

HISTORICAL REVIEWS

HEAT CAPACITY OF KUKERSITE OIL SHALE: LITERATURE OVERVIEW

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***Abstract.** The purpose of the present paper has been to get an overview of, evaluate and systematize the existent data on the heat capacity of kukersite oil shale, as well as to find it out whether there is a need for new data. The study has revealed that the respective information is contradictory and that systematized experimental data on the temperature range below the temperatures of the most intensive thermal decomposition of oil shale are lacking. Also, the examination of the relevant public literature indicated that the specific heat capacity of kukersite has been investigated by a number of researchers till the 1970s. Later, the above-mentioned literary material has often been quoted. With the aim of making the existent data on the specific heat capacity of kukersite comparable and understandable, a complete literature review has been performed by us. The literature analysis presented in this paper is based only on original sources.*

***Keywords:** kukersite oil shale, heat capacity.*

1. Introduction

Oil shales present opportunities for satisfying needs for some of the fossil energy of the world in the years ahead. Oil shale is characterised as an organic-rich sedimentary rock containing solid combustible organic matter in its mineral matrix. The organic matter called kerogen is largely insoluble in petroleum solvents, but when heated, decomposes to yield oil.

Therefore, all the existing technological approaches to oil shale upgrading require its heating to temperatures at which the thermochemical destruction processes of kerogen take place sufficiently fast. Oil shale can be upgraded to oil by either aboveground (ex situ processing) or underground (in situ processing) technology. In both cases, the chemical process of pyrolysis is used to convert the kerogen present in oil shale into shale oil and

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shale oil gas. The decomposition (pyrolysis) of kerogen begins at relatively low temperatures (300 °C), but proceeds more rapidly and more completely at higher temperatures, namely at about 400–500 °C. The amount of heat of pyrolysis reactions in itself is relatively small, and most of the process heat is consumed for heating oil shale. Therefore, data on the heat capacity of oil shales can be considered valuable engineering information in the design of thermochemical conversion processes such as retorting, for example.

The aim of this paper was to prepare an overview of reports on kukersite heat capacity with systematized literature data.

In Estonia, kukersite oil shale is the most important mineral resource. Here, since 1924, eight different technologies/processes of producing oil or/and gas have been applied in the thermochemical conversion of oil shale on a pilot or commercial scale. However, there are relatively few written records from the past of heat capacity data sets on kukersite shale oil which can be found in the publicly available literature.

2. Results and discussion

The section Results and discussion consists of two parts. The first part presents an overview of the literature data found on the heat capacity of kukersite oil shale. In the second part, the original sources of literature used in this study are briefly described.

2.1. Data on the heat capacity of kukersite in literature sources

Our literature review revealed that research on the heat capacity of Estonian kukersite oil shale was mostly done till 1959. No newer reports were found. Later literary sources often present only the derived equations from previous works that were published in those years, without further describing them (experimental conditions, temperature ranges, samples, coefficients used in equations). A comparison of the existing data [1, 2–7] demonstrated that although the few values of kukersite oil shale heat capacity [4–6] obtained at temperatures below 100 °C (in the region of measurement) were quite consistent, the respective figures differed about twice when extrapolated up to 350–400 °C. There is only one experimentally obtained heat capacity curve covering the temperature range of 100–900 °C, but this information was presented only graphically, with no tabulated values [7].

Figure 1 shows a comparison of the heat capacity values of kukersite oil shale with an organic content of about 36%. The reason for selecting for demonstration organic content ca 36% was the fact that all research teams used samples of the typical Baltic oil shale that contained organic matter this much. In addition to the measured literature data, the extrapolated and/or calculated values of heat capacity are presented. The calculations were performed by us using equations found in literature sources [1, 2–7]. The equations were derived for the recommended temperature regions based on experimental results.

