THESIS ON CHEMISTRY AND CHEMICAL ENGINEERING G44

Thermochemical Destruction of Graptolite Argillite

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This dissertation was accepted for the defense of the degree of Doctor of Philosophy in Chemistry and Materials Technology on March 17, 2016

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Defense of the thesis: April 26, 2016, at 12.00
Lecture hall U06-201
Tallinn University of Technology, Ehitajate tee 5, Tallinn

Declaration:

Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology, has not previously been submitted for doctoral or equivalent academic degree.

Galina Sharayeva

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ISSN 1406-4774
ISBN 978-9949-23-923-8 (publication)
ISBN 978-9949-23-924-5 (PDF)

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Sharayeva, G.; Luik, H.; Luik, L. Effect of of Different Temperature-Time Combinations in Kerogen Pyrolysis to Thermobitumen and Oil. International Journal of Environmental Engineering, 2015, 2 (1), 174−181.

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Johannes, I.; Tiikma, L.; Luik, H.; **Šarajeva, G**. Thermal Extraction of Oil from a Utah Green River (USA) Oil Shale in Autoclaves. International Journal of Engineering and Applied Sciences (EAAS), 2015, 6 (5), 23−35.

THE AUTHOR'S CONTRIBUTION TO THE PUBLICATIONS

I The author carried out the experimental part, participated in data processing and in discussion of the results.

II The author carried out the experimental part, interpreted the results and wrote the manuscript.

III The author carried out the experiments, participated in the interpretation of the results. The paper was written by the author together with co-authors.

IV The author planned some series of experiment, carried out part of experimental work and interpreted the results.

V The author planned series of experiments, carried out part of experimental work and interpreted the results.

LIST OF ABBREVIATIONS

AlHC	Aliphatic hydrocarbons
FAP	Fischer assay pyrolysis
FT-IR	Fourier Transform Infrared Spectroscopy
GA	Graptolite argillite
GC-MS	Gas chromatography-mass spectrometry
HPHet	High polar heteroatomic compounds
LPHet	Low polar heteroatomic compounds
MAHC	Monoaromatic hydrocarbons
MFAP	Modified Fischer assay pyrolysis
MM	Mineral matter
OM	Organic matter
PAHC	Polyaromatic hydrocarbons
SEM	Soxhlet extraction method
SFE	Supercritical fluid extraction method with CO_2
SR	Solid residue
TB	Thermobitumen
TBO	Mixture of thermobitumen and oil
TLC	Thin layer chromatography

INTRODUCTION

Oil shale belongs to the strategic resources of Estonia and oil shale industry plays a significant role in Estonian economics. The Kukersite oil shale has been used as source of energy and oil since 1924. Up to now, a billion tons of Kukersite has been consumed already. Shale oil is a valuable product that can be used for production of liquid fuels and chemicals.

Increasing consumption of petroleum products in industrialized countries is today's reality. Absence of petroleum reserves in our region and unexpected price of petroleum products in world market forces to find alternative ways to ensure Estonian energy security. Sustainable oil shale industry basing on thermochemical processing of the local oil shale resource strengthens energetic independence of Estonia and lessens the need for importing the petroleum products. In this context, sufficiency of the oil shale reserve and development of oil shale liquefaction methods towards higher shale oil yield are important as a basis for sustainable economy.

Oil shale does not contain oil like oil sands. Shale oil can be obtained from oil shale as a result of thermochemical destruction. Organic matter (OM) in oil shale being disproportioned between liquid, gaseous and solid phases, also gaseous and solid by-products are formed. Pre-existent industrial oil shale liquefaction technologies in Estonia and other countries are basing on semi-coking in retorts of different configuration. Kukersite oil shale is liquefied using Kiviter, Petroter and Enefit processes. Industrial retorts are modelled by laboratory Fischer assay pyrolysis (FAP) to estimate the oil yield and its composition. Industrial shale oil yield amounts to 1 barrels per 1 ton of oil shale, making only 70-75% of that attainable in FAP. Spent shale, characterised by as high as 15% residual carbon content, sent to the landfills or combusted to compensate the energetic balance of process represents hazardous residue or source of greenhouse gases.

Besides Kukersite there is another oil shale in Estonia – graptolite argillite (GA), known also as Dictyonema shale, the reserve of the latter one (estimated by 70 billions tonnes) considerably surpasses that of Kukersite remained (4.7 billions tonnes) [1]. Both the OM and mineral matter (MM) of GA are differing compared with Kukersite. GA contains less OM and is richer in heteroatoms as oxygen, sulphur and nitrogen. GA has not found industrial utilisation yet. Besides its oil potential enclosed in OM, MM of GA is rich in various metals including radioactive, rare-earth and noble ones.

Compared with Kukersite GA gives very low oil yield per shale in FAP respectively 23 and 1-2% only [2]. That is why the semi-coking is not prospective method to be used in industrial-scale liquefaction of GA Alternative to semi-coking technologies should be worked out to effective utilisation of GA. The technology to be worked out should led to the minimum residual content of carbon in spent shale that becoming easily leachable for metals separation.

1 LITERATURE REVIEW

1.1 Oil shale

Oil shale is a sedimentary rock containing various amounts of solid OM dispersedly bound in a mineral matrix. Oil shales from different deposits vary in their geological period of deposition, mineral contents and types, and chemical composition of OM [2,3]. Oil shale deposits are found on all continents; the reserves are more evenly distributed compared to petroleum and for many countries, oil shales represent practically the only type of fossil fuels. Total world resources of shale oil are estimated by Word Energy Council conservatively at 4.8 trillion barrels that surpassing the amount of crude petroleum in the world [4].

Majority of oil shales contain OM derived from varied types of marine and lacustrine algae, with some debris from land plants, depending on the depositional environment and sediment sources. OM in the oil shale is a complex mixture and is derived from the carbon-containing remains of algae, spores, pollen, plant cuticle, corky fragments of herbaceous and woody plants, plant resins, and plant waxes, and other cellular remains of lacustrine, marine and land plant [1,3].

The structure of OM is mainly solid cross-linked macromolecules which are largely insoluble in conventional solvents. However, the durable steric structure of kerogen can be pyrolytically cracked above 350 °C in special reactors. Prior to oil Thermobitumen is formed [5]. FAP is the standard method of evaluating the oil potential of solid fuels. However, the maximum possible obtainable oil yield is often much higher obtained by using thermal dissolution or hydrogenation methods. The minor part of OM not incorporated to the structure of kerogen, bitumoid, can be separated from oil shale matrix as extractables by using low-boiling solvents. The can be observed as a mobile phase inside a macromolecular network containing various bitumoid biomarkers for elucidating the genesis of the OM in oil shale and the degree of its maturity.

Oil shale basic MM could be of two types. The first type is carbonateous, which contains a high proportion of carbonate minerals (such as calcite and dolomite). Oil shales with such a mineral composition are hard formations that are resistant to weathering. The second type is siliceous, which gives usually dark brown or black colour to oil shale [5]. They are deficient in carbonate minerals but plentiful in siliceous minerals (such as quartz, feldspar, clay, chert, and opal). These shales are not as hard and weather-resistant as the carbonate shales. In addition to basic mineral part of oil shales there are different minerals as pyrite, gypsum and others [5].

1.2 Characterization of Estonian graptolite argillite

GA is also known as Dictyonema shale, alum shale or black shale. The name *'dictyonema'* was given after the benthonic root-bearing *Dictyonema flabelliforme*, which turns afterward to a planktonic nema-bearing *Rhabdinopora* *flabelliformis* [6]. GA is a formation of the Tremadoc stage (Pakerord and Varangu regional stages) of the Early Ordovician. The basin that contains the Dictyonema shale spreads from Norway, Denmark, Southern Sweden, and Estonia to the Leningrad Region [7]. The total amount of available black shales is really immense in Baltoscandian region. Only in Estonia GA deposits shown in Fig. 1 have been estimated as 70 billion of tons, surpassing several tens times the existing reserve of Kukersite [8].

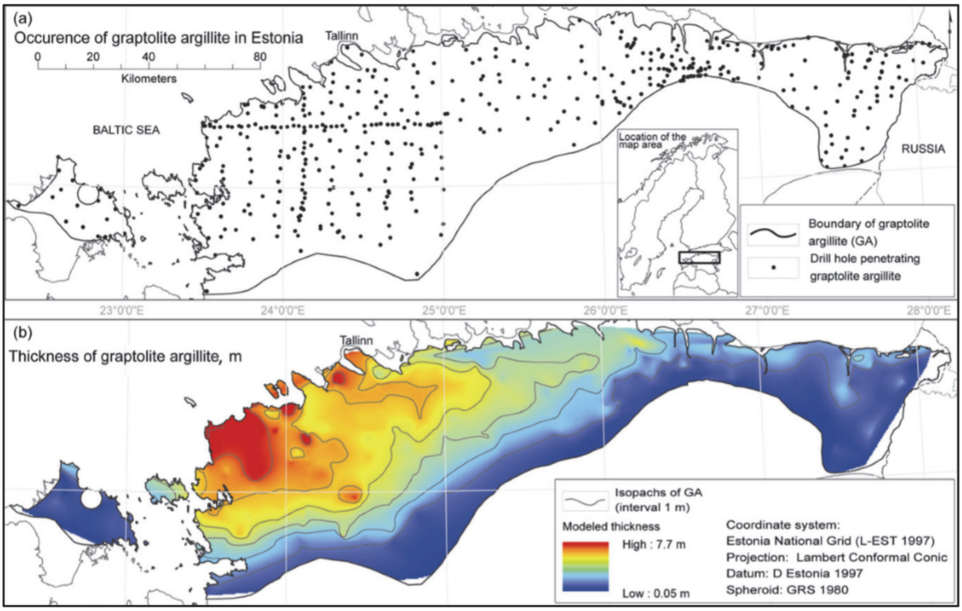

Figure 1. Location map of Estonian GA and location of the drill holes penetrating the GA layers(a). Modeled thickness of GA based on the studied drill holes (thickness grid created by the Natural Neighbour interpolation method, grid cell size 400 m) (b) [8]

Chemical composition of GA is complicated. The mineral part of GA is rich in sulfur, and has low content of calcium, consists of alumosilicates, quartz and clay. The OM of GA shale has sapropelic origin. Compared with Kukersite, it is notable the high content of heteroelements – oxygen, nitrogen sulfur and lower that of C and H. The content of hydrogen is lower than typical sapropel has, but is higher in comparison with humic fuel [9].

Table 1 represents general characteristics of GA from different deposits.

