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PHYSICAL AND THERMODYNAMIC PROPERTIES OF KUKERSITE PYROLYSIS SHALE OIL: LITERATURE REVIEW

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Abstract. *This study presents a literature review of the physical and thermodynamic properties of kukersite oil shale oil (or "synthetic crude oil") as found in public literature. The work showed that although there is nearly a century-old history of shale oil production in Estonia, there are very few data about the thermodynamic properties and only a limited number of property prediction methods related to shale oil produced from kukersite. Publicly available information on the physical and thermodynamic properties of kukersite shale oil originates mainly from the period of 1930 to 1960. The data found are predominantly for the lighter part of the synthetic crude oil, i.e. the part for which the condensation temperatures of the atmospheric distillation curve (average atmospheric boiling points of the fractions) are lower than 300–350 °C. Data and studies can be found about several main physical and thermodynamic properties, such as specific gravity, atmospheric boiling point, molecular weight, enthalpy of vaporization at the boiling point, heat capacity, thermal conductivity, viscosity, surface tension and vapor pressure. But in general, this information is not a systematic set of data intended for determination of thermodynamic properties, but rather it lays out trends and supports the simplest approaches for calculating thermodynamic properties based on "undefined" pseudocomponents (a mixture of compounds that behave similarly).*

Keywords: *kukersite, retort oil, thermodynamic properties, physical properties.*

1. Introduction

Estimates of the depletion of global oil reserves have led to research into the potential for using various alternative resources. One alternative is crude oil produced from oil shale (i.e. a synthetic crude oil or synthetic petroleum), and it is estimated that oil shale resources are equivalent to 2.8–3.3 trillion

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barrels of oil [1]. Thus, oil shale resources contain approximately three times more oil than conventional petroleum reserves (conventional oil reserves contain about 1.2 trillion barrels) [2]. The technologies for obtaining oil from oil shale are based on the thermal decomposition of kerogen (the cross-linked macromolecular organic matter in oil shale) [3]. Low temperature pyrolysis up to about 500 °C (also referred to as retorting, semicoking or low temperature carbonization) has historically been the preferred thermo-chemical conversion process for oil shales with high oil yield per organic matter. During the low temperature pyrolysis or retorting process the organic matter is converted to oil, gas and solid residue. Over the course of the development of shale oil production technologies several hundred different types of retorts (technologies) have been invented, including in situ (below ground) and ex situ (above ground) retorting technologies. However, throughout the long history of oil shale utilization above ground, i.e. ex situ, retorting technologies have been the only production methods used commercially for producing oil from oil shale [3].

The whole crude shale oil produced via oil shale retorting is a complex mixture of hydrocarbons and organic compounds containing heteroatoms, just like petroleum or coal liquids. Crude shale oil from commercial ex situ retorts, or so-called "synthetic crude oil", can be classified by API gravity as an average heavy crude oil. Crude shale oils from different oil shales have wide boiling distributions (generally less than 30% can be distilled below 300 ^{o}C at atmospheric pressure) and wide molecular weight distributions (extending up to 800–1000 g/mol) [4–7]. Usually about 50% of the oil can be used directly as fuel oil. Generally, crude shale oil from ex situ retorts has characteristics in the following ranges: hydrogen/carbon ratio 1.2–1.6, average molecular weight 190–310 daltons, specific gravity 0.8–1.04 (mostly < 1), 30–70% boils higher than 350 ^{o}C, groups of chemical compounds such as nonaromatic hydrocarbons up to 60%, aromatic hydrocarbons 10–50% and heteroatomic compounds 20–60% [3, 4]. Thus, based on its characteristics, crude shale oil is situated somewhere between crude petroleum and coal liquids. Shale oil is more aromatic than petroleum, but not as aromatic as coal liquids [8]. At the same time, shale oil usually contains more olefins than coal liquids and petroleum, and can also contain more heteroatomic organic compounds [4]. Additionally, because shale oil's composition is specific to a given oil shale deposit, shale oils also contain different amounts of heteroatoms, depending on the composition of heteroatoms in the organic matter of the parent oil shale. For example, kukersite shale oil (Baltic basin) contains more than 5% oxygen, El Lajjun shale oil (Jordan) contains up to 10% sulfur, Green River shale oil (USA) contains 2% nitrogen [4]. Therefore, due to the composition of shale oils, the accuracy of using petroleum-based empirical methods for determining the physical and thermodynamic properties of a given shale oil is questionable, at least without a corresponding evaluation of the method's applicability.

