

EFFECT OF ORGANIC MATTER CONTENT AND TYPE OF MINERAL MATTER ON THE OIL YIELD FROM OIL SHALES

ILLE JOHANNES^{(a)**}, HANS LUIK^(a), JØRGEN A. BOJESEN-KOEFOED^(b), LAINE TIIKMA^(a), NATALIA VINK^(a),
LEA LUIK^(a)

- ^(a) Tallinn University of Technology
Department of Polymer Materials
Laboratory of Oil Shale and Renewables Research
5 Ehitajate Rd., 19086 Tallinn, Estonia
- ^(b) Geological Survey of Denmark and Greenland (GEUS)
10 Øster Voldgade, DK-1350K Copenhagen, Denmark

Abstract. *The effect of organic matter (OM) content and type of mineral matter (MM) on the oil yield at retorting of different natural oil shale samples, those demineralized by acid treatment ones, and the kukersite OM flotation concentrate mixed with individual minerals has been described basing on the previously published results. The influence of OM content in Estonian kukersite natural samples and their flotation concentrates on the yield of benzene extract after supercritical water conversion and thermobituminization in autoclaves, and on evolution of hydrocarbons in source rock analysis (SRA) has been studied experimentally. A comparative study has been carried out by plotting the oil yields versus the according OM contents. The variations in the adsorption capacity of oil on MM and in the oil yield from a unit of OM are characterized by the values of intercept and slope of the approximated linear trendlines.*

Keywords: *oil shale, pyrolysis, organic matter, mineral matter.*

1. Introduction

As the reserves of petroleum are being depleted, oil shales become more and more important as an alternative source of liquid fuels. The age and organic matter (OM) content of oil shales can vary in wide ranges, and carbonates, aluminosilicates or silicates can prevail in their mineral matter. Urov and Sumberg [1] have collected together characteristic data for a hundred known oil shale deposits and outcrops. In their monograph the lowest content of

* Corresponding author: e-mail ille.johannes@ttu.ee

conditional OM is 5.4% in the shale from Yarmuk (Syria) Lower Eocene deposit, and the highest is 96.9% in the shale from Olenyok (Russia, Yakutia) Cretaceous deposit. Understandable that higher content of OM should result in more shale oil at pyrolysis. The effect of content and composition of mineral matter (MM) on the oil yield from various oil shales has been studied in several works [2, 3, 5–19]. The oldest and most applied and investigated oil extraction procedure has been laboratory retorting in the device open to the air using the standard Fischer Assay according to ISO-647-74 [4]. The open-air procedures are also derivatographic (TG) and Rock-Eval analysis methods for which the sample mass is five orders less than in the standard pyrolysis procedure, and changes in the mass loss or evolution of volatiles are monitored in an inert atmosphere under the chosen programmed temperature regime. Besides, oil shale sub- and supercritical dissolution and thermobituminization in autoclaves have been investigated. The MM content in the initial samples has been varied selecting a row of the appropriate natural shales, treating the initial shales with acid solutions, or mixing OM concentrate and different minerals.

This work discusses the effect of OM content on the oil yield at retorting of different oil shales basing on the results of previously published investigations and describes our experimental results concerning the effect of OM content on the yield of benzene extract after autoclaving liquefaction of Estonian oil shale (kukersite) using water-conversion under supercritical conditions and low-temperature thermobituminization, and also open to the air source rock analysis (SRA) method. The relationship of oil yield from initial samples versus OM is approximated to a linear trendline $Y_1 = a + b[\text{OM}]$ where the slope b characterizes the mean oil yield from the OM unit under the pyrolysis conditions studied, and the ratio $-a/b$ shows the content of OM below which no oil can be extracted because of its adsorption and coking on the surface of MM.

2. Discussion of the previous results

2.1. Retorting

Determination of the actual OM content in shales has been difficult, especially because of the necessity of taking into account the water in crystal hydrates in case no sufficient data were available. So, in the majority of investigations the so-called conditional organic mass, $\text{OM} = 100 - A^d - (\text{CO}_2)^d$, corresponding only approximately to the actual OM content, or the total organic carbon (TOC) have been applied.