Table 1 General characteristics of GA [2]

Deposit	Analytical moisture, %	Ash*	CO_2 of carbonates*	Conditional organic mass*
Estonia, Maardu	1,0	79,2	0,2	20,6
Estonia, Aseri	1,8	79,1	0,3	20,6
Estonia, Toolse	1,3	80,5	0,1	19,4

*Per dry mass, wt. %

GA is characterized by high to very high concentrations of U (up to 1200 g/t, Mo (1000 g/t), V (1600 g/t), Ni, Re and other heavy metals. The total amount of uranium (elemental U) that has been eroded and re-deposited reaches 1.798 million tonnes (at an average content of 95 g/t), zinc (Zn) 22.716 million tonnes (average 1200 g/t), lead (Pb) 6.625 million tonnes (average 350 g/t), molybdenum (Mo) 4.448 million tonnes (average 235 g/t) and vanadium (V) 13.251 million tonnes (average 700 g/t) [8].

GA and its mineral residues from pyrolytical transformations may be used to produce building materials such as bricks, drain-pipes, gas concrete, expanded-clay aggregates, coloured decorative plates and admixture with limestone may be used to produce cement clincer and used as fertilizer and plant growth stimulant [10].

The oil potential of solid fuels is usually estimated as produced in Fischer assay by semi-coking. Calculated oil potential of GA is 2 billions of tons while that of Kukersite oil shale is 0.594 billions of tons the both amounts being estimated basing on semi-coking oil yield [10, 11]. Oil Shale Symposium in Tallinn in 2009 reported the potential availability in Sweden of 4,5 billions barrels oil from rock with a 10 % OM cut off [12]. OM content in GA is lower than that in Kukersite oil shale, but MM of GA could be a valuable feedstock.

In fact, the oil yield in Fischer assay semi-coking is as high as 23,3% for Kukersite but is very low for GA (1-2 %). It was found that the yield of shale oil from GA increases with increasing the OM content in oil shale sample and the increase in oil yield was due to formation of aromatic and heteroatomic compounds [13-16]. The same tendency was noticed also in fast pyrolysis conditions of GA [16]. Urov et al. [18-19] demonstrated that both the yield and the composition of products formed as a result of GA semi-coking can be significantly influenced in the presence of additives as carbonates, alumosilicates and pyrite. The composition of aliphatic hydrocarbons (AlHC) in GA semi-coking oil was investigated and compared with that of Kukersite shale oil [19]. In [21] GA was submitted to semi-coking in Fischer assay up to different final temperatures from 400 to 520 °C and it was demonstrated that the oil yield at 430 °C is the same as 520 °C (22,2% on OM basis) and does not increase with increasing the final temperature. Investigation of the composition of shale oil obtained in GA semi-coking demonstrated higher content of branched-chain hydrocarbons and aromatic compounds and lower content of straight-chain hydrocarbons compared with Kukersite semi-coking oil [22-24]. Investigation of the composition of shale oil obtained in other conditions of pyrolysis resulting from GA self-ignition demonstrated that this oil differs fro0m that produced in semi-coking by the lower content of monoaromatic hydrocarbons (MAHC), aliphatic olefins and considerably higher concentration of polyaromatic hydrocarbons (PAHC) [25]. In [26] it was established that in black shales metals are tightly bound into very stable organic structures like metalloporphyrins. The latter organic structures are often low in hydrogen and that is why the yield of oil in semi-coking is very low or even nil. Consequently, the industrial technology and aggregates developed for Kukersite oil shale liquefaction are not prospective to be used for GA liquefaction. Alternative oil generation methods basing on using solvents and reagents should be worked out. Aromatic porphyrin rings can be destroyed by using severe thermochemical destruction methods. For example, hydrogenation is one of such methods destroying the rings and making, simultaneously, the metals easily leachable. It is established that hydrocracking/hydrogenation process can considerably increase also the shale oil yield. In [12,27] the HYTORT hydrogenation/thermal dissolution technology for oil production was represented and multimetal potential of the spent shale that remains after generating about 5,5% of oil is stressed. GA has been submitted to the thermal dissolution in the temperature interval 250-300°C in the medium of water, alkali solution and benzene, but as a result low yields of oil (5-16% per OM) were obtained [28]. The liquids yielded were characterized by a high content of aromatic and heteroatomic compounds. In [29] the results of GA destructive catalytic hydrogenation and conversion with water are described. The yield of oil was elevated up to 40% per OM the oil being characterized by a high content of aromatic hydrocarbons

As it can be seen from the said above, thermochemical liquefaction of the low-grade GA with a view of obtaining petroleum substitutes is investigated not much and needs further development.

1.3 Comparison of graptolite argillite with Kukersite

Estonian Kukersite and GA formed in Lower Paleozoic belong to the most ancient ones in the world. The source material of both kerogens is of marine origin. Kukersite is characterised by an extremely low bitumoid content arising from its allochthonous origin and sedimentation under conditions of oxidizing atmosphere. GA which proceeded formation under the influence of sulfate-reducing microbes, contains less kerogen and yields considerably more extractables in Soxhlet extraction method (SEM) [30]. Main structural units of OM of sapropelites and their pyrolysis oils are straight and, in less measure, branched carbon chains, precursors of which were fatty acids and isoprenoid structures, respectively, being transformed to bitumoid and kerogen pyrolysis oil composition as paraffins, olefins and ketones. The corresponding structures of oil shale have been formed by fossilization of the most stable components (fatty acids) of biological source material. The hydrocarbon chains in ancient oil shale kerogens have mainly odd carbon numbers [31]. GA is a brown lithified clay belonging to the formation of black shales of sapropelic origin, whose OM is rich in heteroatoms [6]. The main characteristics of GA and Kukersite oil shales are given in Table 2.

Table 2 The main characteristics of GA and Kukersite

Characteristic*	GA	Kukersite
Age, millions years	480	460
MM	Alumosilicates	Carbonates
Analytical moisture, W^a, %	1.4	0.6
Ash (per dry mass), $A_{d,}$ %	83.9	37.2
OM, %	16.0	50,5
CO_2 of carbonates, %	0.1	12.3
Semi-coking oil yield, % on oil shale	2.1	23.3
Elemental composition of OM, %		
C	73.0	79,3
H	9.2	9.5
N	1.2	0.1
S	1.7	0.2
O	14.9	10.9
H/C molar ratio	1.51	1.44
O/C molar ratio	0.16	0.10

*measured for the samples used in work

Oil yield per OM can vary widely between oil shales from different deposits. On the basis of solvent swelling experiments [32] concluded that oil yield is usually higher for oil shales with OM consisting of Type I kerogen than for those with Type II kerogen. Kerogen, which makes up most of oil shale's OM, is a highly cross-linked, organic, macromolecular material [33]. Depending on the oil shale kerogen type, loosening or tightening of the kerogen structure can occur in the temperature region before an active pyrolytic volatilization of oil. Solvent swelling experiments [34] on thermally pre-treated oil shales have indicated that the high oil yield kerogen (Type I) of Estonian Kukersite oil shale, which possesses softening pyrolysis behaviour, shows a tendency for pre-pyrolysis structural loosening [35]. The characteristic is qualitatively similar to that of high tar yield softening coals. On the other hand, the low oil yield kerogen (Type II) of GA, which possesses non-softening pyrolysis behaviour, shows a tendency for pre-pyrolysis structural tightening [36].

1.4 Thermochemical destruction

1.4.1 Pyrolysis

Pyrolysis is a thermochemical decomposition method of organic material at elevated temperatures in the absence of oxygen. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. FAP is the simplest and most widely studied process for recovering oil from oil shale.

Often MFAP is used to modify products yield and composition. During the retorting process, the OM is converted to oil, gas and SR (semi-coke).

The yield and composition of pyrolysis products depend on material pyrolysed and pyrolysis conditions – temperature and heating rate, the content of gaseous atmosphere and its pressure, process duration. Depending on operation conditions, the pyrolysis process can be subdivided into conventional pyrolysis (slow pyrolysis), fast and flash pyrolysis [37] or into low-temperature pyrolysis up to about 500°C and high-temperature pyrolysis (gasification) [2].

Thermal destruction of GA depicted in Fig. 2 reveals endothermic and exothermal effects, published by Siirde in [9]. The endothermic effect takes place at 100-110° C, and is connected with moisture separation. The second endothermic effect at 205-250°C conducts with gas separation. Active destruction of OM proceeds in the 300-450°C interval. Majority of products (oil, gas and pyrogenetic water) is generated during this process. Subsequent increasing of temperature gives destruction of MM. Thermograms show that the last big endothermic effect occurs at 550-600°C with separation of constitutional water from alumosilicates.

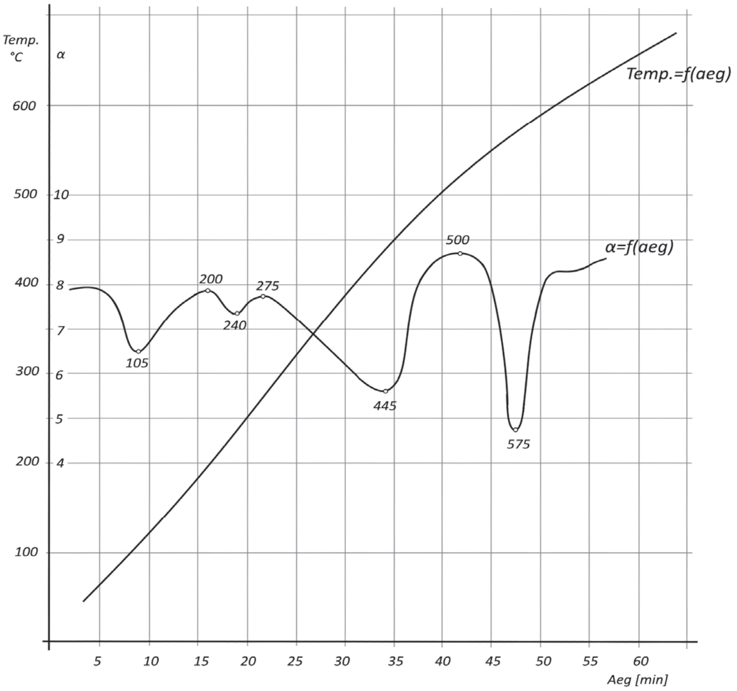

Figure 2. Thermogramm of GA from Maardu deposit [9]

1.4.2 Thermochemical dissolution

Thermal dissolution, i. e. heating in the presence of solvent is one of the alternatives to “dry” pyrolysis. Thermal dissolution could be conducted in autoclaves with both subcritical and supercritical solvent, reactive and non-reactive fluids, and also hydrogen-donor solvents that can provide hydrogen in the conversion process [4]. The process of thermal dissolution is conducted at lower compared with “dry”pyrolysis temperatures (330-400°C) to favour thermobitumenisation and minimize gas production.