Shale oil has been produced in Estonia for almost a century and many different processes (technologies) have been used [9]. The technologies used in industry have been retort generators (Kiviter process) (since 1925), tunnel ovens (1926–ca 1980), Davidson rotating retorts (1931–1961), chamber ovens (1948–1987) and solid heat carrier retorts (Galoter process) (since 1963). From the different retorts and different process regimes kukersite shale oil with somewhat different parameters is obtained, in terms of both physical and chemical properties. Compared to the group composition of petroleum, kukersite contains more olefins and aromatic hydrocarbons, especially in lighter fractions (fractions with lower boiling points) [10–12]. The main component of petroleum is various paraffins, whereas shale oil generally contains few paraffins. One unique attribute of kukersite shale oil is the high content of phenolic compounds (over 30%) [13]. These differences in composition suggest that before using petroleum-based prediction methods it would be necessary to access the accuracy of these methods for kukersite shale oil. Thus, the present article is a literature review of publicly available information about the physical and thermodynamic properties of shale oil produced from kukersite.

2. Analysis and discussion

2.1. General overview of kukersite shale oil studies

The literature review indicated that the most systematic experimental data on the thermodynamic properties of kukersite shale oil and the physical properties necessary for predicting those properties was measured by Kogerman and Kõll at the beginning of the last century [14]. This assessment is made with the objective of predicting thermodynamic properties in mind, since for prediction a thermodynamic or physical property of interest should be related to at least two conveniently measurable properties (of which one describes preferably molecular size and another energy, or structure). The experimental data was presented in 1930 in the book "Physical properties of Estonian shale oils" [14]. Data was given for narrow boiling fractions that were taken at 25 °C intervals from the whole crude oil. The crude shale oil was produced with one specific retorting technology – a Kiviter-type experimental retort (Kohtla-Järve experimental generator). The data presented cover fractions with average boiling points in the range of 150–300 °C. This book provides average property data of the fractions, but not correlations and relationships. The data given in the book contains specific gravity and viscosity at different temperatures (20, 30, 40, 50, 60, 70 ^{o}C), molecular weight and specific heat and surface tension at 20 ^{o}C. And additionally, the fractions' average atmospheric boiling points, thermal expansion coefficients and heats of vaporization at the boiling point were found by calculation. No chemical characteristics, such as elemental composition, amounts of different functional groups or compound classes (paraffins, olefins, aromatics, etc.), were provided for these fractions. It is worth noting that Kogerman's and

Kõll's work was published before the beginning of the systematic characterization of the thermodynamic and physical properties of petroleum-based hydrocarbons. The beginning of that process could be considered the year 1933, when Watson and Nelson developed two empirical figures that contained the dependence of molecular weight on boiling temperature and the characterization parameter K_w or API gravity [15]. The data obtained by Kogerman and Kõll are partially or entirely given in later compilations, for example, in the appendix of Kogerman's own 1931 monograph "On the chemistry of the Estonian oil shale kukersite" (the appendix is titled "Physical properties of Estonian oil shale") [16]; Luts's 1934 book "Der estländische Brennschiefer-Kukersit, seine Chemie, Tehnologie und Analyse" (in German) [17] and Kollerov's compilation "Fiziko-khimicheskie svoistva zhidkikh slantsevykh i kamenougolnykh produktov" (1951, in Russian) [18].

In the book "Der estländische Brennschiefer-Kukersit, seine Chemie, Tehnologie und Analyse" published by Luts in 1934, one chapter is dedicated to the physical and thermodynamic properties of distillation products from Estonian shale oil [17]. In addition to some data taken from the book by Kogerman and Kõll [14], formulas are given for calculating the heat of combustion and hydrogen content from specific gravity. What could be considered the most important contribution is the correlation for molecular weight based on average boiling point for phenol-free wide technical fractions obtained in the boiling range of about 30–300 °C: light gasoline (34–185 °C), automobile gasoline (46–173 °C), heavy gasoline (132–193 °C), motor fuel (186–247 °C), diesel (243–297 °C). This is similar to the distribution of industrial distillation fractions for petroleum oils: naphtha (boiling range 60–100 °C), gasoline (boiling range 40–205 °C), kerosene (boiling range 175–325 °C), diesel fuel (boiling range 250–350 °C).