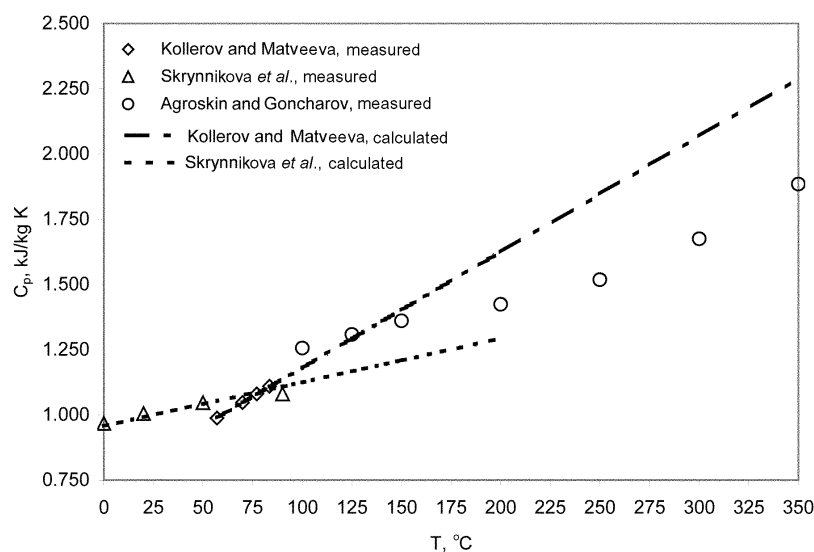


Fig. 1. Literature data on the heat capacity of a typical Baltic oil shale (organic content ca 36%) measured (open points) and extrapolated (dashed lines) up to recommended temperatures by using Equations 1 [4] and 2 [6].

In addition to indicating the degree of consistency of heat capacity data at low temperatures, Figure 1 also reveals the dependence of heat capacity on temperature up to 350–400 °C. The experimental values of heat capacity measured by Agroskin and Goncharov [7] show that the heat capacity of oil shale monotonically increases with temperature increasing up to 350 °C. The experimental data lie between the two curves extrapolated from Equations (1) and (2). These types of increasing trends can often be observed in the case of fossil fuels, but not always [8–12]. A comparison of the heat capacity values extrapolated from Equations (1) and (2) shows them to differ. These values are higher when the equation derived by Kollerov and Matveeva was used.

Based on the respective independent measurements, two research groups (Kollerov and Matveeva [4], and Skrynnikova et al. [6]) also proposed equations to calculate the heat capacity of kukersite, taking into account the organic content of oil shale and temperature. To compare the performances of both equations, calculations were done by us and the results are presented in Figure 2. This figure compares experimental data on the heat capacity of kukersite with different organic contents with the respective values calculated on the basis of Equations (3) and (4) proposed by the two research groups.

In Figure 2 it can be observed that the higher the kerogen content of oil shale, the higher the value of heat capacity. The ratio of the heat capacity of kukersite kerogen to the heat capacity of the mineral matter was roughly estimated by us to be 1.5 (at room temperature). This suggests that most likely

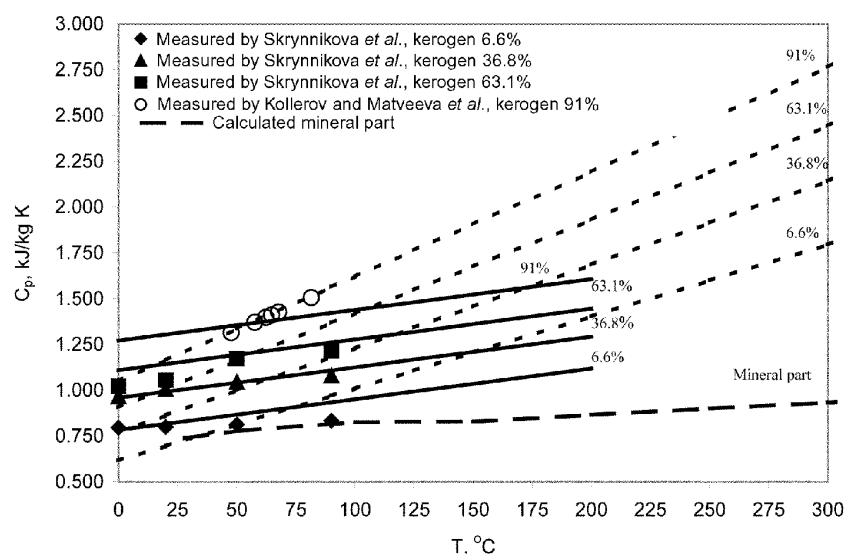


Fig. 2. The measured literature data on kukersite kerogen with various concentrations (solid and open points) compared to extrapolated values from Equations 3 [5] (solid line) and 4 [6] (dotted line). The heat capacity of kukersite mineral part was calculated by us for comparison (dashed line).

the heat capacity behavior of kerogen determines, to a large extent, the total heat capacity behavior of oil shale as a function of temperature. To confirm this observation, the dependence of mineral part heat capacity on temperature is also presented in Figure 2. It can be seen that the heat capacity of kerogen depends on temperature more than that of the mineral part.