In recent years, the use of supercritical fluid extraction for the removal of organic compounds from different solid matrices has attracted much attention. This technique has some advantages over more conventional separation techniques, largely due to the unique physical properties of supercritical fluids. Supercritical fluids exhibit a liquid-like density, while their viscosity and diffusivity remain between gas-like and liquid-like values. Also the recovery of a supercritical solvent after extraction can be carried out relatively simply by cooling the reactor with reducing the pressure and evaporating the solvent.

The extraction of valuable materials from solid substrates by means of supercritical gases has been carried out on a commercial scale for more than a decade. Large-scale processes are related to the food industry like the decaffeination of coffee beans and black tea leaves and the production of hops extracts. The extraction fundamentals of fossilized OM of kerogen and kerogen-like formations from oil shales was published in [38].

Thermochemical dissolution of oil shale kerogen using the supercritical fluid extraction method has been applied for a variety of reasons. The primary reason includes an increase in the production of liquid fuels from oil shale, another shows promise for improving in oil quality due to the selective nature of solvents [39].

The most attractive solvent for both sub- and supercritical extraction is water, because of the specific properties for hydrolysis, hydrothermal, and oxidative processes and availability of this solvent. Supercritical water acts not only as a solvent but also reacts with the double and triple bonds of the decomposition products resulting in alcohols and aldehydes [40]. The influence of the other solvents as toluene, tetralin [41,42], methanol, ethanol [43,44], phenol, and others and also the mixture of solvents were investigated [45]. The sub- and supercritical thermal dissolution was applied for Kukersite [43,44], Moroccan [46], Chinese [47], Turkish [48], US [41] and Australian oil shales [42]. The efficiency of solvents on the various objects was characterized by yield and composition of oil. The extent of dissolution and cracking depends on the chemical composition of solid fuel used for processing, dissolution conditions, and on the solvent composition and properties. The essence of the thermal dissolution process consists in action of solvents on oil shale at high temperatures causing depolymerisation, dissolution, and cracking of the dissolved OM of the fuel [49].

1.4.3 Hydrogenation

It is generally recognized that the higher the hydrogen content of the OM in solid fuel the higher the yield of oil. This knowledge has stimulated the use of hydrogen-adding process in the shale oil production and upgrading.

Hydrogenation is the technique, which can be practised in processing both solid fuels and fractions of distillation or chemical separation derived from petroleum, bitumens, as well as from coal, oil shale and other solid fuels. As a result of hydrogenation the chemical composition and the qualities of the syncrude obtained will be closer to those of the light natural petroleum. Hydrogen can be introduced into the process either directly from the gas phase or from any hydrogen-donor. A catalyst could be used to activate the hydrogen.

Shale oil differs from crude petroleum and is characterised as highly unsaturated and rich in heteroatomic compounds. The latter ones make necessary additional treating [50]. An important concept in thermochemical decomposition is formation of volatile and nonvolatile reactive radical components as a result of bond breaking in the macromolecular structure. Reactions between radical components can lead to char formation, if the radical species involved are located on large fragments of the network structure. Stabilization of radicals by hydrogen can result in volatiles, if the hydrogen capping of the structure prevents their incorporation into a new structure [3].

FAP and the assay for hydropyrolysis (HYTORT) tests on samples from several oil shale resources are represented in [51]. Results of hydropyrolysis tests are given in Table 3 (100 grams sample were used).

Table 3 Oil yields from hydroretorting of different oil shales samples [51]

Oil shale sample	Oil yield (gal/ton)		
	FAP	Hydroretortong assay	Increasing times
Sweden – Billingen	3.8	17.5	4.6
Sweden – Naerke	10.9	32.3	3.0
Sicily	4.4	12.2	2.8
Indiana – New Albany	12.5	28.2	2.3
Montana – Heath Formation	16.2	33.6	2.1
Canada – Kittle	10.0	21.1	2.1
Jordan – El Lajjun	32.8	57.0	1.7
Brazil – Lower Irati	19.4	32.7	1.7

The results obtained at 538°C at H_2 pressure 7 MPa and duration 30 min indicate that the HYTORT process can produce oil yields even over 400% of those obtained by conventional retorting. In most cases oil yields increased 2-3 times in comparison with FAP. These results demonstrate that oil shale resources which would normally be considered too lean for commercial exploitation by conventional retorting process could be exploited with using HYTORT process.

1.5 Aims of the work

Basing on the literature review above, GA represents peculiar oil shale compared with Kukersite and other oil shales found industrial liquefaction already. Effective liquefaction of GA needs alternative thermochemical methods.

The main goals of this work include working out physical-chemical and technological fundamentals for GA upgrading with obtaining higher shale oil yield compared with traditional semi-coking, investigation of shale oil composition formed using various methods and different conditions of thermochemical destruction, and comparing GA shale oil composition with Kukersite shale oil.

2 EXPERIMENTAL

2.1 Methods

2.1.1 Methods of bitumoids extraction

2.1.1.1 Soxhlet extraction method

Exhaustive Soxhlet extraction method (SEM) as a traditional debitumenisation method using chloroform and benzene- methanol mixture in special extractors was carried out with obtaining bitumoids A and C, respectively. The solvent was heated to reflux. During each cycle, a portion of compounds dissolved in the solvent. The process continued until the colourless solution was returned to the distillation flask.

2.1.1.2 Supercritical carbon dioxide extraction

The yield of bitumoids obtained in SEM being very low, an alternative method of debitumenisation was worked out to be convinced the yield of bitumoid being ultimate by using SEM or could it be enhanced.

Oil shale samples were submitted to low temperature supercritical flud extraction in an autoclave with using CO_2 (SFE) at three different temperatures. A rocking 500 cm^3 stainless steel batch autoclave supplied with a manometer and gas valves was used. Starting with 100 g, the same portion of oil shale was extracted consecutively at 40, 100, and 150°C and initial carbon dioxide pressure 9 MPa during 2 hours. At the end of heating, the system was cooled down to the ambient temperature. Carbon dioxide was then released from the autoclave via gas valve and the autoclave was opened. The extractables formed were diluted with diethyl ether and the filtration cake was treated in the autoclave at the following temperature. Diethyl ether was evaporated and the extract yields were determined by weight analysis.

2.1.2 Laboratory methods of thermochemical destruction

2.1.2.1 Fischer assay tests

The samples were submitted to the pyrolysis in a Fischer assay following standard and modified regimes.

FAP standard conditions followed ISO 647-74: heating 50 g of oil shale in aluminium retort up to 520 ^{o}C during 90 min.

MFAP was conducted at varied temperatures in-between 320-525 ^{o}C with residence times 20 and 60 min.

As a result of pyrolysis series demonstrated in Fig. 3, oil as condensable volatiles, solid residue (SR), non-condensable gas, water and non-volatile solvent-soluble thermobitumen (TB) were quantitatively yielded. Upon cooling of the volatile matter, condensable material was collected in a round-bottomed flask. The condensate contained all the oil as well as water. Oil and solvent solubles (TB) were summarized and calculated as total TBO.

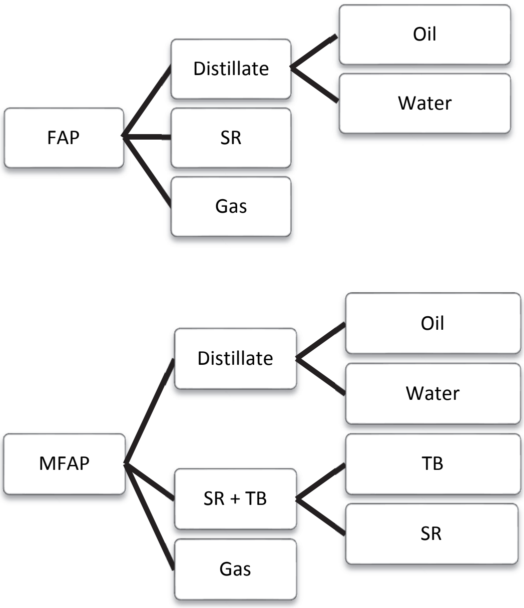

Figure 3. Scheme of GA pyrolysis and products separation

2.1.2.2 Low temperature pyrolysis in autoclaves

Pyrolysis of GA without solvents was carried out in glass test tubes placed in 58 cm^3 autoclaves. In each experiment about 12 g of the air dried and powdered GA were used. The samples were placed into a cold muffle oven. The constant nominal temperature varying from 340 to 420 °C was attained for the period of 60 minutes. The pyrolysis duration was measured from the time when the muffle oven reached the nominal temperature prescribed. Efficiency of the liquefaction process was evaluated by the yield of pyrolysis products as TBO, SR, gas and pyrogenetic water.

Gas yield formed was determined by the weight loss of glass test tubes with the sample after discharging gaseous products from the open autoclave at room temperature. The liquid products consisting of TBO and water were extracted exhaustively with boiling benzene in a Soxhlet extractor. The water phase was gathered and weighted as drops on the walls of the test tube, and condenser of Soxhlet extractor after the azeotropic mixture of water and benzene was decomposed. The mass of moisture in the initial samples and SR were weighted by drying at 105 °C during 2 h. The content of OM in SR was measured as weight loss in incineration at 550°C during 2 h. The solvents applied were removed from TBO solutions in a vacuum rotation evaporator at 70 °C.

2.1.2.3 Thermochemical dissolution with solvents

2.1.2.3.1 Thermochemical dissolution with solvents

Thermochemical dissolution experiments were carried out in 20 cm^3 autoclaves charged with powdered sample of GA with addition of applied solvent or reagent or mixture of them. Benzene, toluene, hexane, cyclohexane, isopropanol, methanol and ethanol were used as solvents. The autoclave was placed in a muffle oven and heated to the nominal temperature. After the end of the heating time the autoclave was left at ambient temperature for cooling and opened on the next day. TBO was washed out from the autoclave by solvent extraction using benzene. SR was weighted as solvents insoluble material, gas and pyrogenetic water from were calculated from the difference. Thermochemical dissolution in case of the solvents used was carried out in unified experimental variables: 360 ^{O}C, 4 h, oil shale-to-solvent weight ratio 1:2. TBO was separated from SR by extraction with benzene.