The majority of publically available kukersite shale oil data (also referred to more generally as Baltic basin shale oil data) is summarized in Kollerov's compilation "Fiziko-khimicheskie svoistva zhidkikh slantsevykh i kamenougolnykh produktov" [18]. This is a broader compilation on the physical and thermodynamic properties of oils obtained from solid fossil fuels in which data obtained by Kogerman and Kõll [14] is given along with data about kukersite shale oils produced in tunnel ovens, chamber ovens and retort generators (Kiviter process). This data is more abundant for wide technical fractions (gasoline, diesel and other wider oil fractions) than narrow fractions. Again, the fractions are characterized only by average properties and no information on or links to chemical characteristics are provided. Average physical and thermodynamic properties of kukersite shale oil fractions are presented in the book in tables and in many cases represented as graphical and/or equation based relationships. And yet, three-parameter relationships are given only as a few figures, and only for general liquid organic compounds. Because it is a compilation, data is not really presented systematically and the data is not supported with enough additional information to assess its quality. Data, graphs, equations and assessments are

presented for kukersite (or Baltic basin) shale oil properties such as specific gravity, molecular mass, boiling point, thermal conductivity, heat capacity, enthalpy of vaporization, vapor pressure and surface tension. A chapter in the book "Khimiya i tekhnologiya produktov pererabotki slantsev", published a few years later, in 1954 (in Russian), gives additional data and linear empirical relationships for the temperature dependence of specific gravity, heat capacity and thermal conductivity of Baltic basin shale oil [19]. The experimental data are on four narrow boiling range fractions and one wider boiling range oil fraction of neutral oxygen-containing oil substances, and on two fractions from chamber oven oil. However, the boiling ranges of these fractions are not specified and the fractions are characterized only by average properties (molecular weight, average boiling point, specific gravity and kinematic viscosities at 20, 50, 75 ^{o}C). This book also contains two more chapters related to properties of general liquid organic compounds, one addressing the Bachinski relationship of viscosity and the other Kollerov's K factor [20, 21].

The most important subsequent overview could be a chapter in the book "Khimiya i tekhnologiya slantsevoj smoly" (1968, in Russian) which, based on Kollerov's book, presents both equations and graphs for predicting the physical and thermodynamic properties of shale oil [22]. Later experimental data on physical and thermodynamic properties, such as boiling points, specific gravities and molecular weights, can be found in a limited form in several works; however, these in and of themselves are not studies about thermodynamic properties, but parts of studies about the chemical composition of shale oil. Worth mentioning is also a later determination of viscosity for wide fractions [23–25].

In conclusion, searching the literature showed that publically available data on the physical and thermodynamic properties of shale oil produced from kukersite oil shale is mostly from the time period between 1930 and 1960. This was the age which was dominated by graphical relationships. Relatively little systematic experimental data was found for narrow boiling range fractions, or data for fractions with a boiling range smaller than 30 ^{o}C (about 50 °F). Experimental data can generally be found for the lighter portion of oil for which the condensation temperatures of the atmospheric distillation curve (the average atmospheric boiling points of the fractions) are lower than 300 ^{o}C. It must also be acknowledged that the respective studies/measurements have not historically been carried out with the development of prediction methods in mind. The data found can acceptably be used for correlations based on undefined fractions, or pseudocomponents described by average parameters, and this only in a relatively limited form.

The next subsection (section 2.2) gives a short overview of some basic aspects related to the prediction of the thermodynamic properties of oil fractions in the context of existing kukersite shale oil data. The following two subsections provide more specific information about two basic compilations of data. In subsection 2.3, a more detailed description of the

experimental methods and the original data are presented from Kogerman's and Kõll's "Physical properties of Estonian shale oils" [14]. Subsection 2.4 gives some observations about Kollerov's compilation "Fiziko-khimicheskie svojstva zhidkikh slantsevykh i kamenougolnykh produktov" [18], and the main graphical relationships and equations related to kukersite shale oil are presented as a table.

