VAPORIZATION PARAMETERS OF PRIMARY PYROLYSIS OIL FROM KUKERSITE OIL SHALE

VAHUR OJA[*]

Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

Abstract. *The objective of this study was to obtain vapor pressure and heat of vaporization values of the less volatile heavy end of the Kukersite oil shale primary pyrolysis oil and therefore to have a quantitative insight into the vaporization ability of the oil during the pyrolysis process. The shale oil was produced via rapid pyrolysis in a laboratory scale reactor and collected in a solvent filled cold trap. The solvent together with lighter oil constituents were evaporated in a vacuum oven. The prepared low-volatile oil fraction for vapor pressure measurements was estimated to be about 60% by weight of the total oil of pyrolysis. A non-isothermal modification of the conventional Knudsen effusion technique was applied to track vapor pressure as a function of the evaporative loss of progressively heavier oil constituents, starting at a several percent mass loss. From the data, atmospheric boiling point values of progressively less volatile oil were derived, indicating that the boiling point increases above 550 °C (above the retorting temperature) only when about 75 wt% of the oil has vaporized.*

Keywords: *Kukersite oil shale, retorting oil, vapor pressure, heats of vaporization, boiling points.*

1. Introduction

Worldwide oil production from oil shale has a long, yet very chaotic, history with considerable ups and downs. A few decades ago, there were commercial-scale activities present in only a few countries, and one of them was Estonia [1]. As a result of increasing interest in alternative liquid fuels resources, possibilities for commercial utilization of oil shale reserves have received wider attention, causing an increase in local oil shale upgrading activities around the world. Oil yield per unit of organic matter of oil shale can vary widely between oil shales from different deposits [2, 3]. It is usually higher for oil shales with organic matter consisting of Type I kerogen than

---

[*] Corresponding author: e-mail *vahur.oja@ttu.ee*

for those with Type II kerogen [2]. Kerogen, which makes up most of oil shale's organic matter, is a highly cross-linked, organic, macromolecular material [4]. Depending on the oil shale kerogen type, loosening or tightening of the kerogen structure can occur in the temperature region before an active pyrolytic devolatilization of oil shales. Solvent swelling experiments [5] on thermally pretreated oil shales have indicated that the high oil yield kerogen (Type I) of Estonian Kukersite oil shale, which possesses softening pyrolysis behavior, shows a tendency for pre-pyrolysis structural loosening [6]. This characteristic is qualitatively similar to that of high tar yield softening coals [7]. On the other hand, the low oil yield kerogen (Type II) of Estonian Dictyonema oil shale, which possesses non-softening pyrolysis behavior, shows a tendency for pre-pyrolysis structural tightening [8]. This trend is qualitatively similar to that of low tar yield non-softening coals [7]. These modes of action are an example of similarities in the underlying principles that cover oil shale and coal pyrolytic behaviors.

Similarly to coal pyrolysis modeling, oil shale pyrolysis modeling could have the benefit of quantitatively characterizing both the chemical and physical processes of pyrolysis. The vapor pressure of coal primary tar species is one of the key parameters in coal pyrolysis modeling. Advanced models of pyrolysis utilize the coal tar vaporization process as one of the key phenomena because the ability of tar to evaporate determines several key features of the pyrolytic process (tar yields, char yields, gas yields, tar molecular weight distribution) [7, 9]. The models are the Functional Group-Depolymerization,Vaporization, and Cross-linking Model [10], the FLASHCHAIN Model [11], and the Chemical Percolation Devolatilization Model [12]. On the basis of organic matter content, pyrolysis tar or oil (for pyrolysis products condensable at room temperature the term oil is preferred in oil shale research instead of tar) is the dominant product of the pyrolysis of high oil yield, softening oil shales, such as Kukersite oil shale (with a typical Ficher assay oil yield of 70 wt% on an organic matter basis [3]). Similarly to coal pyrolysis, the ability of the primary oil to evaporate from oil shale particles at different heating rates and pressure conditions should determine the aforementioned key features of the Kukersite oil shale pyrolysis. However, the vapor pressure information for Kukersite oil shale primary oils (similarly also to the case of the industrial retort oils with a molecular weight above 200–250 daltons), was not found in the open literature. Also, there is no vapor pressure information available on primary tars of oil shales from other deposits.