Plot of the oil yields (Y_{OS}) from initial samples versus the conditional OM values of 94 oil shale samples under the standard retorting conditions characterized in [1] demonstrates a roughly (regression coefficient $R^2 = 0.78$) linear relationship (Fig. 1, curve 1)

$$Y_{\text{OS}} = -2.62(\pm 0.87) + 0.465(\pm 0.026)\text{OM}. \quad (1)$$

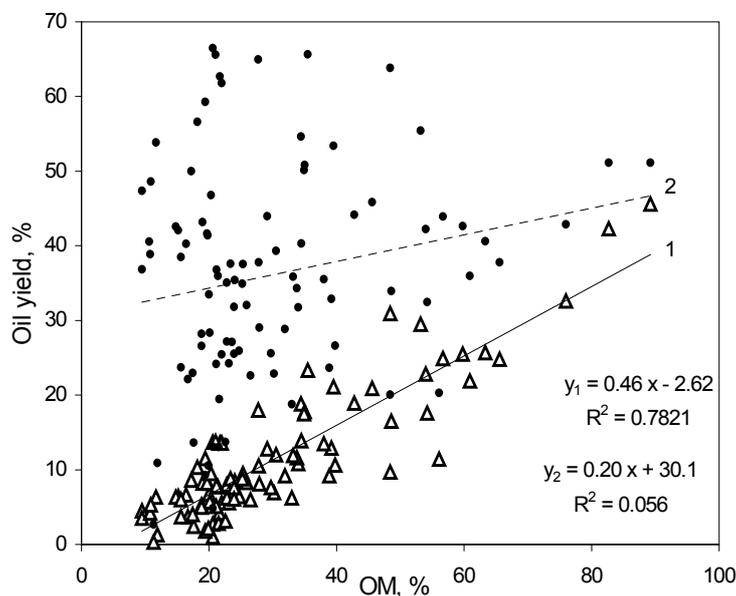


Fig. 1. Effect of OM content on the oil yield at retorting of world oil shales from initial samples [1] (Δ , trendline 1) and from their OM (\bullet , trendline 2) *.

According to Eq. (1) oil cannot be distilled at retorting if the OM content is below 5.7% ($2.62/0.46$). Presumably, all the small quantity of oil formed from OM of more poor shales adsorbs and cokes on the prevailing MM. The noteworthy dispersion of the oil yields from the linear trendline 1 can be caused mainly by different compositions of both OM and MM of the oil shales. Therefore, the oil yield from OM of different samples is not a constant value. Despite the wide diffusion and very low regression coefficient of the oil yield from a unit of OM (Y_{OM}) in Fig. 1 curve 2, a slight tendency to increase with increasing content of OM is revealed as follows:

$$Y_{OM} = 30.1(\pm 3.0) + 0.198(\pm 0.090)OM. \quad (2)$$

Unfortunately, the extreme variation of the oil yields at any value of OM allows to choose any alternative group of samples with fewer experimental points indicating, on the contrary, that the increase in OM content decreases or has no influence on the oil yield. For example, the data given in a recent paper by Oja *et al.* [5] on the oil yield from five different shales under standard Fischer Assay can be compared. In the range of the shales tested (Fig. 2) the effect of OM content on the oil yield from initial samples ($b = 0.757$) is 1.6 times more intensive than the average effect in Fig. 1 ($b = 0.46$). But the oil yield from OM reveals a sharp increase from 20 to 60% near 20% of OM and thereafter is almost independent of OM content.

* Here and further in the figures, except Fig. 7, open symbols show the yields from initial samples and closed ones from initial OM.

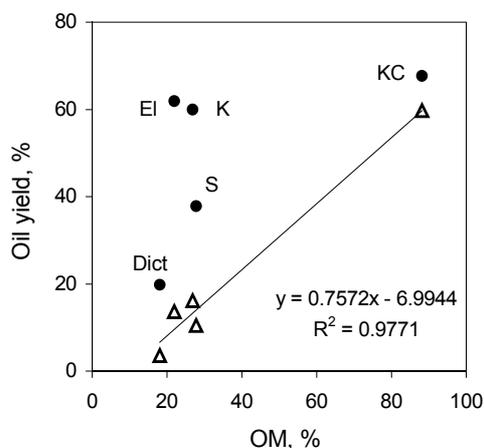


Fig. 2. Effect of OM content on the oil yield from different initial samples (Δ , trendline 1) [5] and from their OM (\bullet): Dict – Dictyonema argillite (Estonia), El – El-lajjun (Jordanian), S – Saveljev (Volga basin, Russia), K – Kukersite (Estonia), KC – Kukersite OM concentrate.

Likewise, the oil yield from different layers of Jordanian El-lajjun deposit (Fig. 3) taken from paper [6] is proportional ($R^2 = 0.929$) to the total organic carbon content (TOC) in the samples, but there is no regularity in the high oil yield, $83(\pm 16)\%$ from TOC, which even rather decreases with increasing TOC.

