1} = 0.9744\exp(-0.2697\rho).$$

The author should use the relation to check and confirm the reliability and accuracy of the measured heat capacity data.

(8) 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)

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

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

$$C_P(T) = C_0 + C_1 T + C_2 T^{-2}$$

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.

$$C_P(T) = C_0 + C_1 T + C_2 T^{-1/2} + C_3 T^{-2} + C_4 T^2 .$$

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

$$C_P(T) = C_0 + C_1 T + C_2 T^{-2} + C_3 T^{-0.5} \quad ,$$

$$C_P(T) = C_0 + C_1 T^{-1} + C_2 T^{-2} \quad .$$

$$C_P(T) = C_0 + C_1 \ln T + C_2 T^{-1} + C_3 T^{-2} + C_4 T^{-3} .$$

have been applied for heat capacity.

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

$$C_P(T) = C_0 + C_1 T + C_2 T^2 + C_3 T^{-1} + C_4 T^{-2}$$

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).

$$C_P = 3\frac{R}{M}\sum_{i=1}^{N} C_i x_i^2 \frac{e^{x_i}}{\left(1-e^{x_i}\right)^2},$$

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.

Minor comments:

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

(2) 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.

(3) 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.

(4) I am recommending to change “non-contact” to “contact- free”, although the meaning is the same. This is commonly accepted terminology.

(5) 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.

(6) 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).

(7) 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.

(8) 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).

(9) Tables 10, 22, 23,26 should be deleted, this information should be moved to the text, too many small and not informative Tables.

(10) 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.

(10) 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.

(11) 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”.

(12) The same equation has been used in different parts of the Theses in different form. For example, eq. (20).

(13) 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.

(14) Table 39. Please change the numbers presentation, the commas should be changed to dots.

(15) 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.

(16) 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"

(17) 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)."

(18) 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.

(19) 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 $\beta_T = \frac{1}{C_P}\left(\frac{\partial C_P}{\partial T}\right) = \left(\frac{\partial \ln C_P}{\partial T}\right)$ or for thermal conductivity $\beta_T = \frac{1}{\lambda}\left(\frac{\partial \lambda}{\partial T}\right) = \left(\frac{\partial \ln \lambda}{\partial T}\right)$.

(20) The subsection "1.4 Outline of the Thesis" should be moved to right before Chapter 1.

(21) 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.

(22) Also, Chapter 2 should be combined with Chapter 1. Too many small subsections in the Thesis

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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*