2.1.2.3.2 Water conversion with additives

Water conversion experiments were carried out in 20 cm^3 autoclaves charged with powdered shale with addition of water or mixture of water with reagents. The autoclaves were placed in a muffle oven and heated to the nominal temperature. After the end of the heating time the autoclaves were left at ambient temperature for cooling and opened on the next day. TBO was washed from the autoclave by consecutive extraction with water, benzene and acetone (Fig. 4). SR was calculated as weight of solvent insolubles, gas and pyrogenetic water from the difference.

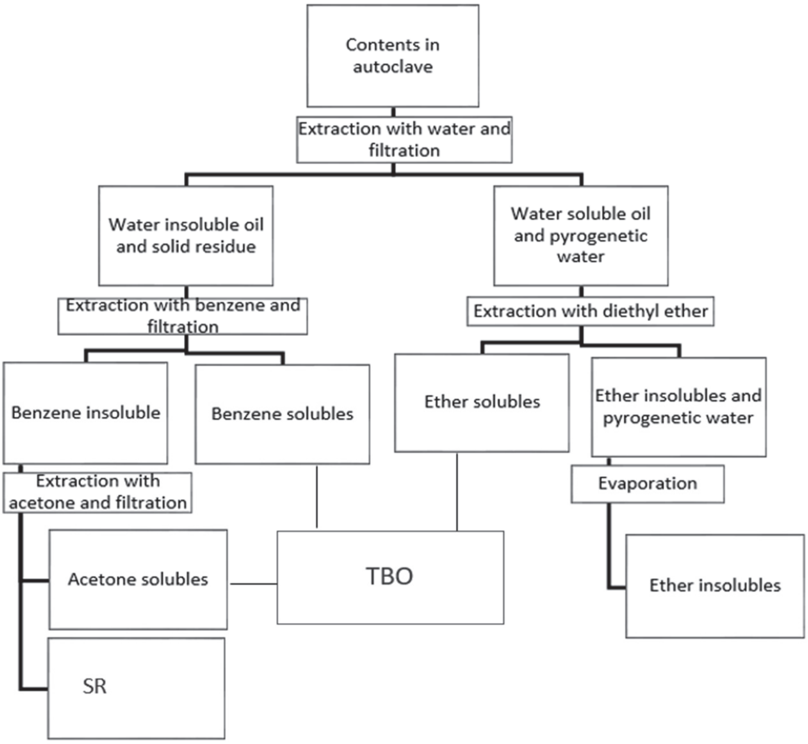

Figure 4. Separation scheme of products obtained as a result of water conversion

2.1.2.4 Hydrogenation

Hydrogenation experiments were carried out in the 500 cm^3 stainless steel batch autoclave supplied with a manometer and gas valves. First of all, the autoclave was filled with 60 g of GA sample. Prior to hydrogen charging the autoclave was twice flushed with inert gas (Ar). The initial pressure of hydrogen charged to the autoclave was 60 at. Autoclave was placed and fixed into electric heater connected to the electric engine and the system was rocked. Temperature of hydrogenation was varied from 350 to 430 ˚C, duration of hydrogenation was 2h. At the end of heating the residual pressure was registered, the system was cooled down to the ambient temperature. Then the gas amount was released from the autoclave via gas valve and the autoclave was opened.

Hydrogenate was washed from the autoclave by extraction with benzene and then benzene was evaporated under vacuum. SR was separated by filtration, dried for solvent removal at 105 ˚C and then weighted. Gas yield was calculated according to the formula

Gas yield =100 - hydrogenate - SR.

2.1.3 Analytical methods

2.1.3.1 Thin layer chromatography

Thin layer chromatography (TLC) was used to separate compound groups in TBO. TLC is a solid-liquid form of chromatography where the stationary phase is normally a polar absorbent and the mobile phase can be a single solvent or combination of solvents.

The electropositive character of the silicon and the electronegative oxygen create a very polar stationary phase. Therefore, the more polar the molecule to be separated, the stronger the attractive force to the stationary phase. The polar stationary phase will more strongly attract like or polar molecules. The equilibrium will be shifted as the molecules remain on the stationary phase. Nonpolar molecules will have a lower affinity for the stationary phase and will remain in the solvent longer. This is essentially how the partitioning separates the molecules. The equilibrium governs the separation, but the component's attraction to the stationary phase versus the mobile phase determines the equilibrium. In general, the more polar the functional group, the stronger the bond to the stationary phase and the more slowly the molecules will move. In an extreme situation, the molecules will not move at all.

In this work, the stationary phase consisted of a finely divided adsorbent, silica gel, used in the form of a thin layer (2 mm) on a supporting material. For this plates 24 cm x 24 cm were used. The mobile phase consisted of an eluting solvent (n-hexane). The samples were about 0,5 g, which was spotted near the bottom of plates.

The TLC plate was propped in a closed container (developing chamber), with the edge to which the spot was applied down. The solvent, which is in the bottom of the container, travels up the layer of adsorbent by capillary action, passes over the spot and, as it continues up, moves the compounds in the mixture up the plate at different rates resulting in separation of the compounds. When the solvent has reached the top of the plate, the plate was removed from the developing chamber, dried, and separated in the plate component groups were visualized under UV light by colour. Five groups of compounds were separated into AlHC, MAHC, PAHC, low polar heteroatomic compounds (LPHet) and high polar heteroatomic compounds (HPHet) the latter ones remaining in startline. The diethyl ether was used to separate groups from silica gel. The amount of groups was determined by weighting after evaporation of diethyl ether.

2.1.3.2 Infrared spectroscopy

FT-IR spectroscopic analysis was used to identify the functional groups composition in TBO.

In this work infrared spectra were taken on an "Interspec 2020 spectrometer".

2.1.3.3 Gas chromatography

Chromatography encompasses a series of techniques that have in common the separation of components of a mixture by series of equilibrium operations that result in separation of the entities as a result of their partitioning (differential sorption) between two different phases, one stationary with a large surface and the other a moving phase in contact with the first. Gas chromatography uses the elution development technique. In this technique, components travel through the column at rates determined by their retention on the solid packing. If the differences in sorption are sufficient or the column is long enough, a complete separation of components is possible. Continued addition of eluant causes the emergence of separated bands or zones from the column. A disadvantage of this technique is very long time interval required to remove a highly sorbed component. This can be overcome by increasing the column temperature during the separation process.

GCMS – Shimadzu QP 2010 Plus gas chromatograph with mass-spectrometer with programming was used.

Quadrupole Mass Spectrometer was used as detector.

2.1.3.4 Elemental analysis

Elemental Vario EL Analyser was used to determine elemental composition of TBO obtained in this work. C, H, N and S were determined directly and O was indirectly calculated from the difference.

2.2 Materials

2.2.1 Initial sample of graptolite argillite

Figure 5. Graptolite argellite

The oil shale sample (Fig.5) used in this work belongs to Maardu deposit. The sample was air-dry finely powdered to give a particle size of 0.04-0.1 mm. Table 4 shows the main characteristics of the given sample of GA.

Table 4 Characterisation of the initial oil shale, %

Characteristic	**Content**
OM^d	16.0
Analytical moisture, W^a	1.4
Ash*, $A^{d,}$	83.2
CO_2 of carbonates (per dry mass)	0.1
Sulfur total S_t	2.9
Sulfate sulfur, S_{SO4}	1.0
Pyrite sulfur, Sp	1.3
Organic sulfur, (dif)	0.6
Elemental analysis of OM^d	
C	73.0
H	9.2
N	1.2
S	1.7
O (by difference)	14.9

* Ash was measured as the weight of residue remaining as a result of combustion at 825°C during 2h.

2.2.2 Reference samples

Air-dry, finely powdered (0.04 - 0.1 mm) and homogenised oil shale samples characterised in Table 5 were used as feedstocks.

Table 5 Characterisation of the reference oil shales, %

Oil shale	US Green River formation Utah basin	Jordanian Attarat	Kukersite
W^a	0.4	0.7	0.6
A^d	65.1	63.1	47.5
CO_2 of carbonates	21.3	15.5	20.2
OM^d,%	13.6	21.4	32.3
FAP oil yield, OM%	56.6	48.6	65.6

2.2.3 Solvents used for separation and dissolution

Benzene, acetone, diethyl ether, and distilled water were used as solvents for separation.

Solvents used in thermal dissolution are represented in Table 6.

Table 6 Solvents used for thermochemical dissolution and their characterization[55]

Solvent	Chemical formula	Critical temperature, °C	Critical pressure, atm	Dielectric constant
Carbon dioxide	CO_2	31.1	73.0	1.6
Hexane	C_6H_{14}	234.2	29.7	2.0
Benzene	C_6H_6	289.0	48.3	1.8
Toluene	$C_6H_5\text{-}CH_3$	318.6	40.6	2.4
Cyclohexane	C_6H_{12}	280.3	40.2	2.0
Isopropanol	$CH_3\text{-}CH(\text{-}OH)\text{-}CH_3$	235.2	47.0	18.0
Ethanol	$CH_3\text{-}CH_2\text{-}OH$	243.0	63.0	27.8
Methanol	$CH_3\text{-}OH$	239.4	79.8	31.2
Water	H_2O	374.1	218.3	80.4

Used solvents are related to non-polar (hexane, toluene, benzene and cyclohexane) and protic polar solvents (isopropanol, ethanol, methanol and water). Non-polar solvents contain bonds between atoms with similar electronegativities, such as carbon and hydrogen. Non-polar solvents are best for dissolving non-polar reactants (such as hydrocarbons). Protic polar solvents can participate in hydrogen bonding, which is a powerful intermolecular force. Additionally, these O-H bonds can serve as a source of protons (H+).

3 RESULTS AND DISCUSSION

3.1 Bitumoids content and composition

Yields of extractables (bitumoids) eluated from oil shales by SEM and stepwise static SFE as well as group composition of the extracts separated by TLC are represented in Tables 7 and 8. Kukersite gives in both processes lower extract yields compared with GA.

One can see that total yields of bitumoid obtained as summarized yields of bitumoids A and C from SEM of Kukersite and GA using chloroform and benzene-methanol mixture consequtively were recovered as 0.79% and 4.88%. Stepwise SFE of Kukersite triplicated the yield of extractables while that of GA oil shale gave extractables less by 30% compared with SEM. It is noteworthy that SFE of Kukersite resulted in higher yields of extractables than those of bitumoids A and C summarized at each process temperature, i.e. 40, 100 and 150˚C. SFE of the GA oil shale at 40˚C resulted roughly in the same extractables yield as that of bitumoid A. So, the extractables obtained at 100 and 150˚C can represent an additional source of geochemical information in Kukersite case and observed as an alternative to the bitumoid C in GA case.