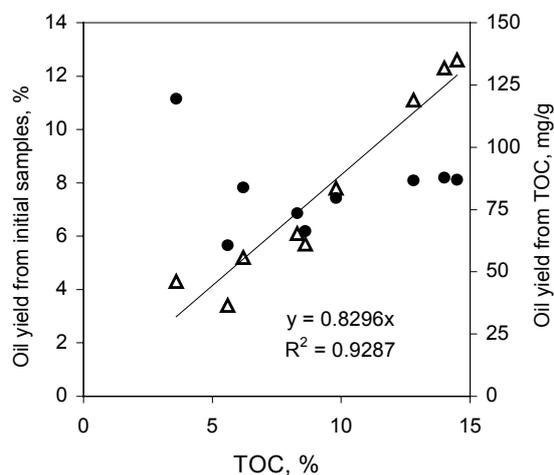


Fig. 3. Effect of TOC content on the oil yield from initial samples (Δ) [6] and from their TOC (\bullet) at retorting samples from different layers of Jordanian El-lajjun deposit.

The pyrolytic behavior of seven Spanish oil shales differing in geological age, depositional environment and source location [7] depicted in Fig. 4 proves the proportionality of the yield of hydrocarbons (HC) from the different shales to TOC whereas the value of b and the HC yield from TOC is roughly 1.2 times lower than the yield of total oil from the TOC of Jordanian shales given in Fig. 3.

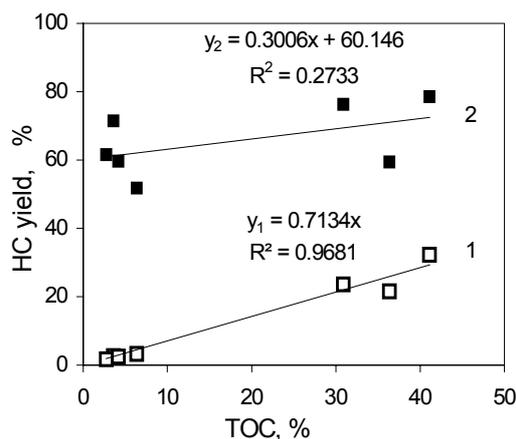


Fig. 4. Effect of TOC content on the yield of hydrocarbons in Rock-Eval analysis of Spanish different oil shales [7] (□, trendline 1) and from their TOC (■, trendline 2).

Borrego with co-authors [7] has studied pyrolysis of the initial and acid-treated OM concentrates of Spanish oil shale using Rock-Eval analysis. The authors have concluded that the adsorptive action of the various clay minerals tested is different and therefore rather difficult to systematize. In addition, montmorillonite has shown to have some catalytic effects in advancing the initiation temperature of kerogen cracking.

So, it can be supposed that the fluctuations in the oil yield from OM or TOC above are caused by the composition of both organic and mineral matter. At that, a higher content of aromatic compounds in OM expressed by a lower ratio of H/C would favor coke formation and decrease the oil yield from OM. The diffuse cloud (R^2 for the linear trendline is only 0.0249) of the corresponding data taken from [1] and depicted in Fig. 5 shows that the H/C ratio, like OM content, has only a trivial increasing effect on the average oil yield from OM.

Basing on the oil yields at retorting of four carbonaceous and three clay mineral oil shales, Sidorovitch [8] has deduced an empirical relationship

$$Y_{OM} = 100H/(O + S + N) + 0.25K + 0.45S, \quad (3)$$

where Y_{OM} – oil yield, K – total content of CaO and MgO in oil shales, H, O, S, N – content of these elements in OM, %.

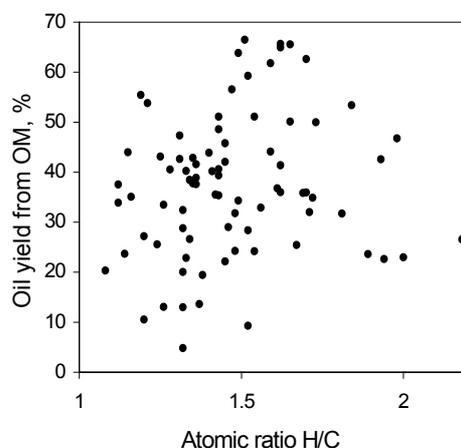


Fig. 5. Effect of H/C atomic ratio on the oil yield from OM at retorting.