The present work was undertaken to get some quantitative insight into vaporization parameters (vapor pressures, heats of vaporization, boiling points) of primary pyrolysis oils from Estonian Kukersite oil shale. The focus is on the less volatile heavy end of the oil (estimated to be about 60% by weight of the total oil of pyrolysis). The approach of the current work was to measure vapor pressures of Kukersite oil shale primary oils as a function of the evaporative loss of progressively heavier oil constituents by using a

non-isothermal Knudsen effusion method [13–15]. This is similar to previous cellulose tar [14] and tobacco tar [15] measurements. In the present study, the further conversion of the obtained vapor pressure curves to vapor pressure curves of evaporating pseudo-components, or to the vapor pressure correlations used in pyrolysis models as seen in [13], was not done due to uncertainty in molecular weight data. The term primary indicates that the oil is a result of primary pyrolytic reactions and has not gone through additional secondary reactions in the hot zone, and therefore, is somewhat different from higher boiling fractions obtained from industrial retorts. Therefore, the present data are informative from a primary pyrolysis oil vaporization point of view, enabling a quantitative insight into the vaporization ability of the oil during the pyrolysis process.

2. Materials and methods

2.1. Materials

The oil shale oil for this study was produced via rapid pyrolysis from Estonian Kukersite oil shale in a laboratory scale reactor. The ultimate analysis of the oil shale sample on a dry basis showed it to contain 34.09% ash, 43.71% carbon, 5.46% hydrogen, 1.77% sulfur and less than 0.5% nitrogen (all in wt%). A detailed description of the oil preparation procedure and characterization were presented in our earlier paper [16]. In short, three identical pyrolysis experiments were performed to collect the oil sample. In each experiment about 2 g of the oil shale from the same source was pyrolyzed in a tubular reactor up to 550 °C. The heating rate of the sample was higher than 5 °C/s and residence time of volatiles in the hot zone was about 3 seconds. The carrier gas used was N_2 with a flow rate of 330 ml/min. The condensable pyrolysis volatiles were collected in a cold trap filled with tetrahydrofuran (THF) at 0 °C. The solvent was then evaporated in a vacuum oven at 40 ± 5 °C. Despite the mild oven conditions applied, it was estimated, with comparison to the corresponding Fisher assay [3] and thermogravimetric analysis data [16], that about 40% by weight of the lighter and more volatile oil fraction was lost in the process (i.e. the oil with a molecular weight greater than 150–200 daltons was collected, see [13]).

The collected low-volatile oil fraction used in vapor pressure measurement experiments constitutes about 60% by weight of the total oil of pyrolysis. Characterization of the low-volatile oil, presented in [16], showed that its elemental composition was the following: 80.05 wt% C, 8.71 wt% H, 0.58 wt% N and 10.66 wt% O + S (by difference). This gave an atomic H/C ratio of 1.3. The low-volatile oil had a wide molecular weight distribution (average molecular weight of 400 g/mol with species up to 1000 daltons). It was also structurally complex, with a considerable amount of OH groups, as seen from FTIR spectra. According to literature, phenolic compounds with roughly linear, long alkyl chains are one of the major types of oxygen-containing compounds in Kukersite oil shale fast pyrolysis tars [17].

Likewise, for Kukersite oils from the solid heat carrier industrial retort, the fraction boiling between 200 and 350 °C (with an average molecular weight of about 250 g/mol) contains about 20 wt% phenolic compounds [18]. Reference [16] indicated that the H/C ratio of oil fractions evaporated progressively at higher temperatures showed a decreasing trend with molecular weight increase; however, the oxygen weight percent stayed between 8 and 9.5 wt%, or the atomic O/C ratio was around 0.08. The data suggested that an average molecule of tar with a molecular weight of 300 g/mol would contain roughly 1.5 oxygen atoms and a tar molecule with a molecular weight of 500 g/mol would have approximately 3 oxygen atoms.