2.2. Some considerations related to predicting kukersite shale oil properties using available data

As mentioned above, the physical and thermodynamic property data on kukersite shale oil fractions can be found primarily by means of average bulk properties. In connection with the fact that the actual composition of oils cannot generally be quantitatively described at the level of individual components, the use of a method for describing oil as a mixture of discrete pseudocomponents (a mixture of compounds that behave similarly) has been widely adopted [12]. The behavior of each individual pseudocomponent is considered as the behavior of a single compound [12]. Oil can be divided into pseudocomponents based on both molecular size (boiling temperature T_b, number of carbon atoms per molecule N_c) and the groups of compounds for a given molecular size (based on chemical characteristics, for instance n-paraffins, isoparaffins, olefins, naphthenes and aromatics). Therefore, there are essentially two approaches for characterizing a fraction for predicting thermodynamic properties: 1) the undefined mixture approach, or average parameter method, which views narrow boiling fractions (or cuts) as individual pseudocomponents that are described by the fraction's average parameters; 2) the defined mixture approach, which divides a narrow boiling fraction or cut, based on the type of compound, into pseudocomponent classes (for petroleum generally three classes are used: paraffins, naphthenes and aromatics). As mentioned earlier, and it is important to emphasize it again here, the publicly available kukersite shale oil data only support the use of undefined mixture, or average parameter, prediction methods.

For petroleum it has been found that to predict the thermodynamic properties of light petroleum fractions (molecular weight < 300 g/mol, boiling point T_b < 350 ^oC) using the average parameter method (undefined mixture method), at least two input parameters are needed (as one-parameter characterization is successful in special cases, for paraffinic crude oil fractions) [12]. It is recommended that these parameters describe the organic component's (single pseudocomponent's) molecular size and energy (or structure) [12]. When these are known, then pseudocomponents can be treated as components whose thermodynamic properties can be calculated using suitable existing equations and correlations. In most cases, average boiling point and specific gravity are used as the two input parameters. One of the simplest ways for dividing oil into undefined pseudocomponents for which the minimum necessary information is known (two known characteristics) is through the constant K factor hypothesis. The K factor

characterizes a fuel fraction's paraffinity and is an empirical relationship between specific gravity and boiling point according to the equation:

$$K_w = \frac{\sqrt[3]{T_b}}{s}. \quad (1)$$

In the most common form of the K factor, called the Universal Oil Products Company (UOP) or Watson characterization factor, T_b is the fraction's average boiling point in °R and S is its specific gravity at 60 °F (15.5 °C). This K factor (also UOP factor, Watson K factor) was put into practice in 1933 by Watson and Nelson [15]. To use the constant K factor hypothesis it is necessary to know the oil's boiling point distribution, found from the distillation curve (from this the oil's mean average boiling point is calculated), and the oil's overall specific gravity (the specific gravity of the whole crude oil). Based on this hypothesis it is possible to find every fraction's (or cut's) specific gravity from its average boiling point on the basis of the value of the K factor calculated from the whole crude oil's average boiling point and average density (assuming that the K value is the same for all fractions).

To evaluate the constant K factor hypothesis for kukersite shale oil Figure was created. The Figure shows the change in the Watson K factor K_w with boiling point. It also demonstrates that for kukersite oil (data from [14, 18]) the K factor is not constant, rather it decreases rapidly for fractions in the average boiling point range from 50 to 350 °C. At the same time, for

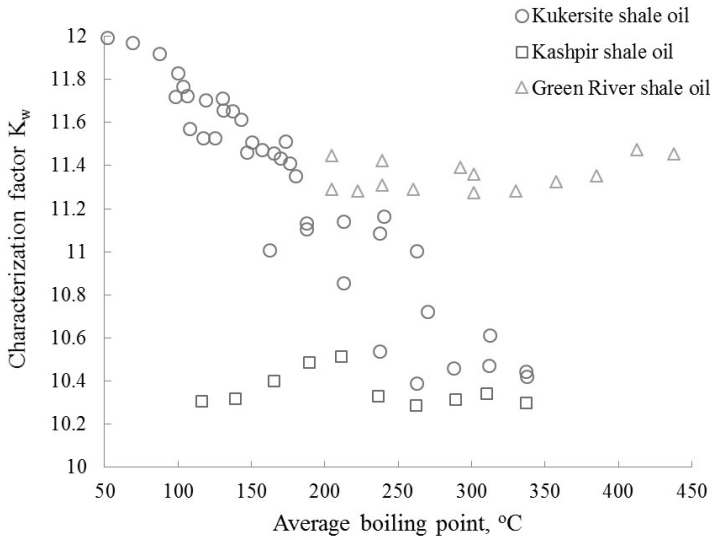

Fig. The change in Watson's characterization factor K_w with temperature for kukersite oil. Shale oils from Kashpir (Russia, Volga basin) and Green River (USA) oil shales are shown for comparison.