As a rule, a statistic equation is valid only in the range of the data applied for its deduction. So, introduction into Eq. (3) content of the elements in 47 oil shale samples published in [1] gives significantly overestimated calculated oil yields as shown by dark points and their linear trendline (curve 1) in Fig. 6. Using the same data from [1] in Regression Analysis Tools for Data Processing in Excel results the relationship with the following coefficients:

$$Y_{OM} = 46.9H/(O + S + N) + 0.59K + 2.44S. \quad (4)$$

As it can be supposed, the oil yields, predicted by Eq. (4) and presented in Fig. 6 as curve 2, depict more realistic results never overcoming 100%. Nevertheless, the correlation of the experimental results and calculated ones

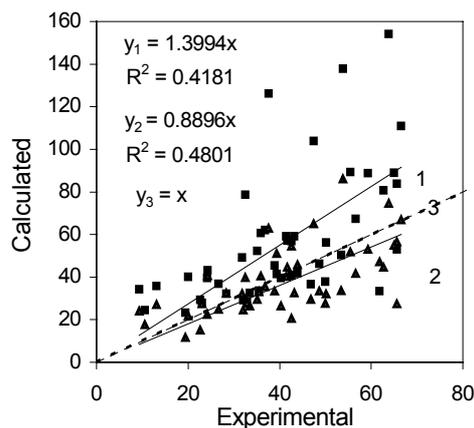


Fig. 6. Comparison of the experimental oil yields from OM at retorting [1] with the data calculated using Eq. (3) (■, trendline 1), Eq. (4) (▲, trendline 2) and diagonal (3) expressing coincidence of the experimental and calculated oil yields.

according to the both equations is unsatisfactory ($R^2 < 0.5$) for the oil shales differing in composition, especially in their mineral matter.

Later Sidorovich [9] has established a correlation between volatiles (V), ash content (A) and OM elementary composition (daf) basing on 26 Russian shale samples as follows:

$$V = (1 - A/100)(7.0H + 0.37O + 1.10S), \quad (5)$$

where the role of noncombustible minerals should be considered in A as clay minerals, siderite, magnesite, and pyrite can give gaseous volatiles during heating.

2.2. Effect of demineralization of oil shales on oil yield

For separation of organic and mineral matters of oil shales several physical and chemical isolation and concentration procedures have been proposed.

It has been found [6, 8, 10, 11] that the conventional hydrochloric/hydrofluoric acid treatment is effective for removing most carbonate, oxide, and monosulphide minerals from sedimentary rocks and leaves kerogen and pyrite largely unaffected. Effective removal of pyrite is usually the main problem because oxidative removal of pyrite is not possible without alterations in the organic composition. The magnitude of the change in the organic matter depends on the chemical nature of kerogen as well as on reaction conditions. The extent of oxidation of oil shales and coals by HNO_3 varies, but introduction of carboxyl groups and additional nitrogen has been noticed. This effect can be minimized by using diluted acid at moderate temperatures for a short time. To eliminate the effect of variations in group and elemental composition of OM, the effect of MM on the oil yield of individual oil shales will be discussed below.

According to Al-Harashsheh [6], the treatment of Jordanian oil shale with HCl increased the ratio of oil to gas as a result of the dissolution of calcite in the oil shale and, at higher concentrations of HNO_3 , the acid reacted with kerogen resulting in higher amount of low molecular weight compounds. Therefore, the amount of noncondensable gases produced by Fischer Assay after treatment with a high concentration of HNO_3 was relatively high. HF was believed to drive off water from oil shale by dissolving clay minerals leading to an increased oil-to-gas ratio.

The results of TGA kinetic analysis of Moroccan oil shale proved [2] that the removal of mineral matter caused a decrease in the activation energies of pyrolysis reactions of oil shale OM.

Ballice and Sert [10, 11] have isolated kerogen from Beypazari (Turkey) oil shale by successive treatments with HCl, HNO_3 and HF. A series of temperature programmed pyrolysis operations established that carbonates of alkali and alkaline earth metal cations affected the reactivity of oil shales on TOC basis. The leaching of these MM with HCl caused a slightly decrease in the conversion to volatile hydrocarbons. The following removal of pyrite with HNO_3 did not affect the reactivity of organic material. However,

removal of the silicates soluble in HF increased the conversion of OM at pyrolysis. It was explained by the inhibitive effect of the silicate minerals and by better heat transfer from outside towards the inside of oil shale particles after complete removal of the mineral matrix.