2.2. Experimental

The Knudsen effusion technique using a continuous temperature change mode [14] was applied to determine vapor pressure curves of oil shale oil as a function of weight percent vaporized (or left in the sample). The general principle of Knudsen effusion techniques involves measuring the rate at which molecules of the evaporating substance are lost through a hole in the cap of a hermetically sealed effusion cell into a high vacuum under molecular flow conditions [19]. The experiments are traditionally performed through isothermal steps [20, 21]. The continuous measurement version of the Knudsen effusion method used in this study is a modification employed for mixtures with a wide range of volatility. The Knudsen effusion apparatus used was identical to the system applied for vapor pressure measurements of biomass tars and biomass related compounds shown in [15, 20].

The experiments involved continuously tracking the rate of oil loss during a series of cooling-heating cycles, carried out with a heating rate of 0.6 °C/min. Since the oil composition changes during the evaporative loss of its lighter components, the temperatures of successive cooling-heating cycles were continually raised from 50 °C to 190 °C to keep the vapor pressure in the range of 10^{-6} to 10^{-3} torr. The maximum temperature of 190 °C was believed to be sufficiently low to avoid significant thermal degradation of the oil sample, at least on the basis of what was observed in coal tar vapor pressure and Kukersite oil shale primary tar vaporization studies [13, 16]. For details on the experimental procedure see [14]. The specific equation applied to convert mass loss rate data to vapor pressure data had the following form [13]:

$$P = 17.1463 \frac{\omega}{t\, A_0\, W_0} \sqrt{\frac{T}{MW}} \, , \tag{1}$$

where P is the vapor pressure, torr; ω is the weight loss in grams during the effusion time interval t, sec; A is the area of the orifice, cm^2; MW is the molecular weight of the effusing vapor, g/mole (or the pseudo-molecular weight of fractions evaporated during the cooling-heating cycle); T is the absolute temperature, K; W_0 is the Clausing probability factor obtained by

interpolation from the table given by Dushman [19]. It was assumed that each evaporated fraction could be considered as a single pseudo-component, described by an average molecular weight. As a first approach, the average molecular weight values of the effusing oil vapors for each cooling-heating cycle were derived from a Field ionization mass spectrometry (FIMS) experiment performed on the whole low-volatility oil sample collected (presented in [16]). The FIMS experiment allowed the molecular weight of the evaporating species to be related to the evaporative loss of oil, both on a mass and mole basis. The following equation was derived:

$$MW = 612.64x + 183.38, \qquad (2)$$

where x is the wt% of oil evaporated. The data showed that molecular weight varies roughly in a linear fashion with mass loss. This trend is similar to that observed in coal tar studies where a roughly linear relationship between molecular weight, measured by a vapor pressure osmometer, and mass loss was derived from the vacuum sublimation data [13]. In the present study, the vaporization of a microgram-sized sample (about 50 µg) in FIMS into a high vacuum with a slow heating rate of 3 °C/min overestimated molecular weight values due to shorter residence times. Therefore, after initial vapor pressure calculations the molecular weight values were adjusted by comparing heats of vaporization (derived from slopes of vapor pressure curves) with pure compound values from literature [22]. Then the vapor pressure calculations were re-performed. As the Knudsen equation (Eq. 1) is quite insensitive to molecular weight values (± 50 g/mol above 250 g/mol results in vapor pressure error below 10% and the error decreases with molecular weight increase), then the molecular weight uncertainty should not lower vapor pressure measurement accuracy considerably.

3. Results and discussion

The prepared whole low-volatile oil was subjected to five successive cooling-heating cycles, while mass loss and mass loss rate (or vapor pressures calculated via Equation (1)) of the oil were tracked continuously. Each of the cooling-heating cycles started with a cool-down step which was then followed by a heating step. The initial sample mass in the effusion cell was 11.91 mg and the sample remaining at the end of the experiment was 4.96 mg. Thus, more than half of the low-volatile oil was examined. Before the first cooling-heating cycle 1.7 wt% of the tar was evaporated at 60 °C in order to make the sample uniform before measurements. In total five cooling-heating cycles were studied, corresponding to 88 wt%, 74 wt%, 64 wt%, 54 wt% and 43 wt% of low-volatility oil left in the effusion cell (at the point where the cool-down step ends and the heat-up step starts), and thus, five vapor pressure curves were obtained. The initial pseudo-molecular weights of evaporating oil at the indicated extents of mass loss were taken as