Kashpir (Russia, Volga basin; data from [18]) and Green River (USA; data from [26]) oil shales the constant K factor hypothesis is a quite acceptable approach. This strongly nonconstant behavior could be attributable to the high content of phenolic compounds and their distribution among fractions [13]. Therefore, the minimum information required for describing kukersite oil using the two-parameter undefined pseudocomponent method would be the oil's distillation curve (boiling point curve) and specific gravity curve, or two other acceptable input property curves.

2.3. Shale oil data measured by Kogerman and Kõll

As mentioned earlier, the most systematic experimental data on the thermodynamic properties of kukersite shale oil, when property determination is the goal, was measured by Kogerman and Kõll [14]. To adequately use or interpret the data one needs sufficient information on the details of the experiments (the information not provided sufficiently in the review given in Kollerov's book). To perform their experiments (for determining physical and thermodynamic properties) Kogerman and Kõll used freshly distilled Kohtla shale oil that was produced in a vertical, heat carrier cross-flow Kiviter retort (Kohtla-Järve experimental generator). The shale oil studied was described as a dark brown liquid which had a green fluorescence and an unusual smell. The sample contained 1.19% water, the specific gravity at 18 ^{o}C was 1.008, the flame point (Martens-Pensky method) was 91 ^{o}C and the viscosity (Engler viscometer) was 6.4 Engler at 50 ^{o}C.

To separate the oil into narrow boiling range fractions (cuts) a 5 liter 26 cm long copper flask, which was equipped with a still head, was used. To avoid decomposition at higher temperatures a pressure of 50 mmHg was used. The distillation rate was two drops per second. 8 oil fractions were collected: the first at the initial boiling point up to 150 ^{o}C (contained 1.17% water) and then 7 fractions at 25 ^{o}C intervals. One significant shortcoming of the data given is the published temperatures of the fractions, which appear to be presented at atmospheric pressure. Neither the fraction temperatures at 50 mmHg nor the calculation of the temperatures at atmospheric pressure from those at vacuum pressures are presented or explained in Kogerman's and Kõll's book [14]. This shortcoming is significant because average boiling point is generally the first choice as an input parameter describing molecular size in property correlations. The data include initial and final condensation temperatures corresponding to fractionation at atmospheric pressure for each fraction, and from these the average boiling points were calculated as the arithmetic mean. After finding the average boiling point the following parameters were measured for every fraction: specific gravity, molecular weight, viscosity, specific heat and surface tension. The thermal coefficient of expansion and the heat of vaporization were also determined by calculation. Because it is necessary to know the measurement method to evaluate the accuracy of the data, these methods are presented in Table 1. In Tables 2–4 the original data from the book by Kogerman and Kõll are given.

Table 1. The measurement and calculation methods used by Kogerman and Kõll [14]

Parameter	Notes
Specific gravity	Measured using a pycnometer and Mohr's balance. For thermo-regulation a water thermostat was used.
Molecular weight	Average molecular weights were determined from the freezing point depression of a stearic acid solution with 2% oil compared to a pure stearic acid solution. The cryoscopic constant was measured using naphthalene and benzoic acid (the average value was 41.8).
Viscosity	Measured using an Ostwald viscometer. Distilled water was used as the reference compound.
Specific heat at 20 °C	Specific heat was determined using a Dewar's flask that was equipped with a heating coil, mixer and thermometer (accuracy 0.1 °C). For every experiment 200 g of oil was used and the temperature was measured every 30 seconds. The heating period was 2 minutes. Distilled water was used as the standard compound.
Surface tension at 20 °C	Measured using the drop method in relation to air. Surface tension values were calculated using the following formula: $\sigma_{20} = 7.30 \cdot S \cdot \frac{AW}{A0}$, where σ_{20} is the surface tension (mg/mm); S is the specific gravity of oil at 20 °C; A_w is the number of drops of pure water; A_0 is the number of oil drops.
Thermal expansion coefficient	Calculated using the following formula: $a = \frac{a-b}{b \cdot (t'-t)}$, where a and b are the specific gravities at temperatures t' and t, respectively.
Heat of vaporization at the boiling point	Calculated by the Trouton equation using a constant value of 20 cal/mol K as the entropy of vaporization.