Group compositition data in Tables 7 and 8 show that all extracts were represented by the same groups of hydrocarbons and heteroatomic compounds despite originated from different oil shales and produced resulting from solvent or fluid extraction processes. Heteroatomic compounds are prevailing over hydrocarbons, particularly in Soxhlet extracts where the content of those amounts to 88% - 92%. Among heteroatomic compounds the polar ones, and in the composition of hydrocarbons the aliphatic ones are prevailing over neutral and aromatic ones, respectively. It can be seen that SFE compared with SEM produces considerably more hydrocarbons and less HPHet compounds.

Table 7 Yields and group composition (% of bitumoid) of SEM extracts

SEM	Yield		AlHC	MAHC	PAHC	LPHet	HPHet
	mg/g	% of OM					
GA							
Bitumoid A	2.80	1.75	7.5	1.5	3.0	5.5	82.5
Bitumoid C	5.00	3.13	5.6	0.6	0.9	1.3	91.6
Σ(A + C*)	7.80	4.88	6.3	0.7	1.9	2.8	88.3
Kukersite							
Bitumoid A	1.63	0.48	19.9	7.6	2.8	14.6	55.1
Bitumoid C	1.03	0.31	10.1	1.6	0.7	1.2	86.4
Σ(A + C*)	2.66	0.79	16.2	5.3	2.0	9.3	67.2

Table 8 Effect of temperature on the yields and group composition (relative %) of SFE extracts.

SFE temperature, ˚C	Yield		AlHC	MAHC	PAHC	LPHet	HPHet
	mg/g	% of OM					
GA							
40	2.34	1.47	26.4	6.2	9.6	20.6	37.2
100	2.40	1.51	20.2	4.1	11.8	23.9	40.0
150	1.06	0.67	30.8	2.2	20.1	22.8	24.1
Σ150	5.80	3.65	25.3	4.6	12.2	22.2	35.7
Kukersite							
40	4.21	0.82	20.1	9.7	18.2	14.2	37.8
100	2.94	0.57	17.6	10.9	13.2	21.5	36.8
150	5.00	0.97	18.9	2.6	10.6	8.6	59.3
Σ150	12.15	2.36	19.1	7.0	13.9	13.6	46.4

Extraction efficiency of SEM and SFE with regard to different compound groups determined is represented in Tables 9 and 10. Extraction efficiency depends on both process variables as temperature, pressure, duration, solvent type and chemical composition of the source matter.

Table 9 Extraction efficiency of different compound groups resulting from SEM (mass % of OM).

SEM	AlHC	MAHC	PAHC	LPHet	HPHet	Total extract
GA						
Bitumoid A	1.31	0.29	0.50	0.96	14.44	17.50
Bitumoid C	1.75	0.19	0.28	0.41	28.67	31.30
ΣA + C	3.06	0.48	0.78	1.37	43.11	48.80
Kukersite						
Bitumoid A	0.96	0.36	0.13	0.70	2.64	4.79
Bitumoid C	0.31	0.05	0.02	0.04	2.68	3.10
ΣA + C	1.27	0.41	0.15	0.74	5.32	7.89

Table 10 Extraction efficiency of different compound groups resulting from SFE (mass % of OM).

SFE temperature, ˚C	AlHC	MAHC	PAHC	LPHet	HPHet	Total extract
GA						
40	3.88	0.91	1.41	3.03	5.47	14.70
100	3.05	0.62	1.78	3.61	6.04	15.10
150	2.06	0.15	1.35	1.53	1.61	6.70
Σ 150	8.90	1.68	4.54	8.17	13.12	36.41
Kukersite						
40	1.65	0.80	1.49	1.16	3.10	8.20
100	1.00	0.62	0.75	1.22	2.10	5.69
150	1.85	0.25	1.03	0.83	5.75	9.71
Σ 150	4.50	1.67	3.27	3.21	10.95	23.60

Higher in temperatures efficiencies were obtained on account of certain compounds groups transformed to the extractables composition resulting from SFE. One can see that SFE performed already at 40˚C, i.e. the lowest temperature used results in considerably higher production of aliphatic, mono- and polycyclic aromatic hydrocarbons and neutral heteroatomic compounds from both Kukersite and GA than SEM with liquid chloroform. Distinction between SFE and SEM efficiencies becomes particularly evident when those compounds in extracts yielded from oil shales at 40˚C are compared with their yields in summarized bitumoids A and C. Further extraction at the temperatures 100˚C and 150˚C yielded additive portions of hydrocarbons and neutral heteroatomic compounds and that is why efficiency of different compound classes on the bases of summarized extract (Σ150^{O}C) with that in total bitumoid (bitumoids A + C) would be compared to obtain comparable and reliable data. Such comparison can be seen in Tables 9 and 10 demonstrating amplified regularities described above. Extraction efficiency of the same compound groups from GA surpasses that of Kukersite.

Generalizing, SFE yields from both oil shales mainly various hydrocarbons and neutral heteroaromic compounds while SEM produces lots of HPHet compounds the efficiencies of extraction always being higher for GA. Productivities of Soxhlet extractor and batch autoclave in case of GA and Kukersite oil shale were 10 - 50 and 120 - 200 mg/h, respectively. SFE leads to higher productivities at lower temperature and shorter process duration.

Homologous n-alkanes, alkylmonoarenes, alkylpolyarenes and alkylalkanones easily extracted by SFE were identified, and new compounds as n-alkanones-3, n-alka- nones-4, n-alkanones-5, n-alkanones-6 and n-alkanones-7 were found in SFE extracts.

GA extracts were characterized by the same homologous series of compounds having, in most instances, longer alkyl chains amounting as an absolute maximum to 31 in n-alkanes. In addition to, homologous carboxylic acids and esters were identified.

3.2 Semi-coking of graptolite argillite in a Fischer assay

As a result of conventional FAP oil in yield 13,3% on OM bases from GA was produced as condensable volatiles. Recoverable oil and TB yields as well as those of SR, gas and water obtained from kerogen as a result of MFAP at constant residence time (20 or 60 min) and varied temperatures are represented in Table 11. The analogous results of FAP for Kukersite are represented in Article II.

One can see common features and dissimilarities between two oil shales tested. With increasing the temperature the yield of SR proportionally decreases and that of gas increases up to twice. Exception is Kukersite MFAP during 60 min where gas yield practically was not changed with temperature rise from 370 to 410 °C.

Concerning regularities of TB, oil and water formation one can notice significant differences.

Table 11 Yield of products from GA in Fischer assay using standard and varied conditions, % on OM

Pyrolysis conditions		Product yields, %					
Residence time	**Max. temp**	**Oil**	**TB**	**TBO**	**SR**	**Water**	**Gas**
20	390	6,7	1,5	8,2	70,5	17,7	3,6
20	440	14,5	0,3	14,8	53,8	23,1	8,3
20	480	17,5	0,2	17,7	51,5	18,9	11,9
20	520	13,3	-	13,3	44,6	27,6	14,5
60	320	0,7	1,1	1,8	80,5	14,4	3,3
60	390	5,1	1,6	6,7	65,9	21,3	6,1
60	440	10,4	0,4	10,8	53,3	27,3	8,6
60	460	13,0	0,3	13,3	49,2	25,5	12,0
60	490	11,4	0,1	11,5	46,3	27,3	14,9

One can see that TB yields at 390-490^{O}C and residence times 20 and 60 min are very low (1,6%). TB maximum has been formed below 390 °C, because with increasing the temperature TB intensively decomposes to oil, gas and water. The maximum oil yield (17.5%) in parallel with the minimum that of TB (0.2%) was obtained during 20 min at 480 °C. GA pyrolysis was accompanied with significant water formation compared with Kukersite (3–5 and 0.6–1.6% per oil shale, respectively). Water of crystallization in mineral part of GA can have its role in larger water formation.

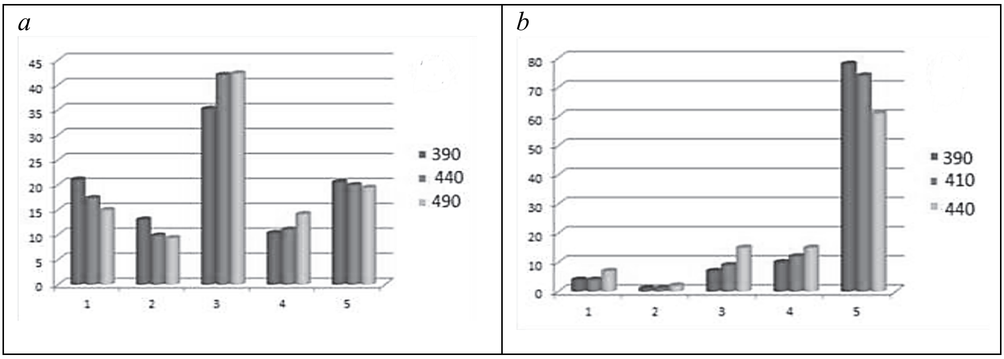

Figure 6. Group composition of TBO of GA (a) and Kukersite (b) oil shales, %. Fractions separated by TLC as follows: 1 –AlHC, 2 – MAHC, 3 – PAHC, 4 – LPHet, 5 – HPHet.

Group composition of TBO is displayed in Fig. 6 and one can see that it is different for GA and Kukersite. In the composition of GA TBO prevail PAHC their yield amounting to 40%. 60–75% of Kukersite TBO make HPHet. The content of hydrocarbons is low. HPHet, dominating in Kukersite TBO make only 20% in GA. Among hydrocarbons PAHC are dominating in Kukersite TBO as well. It seems that temperature has only small effect on TBO composition. With increasing the temperature slightly decreases the content of HPHet and increases that of hydrocarbons (in case of GA, particularly PAHC content).

The individual composition of TLC AlHC and LPHet fractions analyzed by using GC-MS-methods is represented in Appendix 1. One can see that the TBO of GA differs from that of Kukersite mainly by the composition of AlHC and LPHet. Similar compounds were identified in the composition of aromatic hydrocompounds. FAP of both GA and Kukersite yielded homologous alkanes and alkenes. The length of the hydrocarbonaceous chains in n-alkanes derived from GA pyrolysis is longer compared with Kukersite, 31 and 17 carbon atoms, respectively. The phenols and the N containing compounds with aromatic structure are prevailing in GA TBO LPHet fraction.

3.3 Low temperature pyrolysis of oil shales in autoclave

3.3.1 Low temperature pyrolysis of graptolite argillite in autoclave

Yields of the pyrolysis products from the GA obtained in the test series conducted at various nominal temperatures and varied durations are presented in Article III in Tables 1 and 2.