255, 340, 410, 470 and 535 g/mol (estimated from FIMS data). Experimentally measured vapor pressure data of all heat-up and cool-down steps were fitted individually to an integrated Clausius-Clapeyron vapor pressure equation (the simplest two-constant vapor pressure equation). During a cooling-heating cycle the route of the vapor pressure curve during the cool-down step differed somewhat from that of the immediately following heat-up step curve due to the shift in the composition of the oil. Thus, for deriving a cooling-heating cycle vapor pressure equation an arithmetic average of the corresponding integrated Clausius-Clapeyron equation constants of the cool-down and heat-up steps (described as the intercept, which is proportional to vaporization entropy, and slope, which is proportional to vaporization enthalpy or heats of vaporization) was taken. A comparison of the heat of vaporization values obtained (for characteristic values see column 5, Table) with those of pure compounds at the same temperatures (from [22]) suggests that somewhat lower molecular weight values should have been used in the calculations. Therefore values 250, 300, 350, 400 and 450 g/mol were evaluated to be more reliable and re-calculations were performed.

Figure 1 presents graphically the vapor pressure curves obtained (extrapolated vapor pressures up to predicted critical temperatures, predicted by Klincewicz's relation [23]) of five cooling-heating cycles in the form of the integrated Clausius-Clapeyron equation, presented as

$$\ln P = B - \frac{\Delta H}{R\,T} = B - \frac{A}{T}, \qquad (3)$$

where A and B are empirically determined constants; P is the vapor pressure, torr; R is ideal gas constant; ΔH is the heats of vaporization, J/mol; and T is the absolute temperature, K. The heats of vaporization, ΔH, actually the term $\Delta H/\Delta Z$ (the heats of vaporization divided by the difference between vapor and liquid compressibility factors), were assumed to be independent of temperature during the extrapolation out from the measured temperature (or pressure) region. The actual measured vapor pressure curves were measured in the pressure region from $\ln P = -10$ to $\ln P = -6$, given as the natural

Table. Vapor pressure data derived for progressively less volatile Kukersite oil shale oil as a function of mass remaining

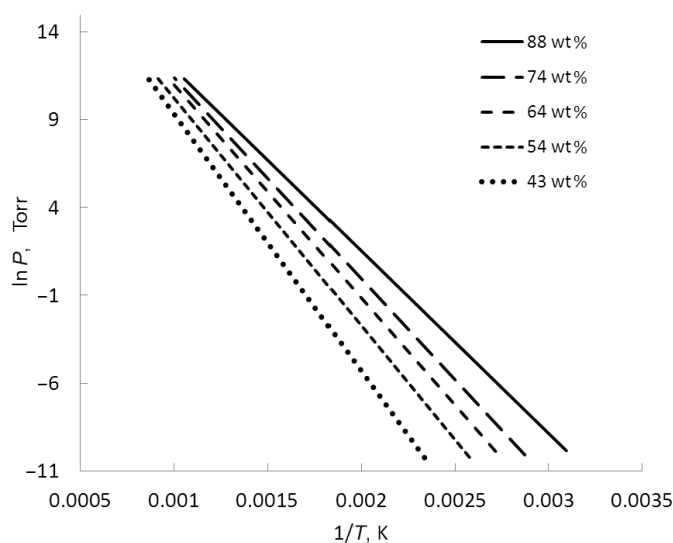| wt% of oil remaining, as % of the prepared low-volatile oil	wt% of oil remaining, as % of the total primary pyrolysis oil	B	A	$\Delta H =$ A*R/1000, kJ/mol	T_b, °C
88	53	22.30	−10388.6	86.5	390
74	44	22.90	−11486.0	95.5	432
64	38	23.18	−12174.0	101	462
54	32	23.23	−12985.0	108	509
43	26	24.00	−14663.0	122	571

Fig. 1. Vapor pressure curves of Kukersite oil shale oil. The legend values are the weight percent of the volatile oil remaining, when expressed as a percent of the pre-prepared low-volatile oil.