Table 2. Data for narrow shale oil fractions obtained from the Kiviter experimental plant (measured by Kogerman and Kõll [14])

Fraction, °C	T_b, °C	d_4^{20}	ΔH, cal/kg	MW, g/mol	σ^{20}, mg/mm	B, 1/°C	C_p^{20}, cal/g °C
150–175	162.5	0.8375	–	126	2.824	0.0009523	–
175–200	187.5	0.8459	69.4	132	2.818	0.0009393	0.548
200–225	212.5	0.8582	68.4	142	2.876	0.0009027	0.504
225–250	237.5	0.8770	60.4	169	2.931	0.0008677	0.507
250–275	262.5	0.8977	60.2	178	2.899	0.0008226	0.500
275-300	287.5	0.9257	56.4	199	2.868	0.0007716	0.502
Kohtla retort	–	–	–	–	3.380	0.0007190	–

Note: T_b – average boiling point; d_4^{20} – specific gravity; ΔH – heat of vaporization at the boiling temperature; MW – average molecular weight; σ^{20} – surface tension at 20 °C; β – average expansion coefficient at 20 °C; C_ρ^{20} – specific heat at 20 °C.

Table 3. The temperature dependence of dynamic viscosity for narrow shale oil fractions obtained from the Kiviter experimental retort (unit is cP) (measured by Kogerman and Kõll [14])

Temperature, °C	Fraction 150–175 °C	Fraction 175–200 °C	Fraction 200–225 °C	Fraction 225–250 °C	Fraction 250–275 °C	Fraction 275–300 °C
20	1.1300	1.3013	1.5960	2.2630	3.7990	8.7410
30	0.9889	1.1033	1.3310	1.8260	2.9240	1.1033
40	0.8557	0.9461	1.1360	1.5060	2.3030	0.9461
50	0.7545	0.8343	0.0977	1.2720	1.8530	8.3430
60	0.5973	0.7332	0.8560	1.0970	1.5540	2.6380
70	0.5973	0.6517	0.7554	0.9430	1.3200	2.1090

Table 4. The temperature dependence of specific gravity (d_4^{20}) for narrow shale oil fractions obtained from the Kiviter experimental retort (measured by Kogerman and Kõll [14])

Temperature, °C	Fraction 150–175 °C	Fraction 175–200 °C	Fraction 200–225 °C	Fraction 225–250 °C	Fraction 250–275 °C	Fraction 275–300 °C
20	0.8375	0.8459	0.8582	0.8770	0.8977	0.9257
30	0.8298	0.8382	0.8507	0.8694	0.8905	0.9187
40	0.822	0.8303	0.8430	0.8620	0.8330	0.9116
50	0.8139	0.8230	0.8356	0.8548	0.8758	0.9047
60	0.8066	0.8149	0.8280	0.8480	0.8694	0.8980
70	0.7987	0.8074	0.8212	0.8403	0.8620	0.8910

2.4. Overview of Kollerov's book

As mentioned earlier, Kollerov's book contains the most extensive information on the thermodynamic and transport properties of kukersite shale oil. More generally, Kollerov's 1951 book "Fiziko-khimicheskie svojstva zhidkih slantsevykh i kamenougolnykh produktov" [18] is a compilation which combined data about the physical and thermodynamic properties of both shale oils and coal oils that were in use in the scientific community in the Soviet Union. A note in connection with this is that in Kollerov's book, the data taken from the publication by Kogerman and Kõll are incorrectly associated with Davidson retort crude oil, but not with Kiviter type experimental retort crude oil. In Kollerov's book, in addition to Kogerman's and Kõll's data, a substantial amount of data is given for Estonian kukersite shale oils produced in industrial tunnel ovens, chamber ovens and Kiviter processes. Most of the data are given for wide boiling range fractions (technical fractions). Data are also provided for dephenolated fractions (fractions from which phenolic compounds have been removed) as well as the phenols. In addition to kukersite shale oil, there are also data given for Kaspir shale oil and coal pyrolysis tars. One shortcoming of the book is that because it is a compilation of data, then information concerning the measurement details of the data is not sufficiently provided. In addition to experimental data, Kollerov's book gives both graphical and equation based options

(one-parameter correlations) for determining thermodynamic properties. The emphasis is on graphical relationships because from 1930 to 1960 prediction methods were mainly presented graphically. Table 5 gives the most important relationships from Kollerov's book for kukersite shale oil.