The results demonstrated that at any temperature series the gas yield increases with time whereas the yield of TBO has a maximum and that of SR a minimum shifting with increasing temperature to shorter durations. The maximum yield of gas achieved is only 2.7%, and the maximum transformation degree of the OM is 7.4% of the dry initial shale.

The better characterization of the process can be obtained when the yields are depicted on the basis of OM. Effect of pyrolysis duration at various nominal temperatures and temperature at various durations on the yields of the main decomposition products – gas, TBO, water, and SR of OM, are presented in Article III Table 1 and Fig. 7.

The experimental data in Article III Table 2 and in Fig. 7 and 8 prove the tendencies prove the tendencies in Table 1. The decomposition of OM starts in the heating stage already before the nominal temperature has been achieved. The yields of gas, SR and W change with increasing both nominal temperature and pyrolysis time up to a characteristic steady state whereas the yield of TBO passes a maximum at several optimal combinations of temperature and time. The yields on OM basis achieve close values: for gas about 16%, for TBO 13.2%, and for water 15%. OM in SR after pyrolysis at most expedient pyrolysis conditions can be reduced not lower than to 58 %. Yield of the target product, TBO, obtained using the low-temperature pyrolysis procedure in an autoclave, s.c. TBO-technology, being even lower than in FAP and MFAP.

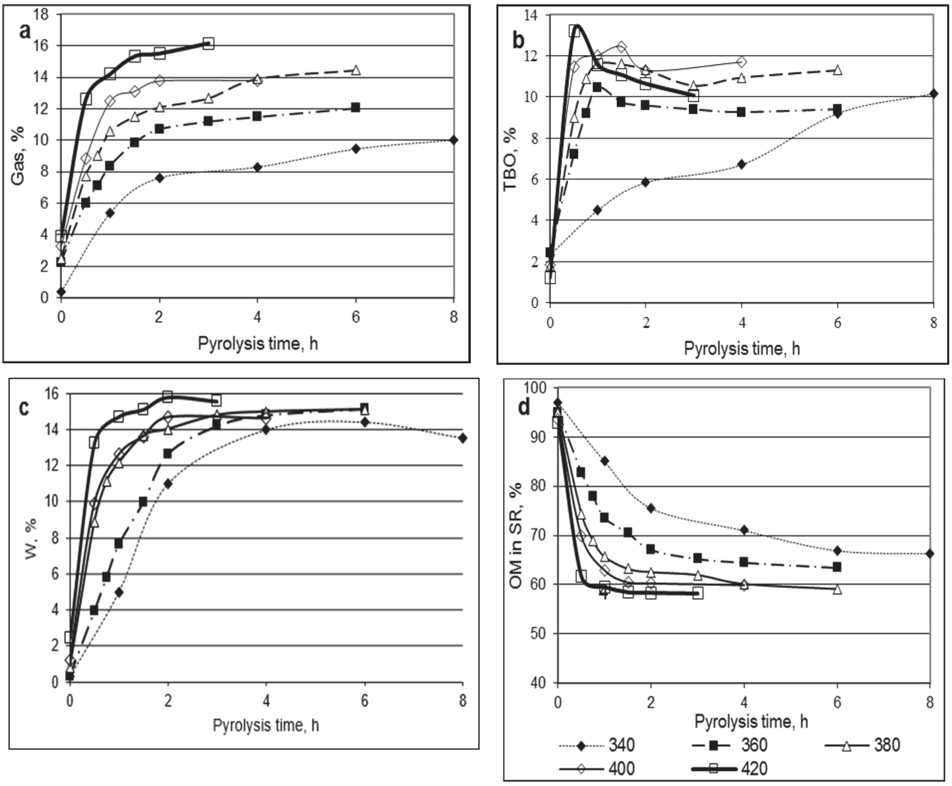

Figure 7. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of gas (a), TBO (b), water (c) and SR (d), % on OM basis at different pyrolysis temperature: 340, 360, 380, 400, 420°C.

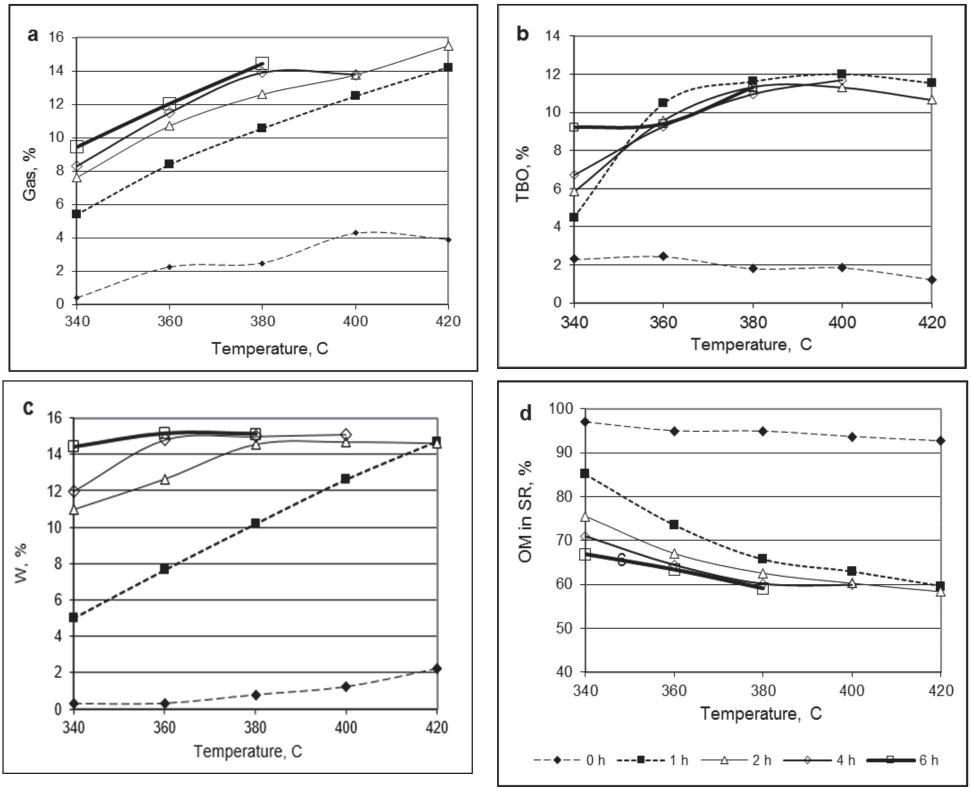

Figure 8. Effect of nominal temperature in autoclavic pyrolysis on the yield of gas (a), TBO (b), water (c) and SR (d), % on OM basis at different isothermal duration: nominal temperature achieving, 1h, 2h, 4h, 6h.

3.3.2 Low temperature pyrolysis of various oil shales in autoclave

The yields of pyrolysis products from GA were compared with those obtained for Kukersite (31.0% OM) [59], US Utah Green River (13.6% OM) [Article V], and Jordanian Attarat (21.4% OM) [Article IV] oil shales. Also, the group composition of their TBO were compared.

The yields of pyrolysis products from the oil shales obtained in autoclave at the identical conditions are given in Fig. 9.

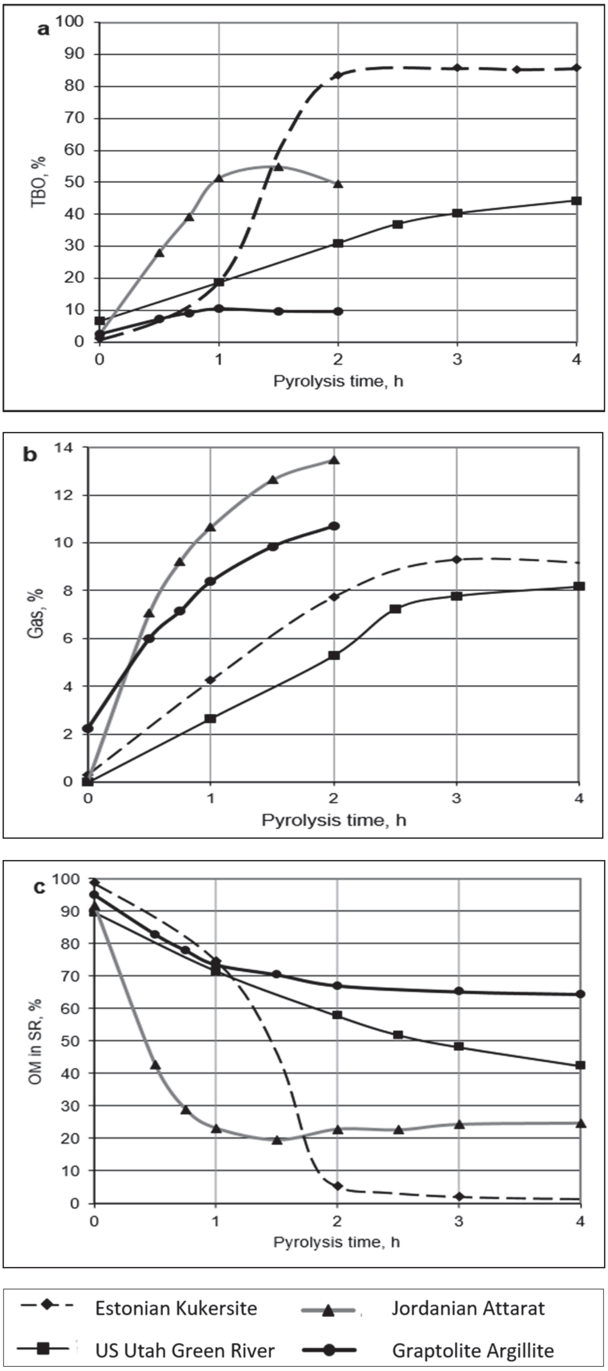

Figure 9. Effect of time on the yields of pyrolysis products (360°C) from different oil shales.

The optimum durations at 360 °C and maximum yields of TBO in their OM basis depicted in Fig. 9a are very different: for Estonian Kukersite about 2 h, 85%, for Jordanian oil shale 1.5 h, 55%, for US Utah Green River 4h and 45%, and for Estonian GA –1h and 10-12% only. At higher temperature the maximum is achieved at shorter time. The angle of inclination gives the possibility to compare the speed of TBO formation. Kinetics of destruction of Estonian Kukersite, US and Jordanian oil shales was described in [52], Article IV and Article V.

The yield of gas from different oil shales (Fig. 9b) increases steadily with temperature and time increasing. The gas yield is higher for Jordanian oil shale and GA (more than 11-13%) and compared with Kukersite and US shales (8-9%).