2.3. Effect of OM content on the oil yield at retorting of model mixtures

The influence of addition 10% of KCl, K_2CO_3 , Na_2CO_3 , $CaMg(CO_3)_2$, Fe_2O_3 or Al_2O_3 to hemicellulose, cellulose and lignin was investigated by Yang *et al.* using TGA [12]. All the minerals demonstrated a negligible influence, except K_2CO_3 whose addition inhibited the pyrolysis of hemicellulose by lowering its mass loss rate by 0.3 wt% / °C, but enhanced the pyrolysis of cellulose by shifting the pyrolysis to a lower temperature. With increased amount of K_2CO_3 added, the weight loss of cellulose in the lower temperature zone (200–315 °C) increased greatly and the activation energies of hemicellulose and cellulose pyrolysis decreased notably from 204 to 42 kJ/mol.

Oja *et al.* [5] have proved that at co-pyrolysis of Estonian kukersite oil shale and its alkaline ash (850 °C) in the 1:2 mix (as it is common in the industrial heat carrier system “Enefit”) under standard Fischer Assay conditions, the total oil yield from OM is decreased by 8–10%, sulphur concentration in the oil shows a few percent decrease while H_2S concentration in retorting gas decreases from 8.8 vol.% to 0.4 vol.%.

The most comprehensive study of the effect of different ingredients of the Estonian kukersite MM on the yield of retorting products in Fischer Assay was carried out by Urov and Vysotskaya [13–19]. For this aim, model mixtures consisting of kukersite flotation concentrate (A^d – 9.3%, CO_2^d – 0.2%), and its main minerals [alumosilicates, carbonates, pyrite, quartz, kaolinite and halloysite, and enrichment residue of Dictyonema shale (Dict. MM)] were pyrolyzed in the range of OM content between 28–90%. The oil yields obtained in this research work are compiled for comparison in Fig. 7.

The results in Fig. 7a confirm an increase in the oil yield from the initial mixes of kerogen with the minerals with increasing OM content. At that, adsorption on quartz (SiO_2), Ca and Mg carbonates and pyrite (FeS_2) is negligible, as far their total trendline (y_1) is strictly proportional to OM content and crosses the zero-point of the axes. The sorption effect of the individual clay minerals is evident in the negative value of the intercept of their total trendline (y_2), whereas its sharper rise with increasing OM (or sharper slope with increasing MM) shows an inhibiting effect of minerals on the OM thermal decomposition into oil. Figure 7b reveals that the adsorption effect at high concentrations of clay minerals is the main reason for low oil yield from OM of poor shales in retorting. At that, the unwanted effect of kaolinite [$Al_2Si_2O_5(OH)_4$] is lower than that of halloysite [$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$] transforming at 75 °C into kaolinite. It agrees with the earlier work [18] where the inter-layer water eluted was supposed to form a new internal surface that caused a higher sorption activity. The effect

of Dictyonema MM (y_3) consisting of the both mineral groups is between the trendlines y_1 and y_2 .

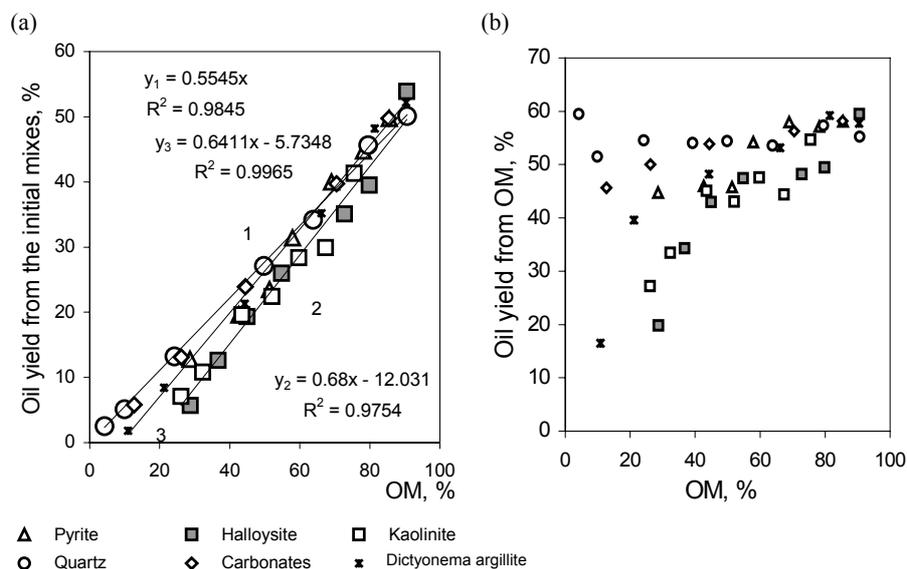


Fig. 7. Effect of OM content on the oil yield from initial samples (a) and OM (b) at retorting of mechanical mixes of kerogen with different minerals. Trendlines: 1 – total for quartz, pyrite and carbonates, 2 – total for halloysite and kaolinite, and 3 – Dictyonema MM.