When using the data of the book, the reader should take note of the characterization factor, or the K factor, and the graphs based on it. For characterizing shale oils Kollerov used a K factor (general form of the equation given by Equation 1) where the boiling temperature was in degrees Kelvin and the specific gravity was d_4^{20}. Although the K factor used by

Table 5. An overview of the parameter relationships for kukersite shale oil given in Kollerov's book [18]

Relationship	Notes
Between specific gravity $\left(d_4^{20}\right)$ and average boiling point (T_b)	Graph $d_4^{20} = f(T_b)$. Empirical equation $T_b = f\left(d_4^{20}\right)$.
Between molecular weight (MW) and average boiling point (T_b)	Graph MW = $f(T_b)$. Empirical equations: 1) Luts's equation is given for calculating the molecular weight (for phenol-free oil) MW = T^2 / 1580, where T is the boiling temperature (K) that corresponds to 50 vol% distilled by Engler distillation. 2) For calculating the molecular weight of tunnel oven and retort generator shale oil fractions MW = 59.5 + 0.38*t + 0,0023*(t–0.95)$^{1.9}$, where t is the boiling temperature (^{o}C).
Between specific gravity $\left(d_4^{20}\right)$ and molecular weight (MW)	Graphs $d_4^{20} = f$(MW).
Between the temperature dependence of the heat capacity and specific gravity $\left(d_4^{20}\right)$	The constants from equation $C_t = C_o + bt$ given as graphs $C_o = f\left(d_4^{20}\right)$ and $b = f\left(d_4^{20}\right)$. Luts's equation is also given in the form C_t = a + 0.0011 (t–20), where t is temperature (^{o}C).
Between enthalpy of vaporization (ΔH) and average boiling point (T_b)	Graphs $\Delta H = f(T_b)$.
Between kinematic viscosity at specific temperatures (ν) and specific gravity $\left(d_4^{20}\right)$	Graphs for viscosity at specific temperatures $\nu = f\left(d_4^{20}\right)$.
Between vapor pressure and temperature	Graphs for wide shale oil fractions: graphed as ln P = f(1/T) lines for different vapor-liquid ratios.

Kollerov has the same general equation form as the Watson K factor (Kw), Watson's and Kollerov's K factors can differ by as much as 17%. This results from the fact that Watson's Kw is calculated using the Rankine temperature unit and the specific gravity at 60 °F (15.56 °C)

3. Conclusions

This review of data available in public literature shows that although there has been almost a century-long history in Estonia of research related to the production of oil from kukersite oil shale, the information on the thermodynamic properties of oil is quite poor. Although data can be found about basic physical and thermodynamic properties (such as the temperature dependence of specific gravity, atmospheric boiling point, molecular weight and enthalpy of vaporization at the boiling point or temperature dependent properties such as heat capacity, thermal conductivity, viscosity, specific gravity, surface tension and vapor pressure), the information is usually not systematic, when the intent is determining thermodynamic properties or evaluating the applicability of a petroleum based prediction method. Likewise, there are few shale oil based correlations and empirical prediction methods for calculating thermodynamic properties.

It is known that for the same oil shale the specific properties, composition and parameters of the oil depend on the retorting conditions used (the technology used): retorting temperature, duration, heating rate and size of the shale pieces. The current trend in Estonia is towards using the solid heat carrier (the heat carrier is the ash) retorting technology, or the Galoter process, for producing retort oil from oil shale. There is very little data about the physical properties of oils from solid heat carrier retorts. The main existing data is for oil from retort generators (Kiviter process), tunnel ovens and chamber ovens.

Thus, so far the publicly available information has been spotty and poor for evaluating the applicability of contemporary prediction methods – studies/measurements were not historically performed with that goal in mind. For using two-parameter correlations the situation is made more complex by the fact that the Watson characterization factor Kw is not constant over a broad distillation range. Therefore, to obtain the input parameters needed for determining the thermodynamic properties of an oil, both a boiling curve (distillation data) and specific gravity distribution are needed.

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