The pyrolysis time for minimum quantity of OM left in SR after pyrolysis using TBO technology (Fig. 9c) corresponds with the conditions for the maximum yield of TBO. About 65% of OM is left in the residue of GA, 40% of US, and 20-25% of Jordanian oil shale. The organic residue of Kukersite oil shale is 2-5% of OM only.

The group composition of TBO obtained at pyrolysis conditions with maximum TBO yield from compared shales is given in Article III.

Comparative pyrolysis of various oil shales in an autoclave and in FAP demonstrated that liquefaction conditions being particulary effective for liquefaction of Kukersite, enhanced somewhat the liquid yield from Jordanian Attarat oil shale only, but had no practical effect in case of the US Utah oil shale and GA. In latter case even less TBO than in FAP was formed.

3.4 Thermochemical dissolution of graptolite argillite in an autoclave

3.4.1 Products yield

The data in Table 12 represent yields of gas, oil and SR obtained in liquefaction process with presence of solvents at 360 °C during 4 h.

Table 12 Products yields obtained in thermochemical dissolution with varied solvents, %

Solvent	TBO	SR	Gas and losses
-	5.1	72.5	22.4
Water	11.4	62.7	25.9
Benzene	22.3	66.3	11.4
Toluene	28.0	63.2	8.8
Hexane	25.5	53.1	21.4
Cyclohexane	30.65	49.5	19.9
Methanol	34.4	53.1	12.5
Ethanol	84.3	17.5	-
Isopropanol	89.5	62.9	-

Solvents used in thermochemical dissolution were all above supercritical conditions, except water. At chosen conditions (360 °C, 4 h) all used solvents gave higher oil yield from GA than in FAP and in dry pyrolysis or water conversion, varying between 22 and 90% (Table 12). Non-polar solvents yield TBO in-between 22,3 and 30,6%. The amount of SR varies from 49,5 to 66,6%). The results of thermal dissolution with alcohols vary significantly. Yields of TBO vary from 11,4 to 89,5% and that of SR from 53 to 63%. Thermal dissolution with isopropanol and ethanol demonstrated exceptionally high TBO yield obtained as a result of incorporation of these alcohol decomposition fragments into TBO. Yield of TBO of thermal dissolution with methanol is higher than that with non-polar solvents. The presence of solvents at supercritical pressures breaks the bonds between kerogen and MM.

Rather additive than synergistic effects were noticed in using benzene-water and ethanol-water binary solvents (Fig.10).

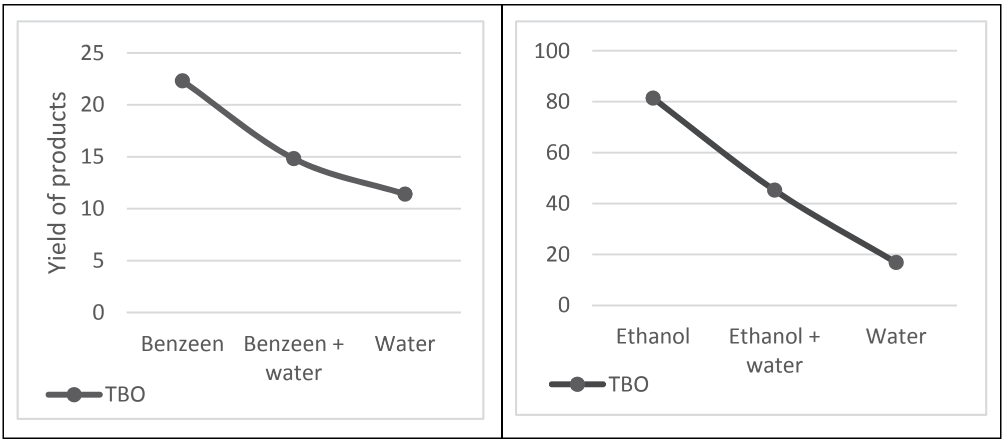

Figure 10. Yield of TBO in thermal dissolution with mixtures of solvents with mass ratio 1:1.

3.4.2 Products composition

Elemental composition of the benzene soluble TBO from dry pyrolysis and from thermal dissolution with methanol, ethanol and mixture of water and ethanol are represented in Table 13.

Table 13 Elemental analysis data, %

	C	H	N	S	O	H/C
Dry pyrolysis	79.7	9.0	0.7	4.9	5.7	1.355
Methanol	82.9	9.1	0.9	1.4	5.8	1.317
Ethanol	82.5	8.7	1.0	0.7	7.1	1.265
Water with ethanol	78.2	8.5	1.0	4.7	7.7	1.304

One can see from Table 13 that there are significant differences in elemental composition of TBO that varying as follows: C - 78.2 to 82.9, H - 8.5 to 9.1, N - 0.7 to 1.0, S – 0.7 to 4.9 and O – 5.7 to 7.7.

The group composition of benzene soluble TBO determined by TLC varies widely (Fig. 11).

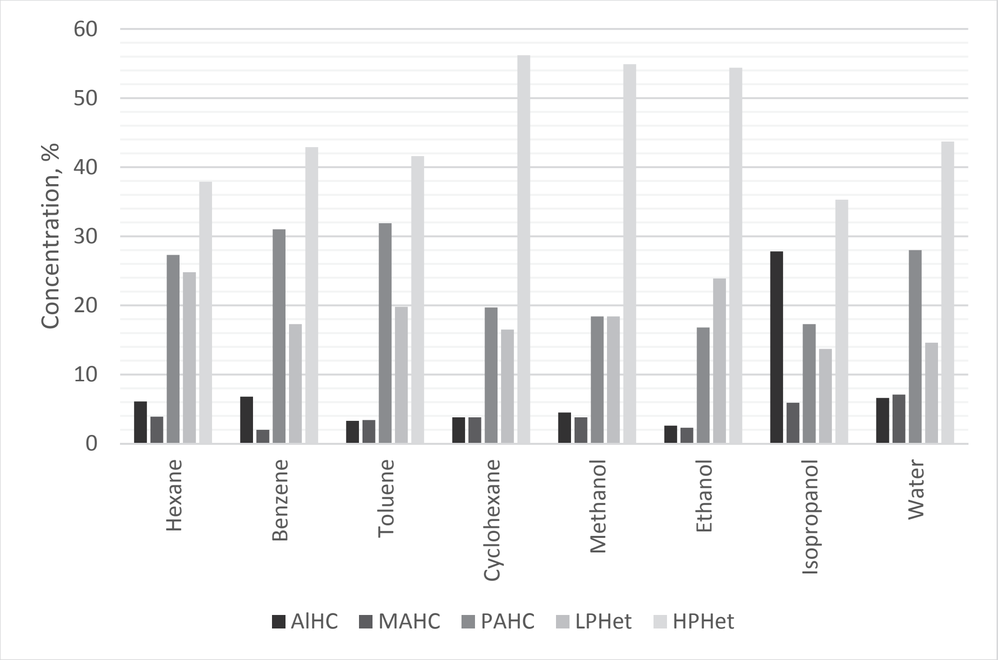

Figure 11. Group composition of the benzene soluble TBO.

Fig. 11 demonstrates, that the HPHet compounds are the dominating fraction in all TBO modifications their yield varying from 35,3% (iso-propanol) to 56,2% (cyclohexane).

Thermal dissolution with using inert solvents as hexane, benzene, toluene and cyclohexane was accompanied with formation of heteroatomic compounds in yield 37.9 to 56.2% and PAHC up to 31.9%.

TBO obtained in the medium of iso-propanol is outstanding by high concentration of AlHC (27,8%) explained by the chemical activity of this solvent.

TBO obtained in GA water conversion was characterised by total content of hydrocarbons as 41,7%. For comparison, the TBO obtained in Kukersite water conversion contained hydrocarbons 27% only [53].

GC-MS-chromatograms of hydrocarbons and LPHet compounds in benzene soluble TBO of thermal dissolution with benzene are represented in APPENDIX A. According to GC-MS n-alkanes with straight alkyl chains C_{12}-C_{33} were formed. Relative concentrations of alkanes in benzene soluble TBO are presented in Fig.12.

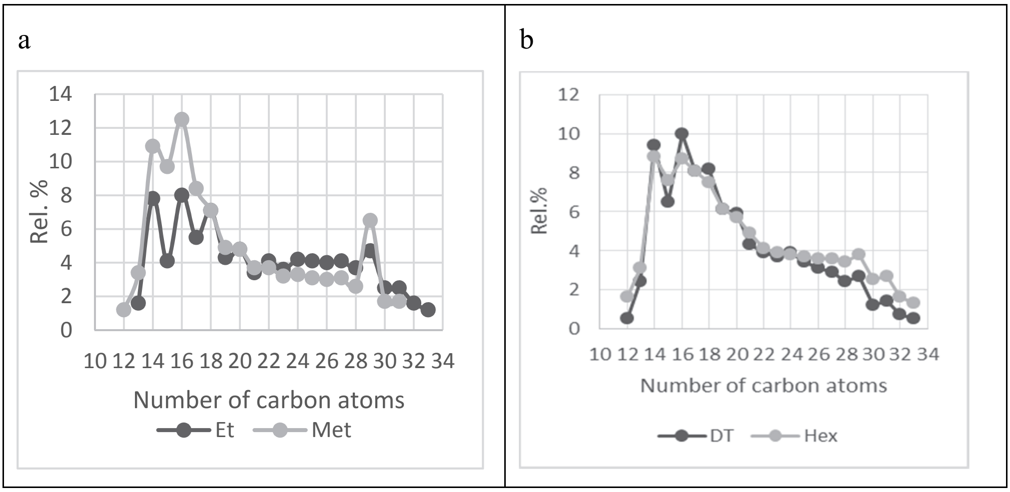

Figure 12. Relative concentration of n-alkanes in benzene soluble nonaromatic hydrocarbons of thermochemical dissolution with a) ethanol and methanol and b) toluene and hexane

One can see from Fig. 12 that the maximum concentration have C_{14} and C_{16}.

3.4.3 Influence of additives on the water conversion products yield

Water conversion resulted in low TBO yield, 11.4% only, being lower than that in FAP. Water is known as a solvent in common use, but in certain conditions its redox potential can be realized by adding reagents.

The reagents used and the yield of TBO, SR and gaseous products in water conversion of GA in their 5% solutions, separated according to the scheme given in Fig. 4 are represented in Table 14.