logarithm of the pressure. Derived values (integrated Clausius-Clapeyron equation constants A and B, enthalpy of vaporization and atmospheric boiling points) are summarized in the Table for each cooling-heating step. In column 2 of the Table the mass loss of the total oil of pyrolysis basis is given for illustrative purposes. The weight of the total oil of pyrolysis was estimated from the observation that the collected lower-volatile oil was about 60 wt% of the total oil formed during pyrolysis. It can be seen that there is, in a larger view, an increase in the magnitude of both entropy and enthalpy terms with mass loss, and therefore, with molecular weight of the vaporizing species. The enthalpy of vaporization is related to the slope of the ln P vs $1/T$ curve and the entropy of vaporization is related to the intercept value of the same curve. The data for the intercept (tabulated in column 3, Table) with mass loss shows values quite close to a kind of linearly increasing trend. The data for the slope (tabulated in column 4, Table) clearly shows an exponentially increasing behavior. The slope values (vaporization enthalpy divided by R, the ideal gas constant) are proportional to vaporization enthalpies of progressively less volatile oil at average measurement temperatures. These temperatures were 75, 100, 125, 150, 175 $^{\circ}$C, respectively.

Figure 2 presents the atmospheric boiling curve of progressively less volatile oil when expressed as a function of the mass left after the lighter fractions were evaporated (tabulated in column 6, Table). The Figure indicates, on the basis of total pyrolysis oil, that when 75 wt% of oil is evaporated, then the 25 wt% of oil which is left has an atmospheric boiling
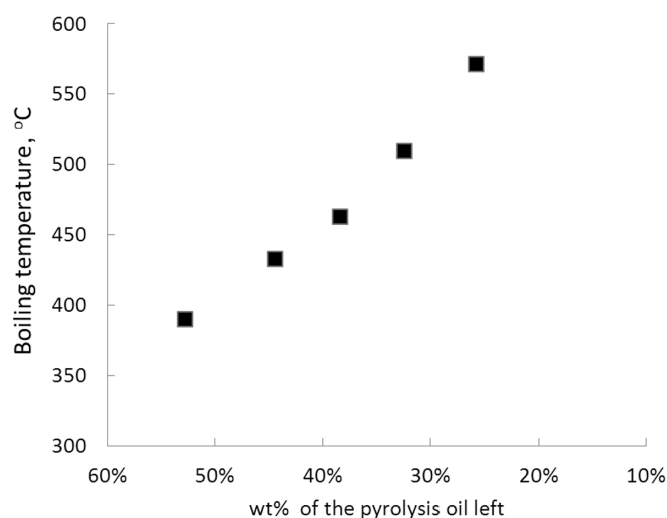
Fig. 2. Atmospheric boiling curve of progressively less volatile oil as a function of the mass remaining after the progressive evaporation of lighter fractions, when expressed as a percent of the total primary pyrolysis oil.

point (T_b) higher than 550 °C, i.e. higher than typical retorting temperatures. This suggests that most of the oil formed is at boiling conditions in an atmospheric pressure retorting (or low-temperature pyrolysis) process.

4. Conclusions

A non-isothermal modification of the conventional Knudsen effusion technique was applied to study quantitatively the vapor pressure of Kukersite oil shale primary oil (or tar), prepared by low-temperature fast pyrolysis. A monotonic increase in vaporization enthalpy and boiling point values was seen as the mass of volatile oil left decreased, or as the molecular weight of the vaporizing species increased. The data show that most of the pyrolysis oil can volatilize below retorting temperatures, since the boiling point rises above 550 °C (above the retorting temperature) only when 75 wt% of the oil has vaporized.