The heat capacity of the mineral part of oil shale was calculated by us applying a simple method for calculating the heat capacity of mixtures on the basis of the equation $C_{p,m} = w_1C_1 + w_2C_2 + w_nC_n$ [13], where C_1 , C_2 and C_n denote the heat capacity of a mineral component, kJ/kg K; and w_1 , w_2 and w_n stand for the mass percent composition of a mineral. The main part of the mineral matter of Baltic oil shales is known and consists of clay (15.0 wt%), calcite (65.3 wt%), dolomite (2.8 wt%), quartz (8.0 wt%), feldspars (6.0 wt%) and pyrite (2.7 wt%), where wt% is mass percentage [4, 14]. The calculations of the heat capacity of kukersite mineral part were performed by us based on the literature data on the heat capacity of mineral part as a function of temperature [15, 16–21].

In conclusion, a comparison of the above data reveals discrepancies between them. Thus, greater deviations seem to appear in the case of extrapolated results at higher temperatures (a trend of curve behavior). In the range of measurement (up to 100 °C) the differences seem to be smaller. This makes estimation of the heat capacity of kukersite difficult. The problem with the comparison of existing data may be caused by insufficient information on measurement methods, conditions included, by the difference in samples com-

position, or by methods of computing heat capacity (for example, finding/deriving a coefficient in the offered equations). As can be seen, the existent material on the heat capacity of kukersite is contradictory. Thus, further investigation would be necessary to have consistent data. The following is an overview of the original heat capacity data found in original sources.

2.2. A short description of the original literature sources used

2.2.1. Investigations by K. Luts

The heat capacity of Estonian kukersite oil shale at room temperature seems to have been first determined by K. Luts in 1944, based on the elemental composition of kerogen and analysis of the mineral part [1]. According to Luts' calculations, the heat capacity of the organic matter of kukersite was 0.36 kcal/kg·°C (1.51 kJ/kg·°C). Then the specific heat of ash was found to be 0.19 kcal/kg·°C (0.80 kJ/kg·°C) by using Kopp's law [1]. Based on this law, the specific heat capacity of dry kukersite oil shale, consisting of 50% organic matter and 50% mineral part, was proposed to be 0.27 kcal/kg·°C (1.13 kJ/kg·°C) [1, 7].

2.2.2. Investigations by Kollerov and co-workers

The heat capacity of a typical technological Baltic oil shale with the kerogen content of 35% (Fig. 1) was determined by Kollerov and Matveeva calorimetrically in an aqueous calorimeter [5]. The characteristics of the sample were the following: W^a 1.54%, A^d 46.50%, CO_2^d 18.50%, $A^d + CO_2^d$ 65.0%, S_t^d 1.86%, C 27.17%, H 3.48% (W^a is the moisture content of an analytical sample, A^d is the ash content, CO_2^d is the carbon dioxide content (dry carbon basis), S_t^d is the total sulphur content, C is the carbon content, H is the hydrogen content). ($A^d = 26.50\%$ is a misprint in the original source [5]). The oil shale sample was pre-heated to 150 °C. Then the heat capacity of the sample was determined at average temperatures from 57.05 to 83.5 °C. Based on these experimental results, an equation to extrapolate and/or calculate the specific heat capacity, C_p , at higher temperatures was derived by the authors applying the method of least squares, and was recommended for use at temperatures up to 300–350 °C (see Fig. 1):

$$C_p = 0.176 + 0.00106 T, \text{ [kcal/kg}\cdot\text{°C]}, \quad (1)$$

where T is the temperature, °C. Equation (1) was formulated for oil shale samples with a moisture content of 1.5%. In case of a sample with a different moisture content, a correction regarding water content must be made [5].