2.4. Effect of OM content on the oil yield in liquefaction using confined systems

All the results above have been obtained using open pyrolysis systems. There have been only few works concerning the effect of OM content on the liquefaction of oil shales in autoclaves. Researchers from China [20] have studied the distribution and maturation behavior of biomarkers hopanoids and steranes released from the kerogen of Estonian kukersite during pyrolysis experiments, performed in gold capsules in the presence and absence of water and kaolinite, montmorillonite, calcite or dolomite at a fixed pressure of 50 MPa and temperature ranging from 240–320 °C. The results show that the maturation rates of hopanoids and steranes increase with mineral acidity but decrease with the addition of water.

3. Experimental

In the frames of the experimental work of the present paper, unlike the earlier investigations above, the content of mineral matter was varied in the range of 30-90% neither by acid treatment of the shale nor by mixing of

different minerals with OM but taking the Estonian kukersite oil shale natural samples from different layers and the flotation concentrates containing 70 and 90% of OM. The composition of the kukersite OM is known to be practically uniform in all its deposits having the approximate empirical molecular formula $C_{421}H_{638}O_{44}S_4NCl$ [20]. Three different liquefaction procedures were studied: low-temperature pyrolysis in autoclaves (thermobituminization), supercritical water conversion in autoclaves, and SRA analysis.

3.1. Thermobituminization

Pyrolysis of kukersite samples (1–4 g) of various OM content was performed in 20 cm³-autoclaves placed in a preheated to 360 °C muffle oven. According to previous investigations concerning thermobituminization of kukersite [21], the four-hour pyrolysis duration was applied, and the mix of thermobitumen and oil formed (TBO) was separated from MM in a Soxhlet extractor with benzene. The changes in the yields of gaseous phase, benzene extract, and solid residue obtained from the initial samples are presented in Table 1. The plot of the extract yield versus OM content is depicted in Fig. 8.

Table 1. Yields of the pyrolysis products in thermobituminization, % from the initial dry samples (360 °C, 4 h)

OM, %	90.1	76.0	59.3	51.0	40.5	31.8
Gas	14.06	8.74	5.63	4.85	3.80	2.32
Benzene extract	74.33	65.13	50.91	43.22	32.10	23.56
Solid residue	11.61	26.13	43.46	51.93	64.10	74.12

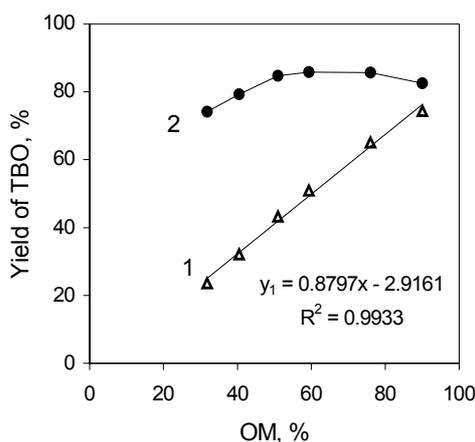


Fig. 8. Effect of OM content on the yield of benzene extract from initial samples (1) and from OM (2) after thermobituminization.

The results obtained prove that extraction of kukersite OM in the form of TBO after low-temperature pyrolysis in an autoclave attains 80% from OM. That is about 130% from the maximum oil yield obtained from the kukersite OM in Fischer Assay (Fig. 2, point K, and Fig. 8, curve 2). The curve 2 reveals a steady decrease in the TBO yield from OM with a decrease in OM content below 50%. Obviously, using more “fatty” samples there is no practical losses caused by TBO adsorption on the solid residue in this procedure.

3.2. Supercritical water conversion

In this series, 60 grams of natural kukersite samples of different OM content were mixed with 120 grams of water. The mix was heated during 2 hours at 390 °C as it was found optimal in previous investigations conducted in a 500 cm³ autoclave [22]. At the end of heating the system was cooled down to the ambient temperature, the autoclaves were opened and the amount of gases was measured. The reaction products remaining in the autoclave were diluted with benzene, and the liquid product obtained was separated from the solid one by filtration. The benzene was removed by rotary evaporation, thus the extract yield being estimated as the weight of benzene solubles. Actually, the extract obtained is TBO, presumably slightly modified by the reaction with SC water. The results of the work are presented in Table 2.