Acknowledgements

REFERENCES

1. Oja, V. Is it time to improve the status of oil shale science? *Oil Shale,* 2007, **24**(2), 97–99.
2. Urov, K., Sumberg, A. Characteristics of oil shales and shale-like rocks of known deposits and outcrops. *Oil Shale*, *Monograph,* 1999, **16**(3), 1–64.
3. Oja, V., Elenurm, A., Rohtla, I., Tali, E., Tearo, E., Yanchilin, A. Comparison of oil shales from different deposits: oil shale pyrolysis and co-pyrolysis with ash. *Oil Shale,* 2007, **24**(2), 101–108.
4. Lille, Ü. Behavior of Estonian kukersite kerogen in molecular mechanical force field. *Oil Shale*, 2004, **21**(2), 99–114.
5. Savest, N., Oja, V., Kaevand, T., Lille, Ü. Interaction of Estonian kukersite with organic solvents: A volumetric swelling and molecular simulation study. *Fuel*, 2007, **86**(1–2), 17–21.
6. Savest, N., Hruljova, J., Oja, V. Characterization of thermally pretreated kukersite oil shale using the solvent-swelling technique. *Energ. Fuel.*, 2009, **23**(12), 5972–5977.
7. Solomon, P. R., Serio, M. A., Suuberg, E. M. Coal pyrolysis: Experiments, kinetic rates and mechanisms. *Prog. Energy Combust. Sci.,* 1992, **18**(2), 133–220.
8. Kilk, K., Savest, N., Yanchilin, A., Kellogg, D. S., Oja, V. Solvent swelling of Dictyonema oil shale: Low temperature heat-treatment caused changes in swelling extent. *J. Anal. Appl. Pyrol.,* 2010, **89**(2), 261–264.
9. Smith, K. L., Smoot, L. D., Fletcher, T. H., Pugmire, R. J. *The Structure and Reaction Processes of Coal.* The Plenum Chemical Engineering Series: New York, 1994.
10. Solomon, P. R., Hamblen, D. G., Carangelo, R. M., Serio, M. A., Deshpande, G. V. General model of coal devolatilization. *Energ. Fuel.,* 1988, **2**(4), 405–422.
11. Niksa, S., Kerstein, A. R. FLASHCHAIN theory for rapid devolatilization kinetics. 1. Formulation. *Energ. Fuel.,* 1991, **5**, 647–665.
12. Grant, D. M., Pugmire, R. J., Fletcher, T. H., Kerstein, A. R. Chemical model of coal devolatilization using percolation lattice statistics. *Energ. Fuel.,* 1989, **3**(2), 175–186.
13. Oja, V., Suuberg, E. M. Measurements of the vapor pressures of coal tars using the nonisothermal Knudsen effusion method. *Energ. Fuel.,* 1998, 1**2**, 1313–1321.
14. Oja, V., Suuberg, E. M. Development of a nonisothermal Knudsen effusion method and application to PAH and cellulose tar vapor pressure measurement. *Anal. Chem.,* 1997, **69**, 4619–4626.
15. Shim, H.-S., Oja, V., Hajaligol, M.R. Vapor pressure measurements of tobacco pyrolysis tar by a non-isothermal Knudsen effusion method. *J. Anal. Appl. Pyrol.,* 2003, **66**(1–2), 183–190.
16. Oja, V. Characterization of tars from Estonian Kukersite oil shale based on their volatility. *J. Anal. Appl. Pyrol.,* 2005, **74**(1–2), 55–60.
17. Derenne, S., Largeau, C., Casadevall, E., Sinninghe Damste, J. S., Tegelaar, E. W., de Leeuw, J. W. Characterization of Estonian Kukersite by spectroscopy and pyrolysis: Evidence for abundant alkyl phenolic moieties in an Ordovician, marine, type II/I kerogen. *Org. Geochem.*, 1990, **16**(4–6), 873–888.

18. Traumann, A., Tint, P., Järvik, O., Oja, V. Management of health hazards during shale oil handling. *Agronomy Research*, 2013, **11**(2), 479–486.

19. Dushman, S. *Scientific Foundations of Vacuum Technique* 2nd ed.; Wiley: New York, 1962.

20. Chen, X., Oja, V., Chan, W. G., Hajaligol, M. R. Vapor pressure characterization of several phenolics and polyhydric compounds by Knudsen effusion method. *J. Chem. Eng. Data,* 2006, **51**, 386–391.

21. Oja, V., Chen, X., Hajaligol, M. R., Chan, W. G. Sublimation thermodynamic parameters for cholesterol, ergosterol, β-sitosterol, and stigmasterol, *J. Chem. Eng. Data,* 2009, **54**(3), 730–734.

22. Chickos, J. S., Acree, W. E., Jr. Enthalpies of vaporization of organic and organometallic compounds 1880–2002. *J. Phys. Chem. Ref. Data,* 2003, **32**(2), 519–878.

23. Owczarek, I., Blazej, K. Recommended critical temperatures. Part I. Aliphatic hydrocarbons. *J. Phys. Chem. Ref. Data,* 2003, **32**(4), 1411–1427.