This research group also measured the heat capacity of concentrated kerogen (organic content 91%) at a temperature up to 80 °C [5], the proposed accuracy of measurements being 1%. The kerogen was obtained by the flotation method from Baltic oil shale. Based on the experimental results, Equation (2) for calculating the heat capacity of 91% concentrated kerogen was also derived by the same authors:

$$C_p = 0.249 + 0.00136 T, \text{ [kcal/kg}\cdot\text{°C]}, \quad (2)$$

where T is the temperature, °C. It was recommended that this equation, with a probable accuracy of 3%, should be applied to calculating the heat capacity of kerogen at temperatures up to 300 °C.

Our belief is that, based on the data above, the same authors [5] offered Equation (3) for a technical calculation of the heat capacity of Baltic oil shale, taking into account organic content and temperature. Such a derivation was based on the permanent content of the ash part of Baltic oil shale:

$$C_p = 0.139 + [(0.001227 + 0.0000054 T) O_m + 0.000906 T], \text{ [kcal/kg}\cdot\text{°C]}, \quad (3)$$

where O_m is the organic content, wt%; T is the temperature, °C; and 0.000906 is the temperature index [5].

Equation (3), with the calculation accuracy of 3%, was recommended for calculating the heat capacity of oil shale samples with a moisture content of 1.5% at temperatures up to 300–350 °C. In case of a sample with a different moisture content, a correction to water heat capacity must be made [5]. The results obtained using Equation (3) are presented by us in Figure 2.

2.2.3. Investigations by Skrynnikova and co-workers

The heat capacity of kukersite oil shale with an organic content of 36.8% (Fig. 1) was measured by Skrynnikova and co-workers. The sample characteristics were the following: organic content 36.8%, W^a 4.2%, A^d 51.4%, CO_2^d 12.1%, C 28.37%, H 3.45%. The measurements were performed using the regular thermal regime bicalorimeter method in the temperature range of 0 to 90 °C [6]. Generally, Skrynnikova and co-workers measured the specific heat capacity of nine kukersite samples with different organic contents, namely from 6.6 to 63.4 wt%. For technological calculations of the specific heat capacity of kukersite oil shale samples with different organic contents at temperatures up to 200 °C, Equation (4) was proposed by the investigators:

$$C_p = 0.178 + 0.00138 O_m + 0.0004 T, \text{ [kcal/kg}\cdot\text{°C]} \quad (4),$$

where O_m is the organic content, %; T is the temperature, °C; 0.0004 is an average temperature index; 0.178 is the index that was explained to denote the heat capacity of the mineral part of kukersite oil shale.

2.2.4. Investigations by Agroskin and Goncharov

Agroskin and Goncharov measured the specific heat capacity of kukersite oil shale with an organic content of 36% (characterized as follows: V_c 30.4%, A^d 51.2% and CO_2^d 12.4%, where V_c is the general bulk of oxidative gas) in the temperature range from 100 to 900 °C [7]. These were the only experimental data found by us which were obtained at high temperatures. The experimental results were presented by Agroskin and Goncharov graphically, with no tabulated data, as a dependence of specific heat capacity on tem-

perature. For this reason, the results could be demonstrated by us approximately in Figure 1.

The authors proposed an experimental method for a reliable determination of the heat capacity of solid fuels in the course of thermal decomposition up to the temperature of 900–1000 °C. For this purpose, the thermometric casing principle was used according to which the difference in temperatures was measured for the researched sample surrounded by a certain shell. To apply this method for measuring the specific heat capacity of fuels in a heating process, several methodical difficulties had to be overcome by the researchers. Some problems were connected with the possibility of heat by-effects, change of heated fuel weight as well as fuel blow-up in a plastic state [7].

3. Conclusions

The literature study showed that the specific heat capacity of kukersite oil shale has been investigated by a number of researchers till the 1970s. Later, the pertinent literature material was often quoted. The major drawback of the research works conducted in 1955–59 on the heat capacity of kukersite oil shale was that experiments were not practically extended to temperatures at which the thermal degradation of oil shale kerogen occurred.

To calculate the heat capacity of kukersite oil shale at higher temperatures, up to 350 °C, a number of equations have been proposed in these research papers. The derivations of these equations were based on the experimental results obtained at temperatures up to 100 °C.

The present study of literature data on the heat capacity of kukersite oil shale shows that further research is highly desirable to eliminate contradictions in the available data and expand the estimating capabilities of the existing equations.

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