Table 2. Yields of the pyrolysis products after SC water conversion, % of the initial dry samples (390 °C, 2 h)

OM, %	90.1	76	59.3	40.52
Benzene solubles	65.2	52.9	39.6	24.5
Water solubles	0.5	0.3	0.2	0.2
Solid residue	17.5	27.6	47.4	65.1
Gas and losses	16.8	19.2	12.8	10.2

For comparison of the influence of OM content on the efficiency of water conversion with the other procedures above, the yield of total liquid products is depicted in Fig. 9.

According to Fig. 9, the minimum content of OM in the initial sample for benzene extraction of liquid products after water conversion, 10.8%, is significantly higher than 3.3% obtained at benzene extraction of thermo-bituminization products (Fig. 8). The fact that water favors adsorption of oil on the solid residue agrees with the previous results from [18, 19] depicted in Fig. 7 in which hallosite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, loosing at 75 °C its crystalline water, has the highest sorption activity. Besides, washing of the filtrate cake with hot benzene in this series could not afford so exhaustive extraction of TBO as Soxhlet extraction.

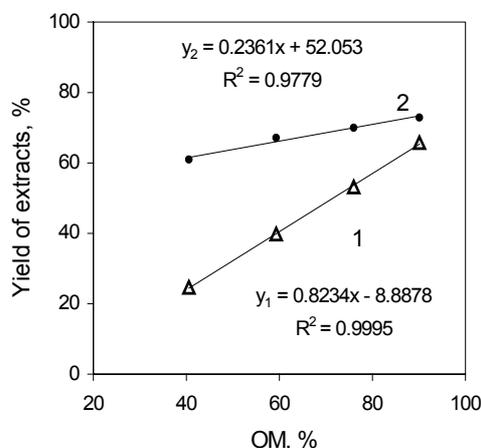


Fig. 9. Effect of OM content on the total yield of solubles in benzene and water from initial samples (1) and from OM (2) in SC water conversion.

3.3. SRA analysis

The advanced modification of Rock-Eval Analyzer, Source Rock Analyzer (SRA), was applied for characterization of the effect of OM content in the Estonian kukersite samples in Geological Survey of Denmark and Greenland. SRA, using a Flame Ionization Detector, determines quantitatively the amount of free hydrocarbons or bitumoids (S1) released at 300 °C and the amount of hydrocarbons (S2) generated through thermal cracking between 300-650 °C under the heating rate $\beta = 25$ °C/min from *ca* 25 mg of samples. Besides, the temperature at which the maximum release of hydrocarbons from cracking of kerogen occurs during pyrolysis (Tmax), and total organic carbon (TOC), hydrogen index (HI = 100S2/TOC), pyrolysable carbon (PC) and residual carbon (RC) are determined.

The results of the SRA analysis of kukersite samples are presented in Table 3 and in Fig. 10.

The data in Table 3 and the trendlines 1 and 2 in Fig. 10 evidence that evolution of hydrocarbons from the initial samples in SRA is not only significantly lower than the yield of benzene extracts from the same samples after using closed devices (Fig. 8 and 9) but it is depressed even in com-

Table 3. Results of SRA

OM, %	32.3	40	59.3	72.4	90.1
TOC, %	23.35	32.36	47.33	54.57	67.05
PC, %	13.47	15.91	18.84	20.96	24.13
S1, mg/g	0.23	0.8	1.63	5.19	7.78
S2, mg/g	162	191	225	247	282
HI	694	590	476	453	422
Tmax, °C	425	425	421	426	429

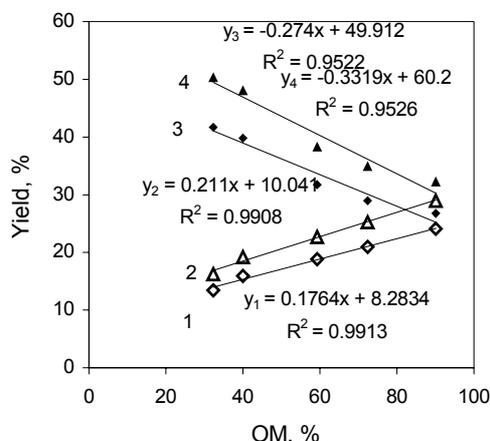


Fig. 10. Effect of OM content on the yield of total pyrolysable carbon (1, 3) and volatile hydrocarbons (2, 4) from initial samples (1, 2) and from OM (3, 4) using SRA.

parison with Fischer Assay (Fig. 1). The positive value of the intercept resulting in negative value for the adsorption characteristic, $-a/b$, suggests that the linear trendline should not be extrapolated towards lower OM concentrations than tested. The surprisingly negative slopes of the trendlines 3 and 4 demonstrate that, inversely to all the results above, an increase in OM content decreases both the evolution of hydrocarbons and total pyrolysable carbon from a unit of OM. Why in SRA the amount of residual carbon from OM of kukersite increases with OM content, needs special investigations.

The TGA results of Aboulkas [3] have shown that activation energy for evolution of volatiles (E) from isolated Moroccan kerogen is lower than that of the original oil shale. A simple possibility for preliminary evaluation of pyrolysis kinetics by approximate calculation of E basing on the data of S1, S2 and Tmax and heating rate was proposed in [23] as follows:

$$x_1 = S1(S1 + S2)^{-1} \quad (6)$$

$$T_1 = 300 + 273 \quad (7)$$

$$x_2 = (S1 + 0.5S2)(S1 + S2)^{-1} \quad (8)$$

$$T_2 = T_{\max} + 273 \quad (9)$$

$$Y_i = \ln[-\ln(1 - x_i)T_i^{-2}] \quad (10)$$

$$X_i = T_i^{-1} \quad (11)$$

$$b = (Y_1 - Y_2)(X_2 - X_1)^{-1} \quad (12)$$

$$E = b \cdot R \quad (13)$$

Introducing the data from Table 3 into the algorithms above, a decrease in E with increasing OM content is obvious for the kukersite samples in SRA pyrolysis (Fig. 10) as well.

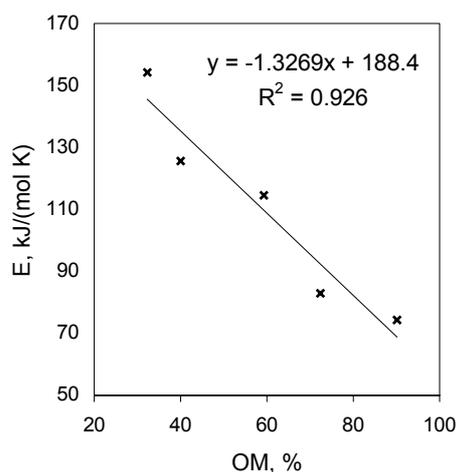


Fig. 11. Effect of OM content on the apparent activation energy for evolution of hydrocarbons from kukersite samples in SRA.

4. Conclusions

The effect of organic matter (OM) content and type of mineral matter (MM) on the oil extraction from different oil shale samples at standard retorting in Fischer Assay, TGA and SRA analysis, autoclavic thermobituminization and supercritical water conversion have been described. The oil yield and adsorption capacity of MM have been characterized by the values of slope and intercept of the approximated linear trendlines of the plots of oil yield from the initial samples versus OM content $Y_{OS} = a + b[OM]$ where the slope b shows the mean oil yield from the OM unit if there is no adsorption on MM, and the ratio $-a/b$ shows the content of OM below which no oil can be extracted because of its adsorption and coking on MM under the pyrolysis conditions studied.

The bulk of experimental results presented in this work has shown that the value of b (g/g) depends mainly on the pyrolysis procedure and increases as follows: SRA, $0.211(\pm 0.012)$ < retorting of world's natural oil shale samples ($n = 98$), $0.465(\pm 0.026)$ < retorting of kukersite kerogen mixed with quartz, pyrite or carbonates, $0.5545(\pm 0.0078)$ < retorting of kukersite kerogen mixed with Dictyonema argillite, $0.641(\pm 0.019)$, < retorting of kukersite kerogen mixed with clay minerals, $0.680(\pm 0.041)$ < benzene extract after SC water conversion of natural kukersite samples with different

OM content, $0.823(\pm 0.013) <$ benzene extract after thermobituminization of natural kukersite samples with different OM content $0.880(\pm 0.036)$.

The adsorption capacity of the solid residue depends on both the pyrolysis procedure and the type of MM. The value of $-a/b$ (%) decreases in the row: retorting of kukersite kerogen mixed with clay minerals (17.6), SC water conversion of natural kukersite samples with different OM content (10.8), retorting of kukersite kerogen mixed with Dictyonema argillite (8.9), retorting of world's natural oil shale samples (5.7), thermobituminization of natural kukersite samples with different OM content (3.3), retorting of kukersite kerogen mixed with quartz, pyrite or carbonates (0).

The oil yield obtained at laboratory standard retorting and TGA of oil shale samples demineralized by subsequent extraction with HCl, HNO₃ and HF agrees satisfactorily with the results obtained at pyrolysis of the mixes of OM and minerals characteristic to oil shale.

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