Table 14 Yield of liquid, gaseous and solid products from GA in water conversion (360°C, 4h) with reagents, % on OM basis

Reagent	TBO				SR	Gas and Water
	Water solubles	Benzene solubles	Acetone solubles	Total solubles		
-	0.76	6.68	4.30	11.74	64.88	23.38
$NaHCO_3$	1.94	20.20	3.74	25.88	43.76	30.36
KOH	1.67	23.81	3.62	29.10	34.52	36.38
NaOH	3.35	26.41	3.60	33.36	32.73	33.91
HCOONa	2.29	37.80	2.91	43.00	16.74	40.26

As it can be seen the yields of TBO were considerably higher than that in conversion with water only. It is known that mineral and organic parts in oil shales are closely related and alkali solution may favour these bonds cleavage. One can see that TBO yield has been increased on account of the benzene soluble compounds.

The most effect on the efficiency of water conversion was demonstrated by using solutions of sodium formate and sodium hydroxide. In the Fig. 13 yields of TBO in different concentrations of the latter reagents are presented.

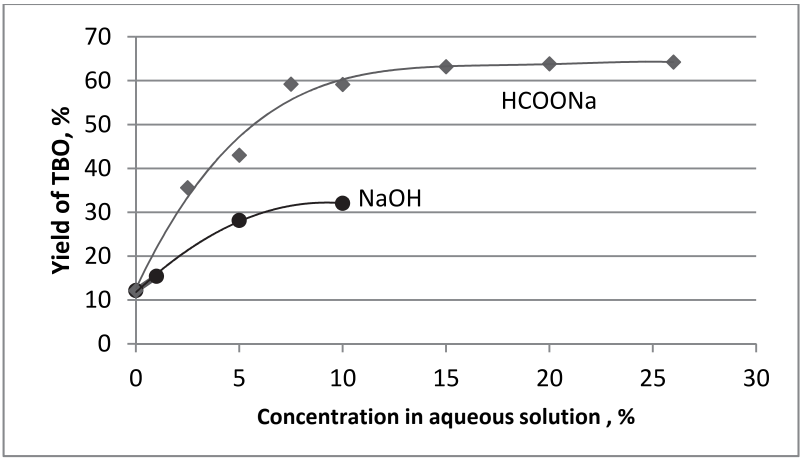

Figure 13. Dependence of TBO yield on concentration of reagent in aqueous solution.

As it can be seen addition of sodium formate increased TBO yield up to 43.0% using 5% aqueous solution and amounted to 63.8% as maximum using 15% solution. Decomposition of sodium formate at elevated temperatures is described according to the equation:

$2HCOONa \rightarrow Na_2CO_3 + CO + H_2$ [54]

High TBO yield obtained can be explained by H-donor and syngas donor abilities of HCOONa initiating different chemical reactions and favouring GA liquefaction.

3.4.4 Influence of additives on the water conversion products composition

Infrared spectra of TBO obtained in water conversion with HCOONa are represented in Fig. 14.

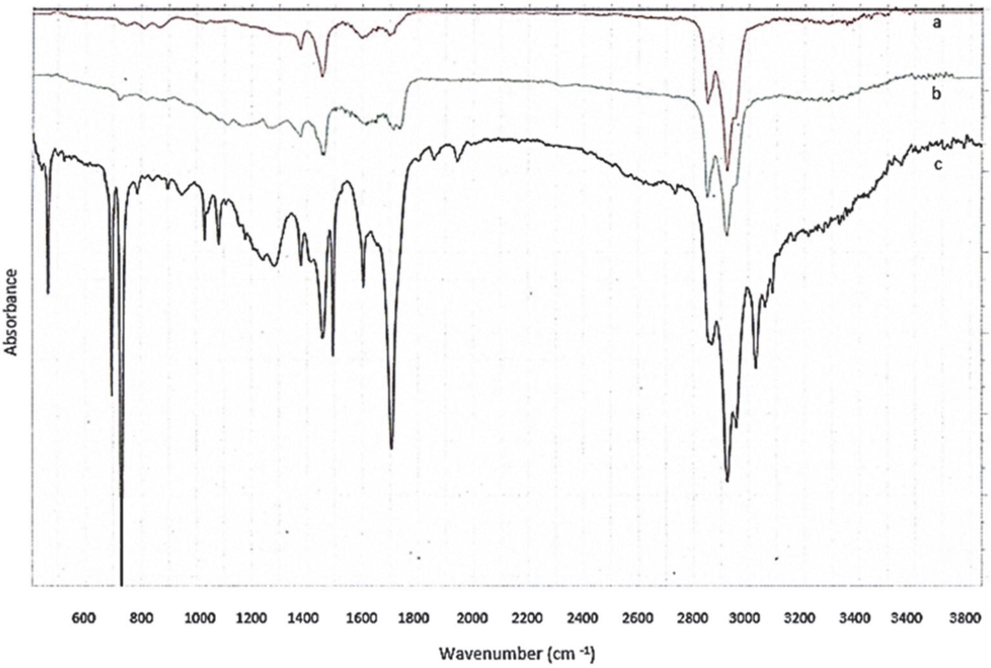

Figure 14. Infrared spectra of TBO obtained in water conversion with HCOONa. a- benzene soluble fraction, b-acetone soluble fraction, c- water soluble fraction.

Infrared spectra of benzene soluble, acetone soluble and water soluble fractions of TBO obtained in water conversion with HCOONa addition have common absorption bands at 725, 750, 1380, 1460, 2860, 2930 and 2960 cm^{-1} caused by methyl and methylene groups in aliphatic chains, absorptions at 1680-1720 cm^{-1} caused by carbonyl groups, broad absorption in the region 3300-3450 cm^{-1} caused by hydroxyl groups and complex absorptions are more intensive in case of water soluble fraction. Absorptions at 750-760, 820, 880, 1020, 1080,1475-1525, 1595-1605, 3020 and 3050 cm^{-1} are typical for aromatic compounds. Water soluble fraction is characterised by specific absorption region at 1145-1270 cm^{-1} caused by ethereal groups. The absorption around 465 cm^{-1} can be refer to the presence of clay mineral microcline.

The results of TLC are given in Fig.15.

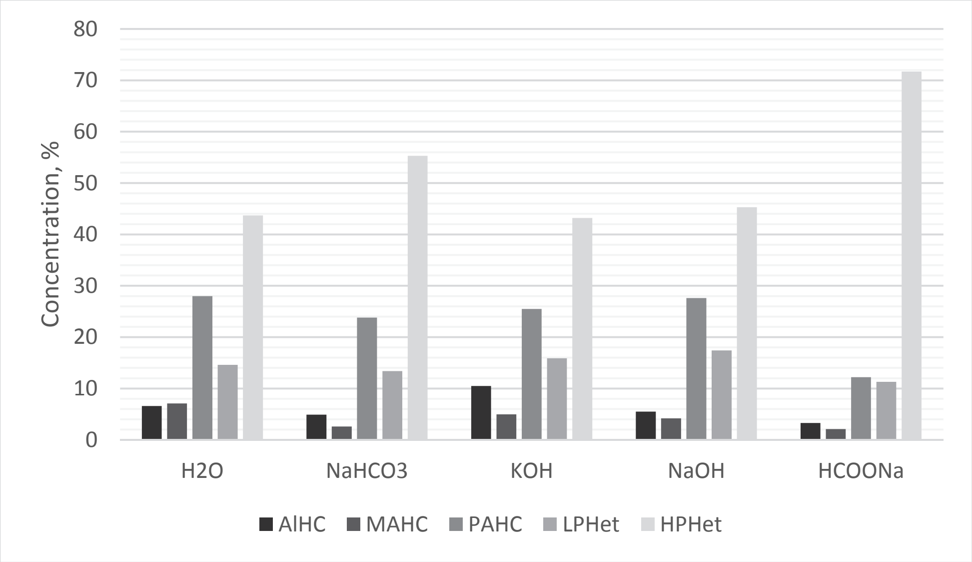

Figure 15. Group composition of the benzene soluble TBO obtained from water conversion of GA in the presence of reagents

Data of the group composition demonstrated that the higher the yield of TBO obtained the higher the content of HPHet in TBO. It can be seen that the main benzene-soluble constituents of TBO are HPHet compounds and PAHC. The benzene-soluble TBO from GA water conversion in the presence of KOH is characterized by maximum content of AlHC (10.5%) and minimum that of HPHet (43.2%).

Compared with FAP and dry pyrolysis in autoclaves 2-4 times higher TBO yields from GA using water conversion with additives were obtained.

3.5 Hydrogenation in an autoclave with molecular H_2

The results of hydrogenation experiments of GA are represented in Fig.16. As it can be seen the yield of hydrogenate has increased in several times in comparison with that of dry pyrolysis in autoclave. The maximum yield was obtained at 390 ^{o}C during 2 h accompanied with decreasing SR content down to 5%. At higher temperatures significance of liquefaction decreases on account of gas formation.

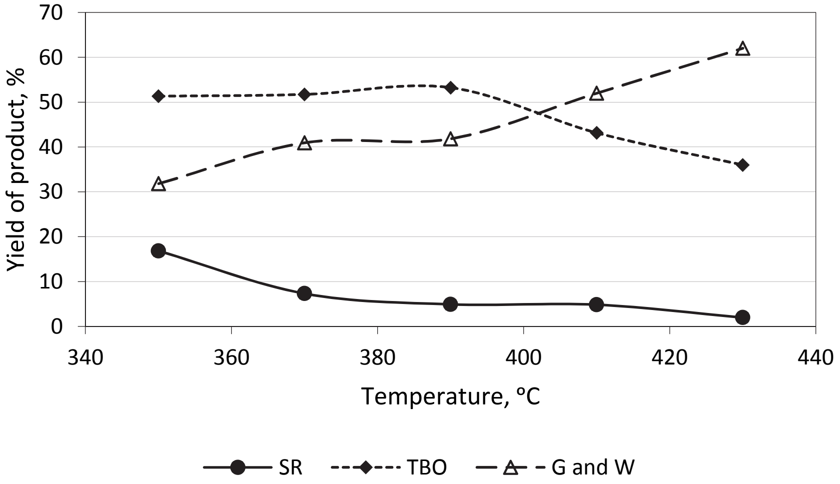

Figure 16. The effect of temperature on the yield of products from GA hydrogenation, % on OM

The results of ultimate analysis of hydrogenates are presented in Table 15.

Table 15 Elemental composition of hydrogenates obtained at different temperatures

Temperature	C	H	N	S	O (dif)	H/C
350	84.41	9.98	1.41	1.65	2.56	1.418
390	84.98	10.71	0.89	2.26	1.17	1.512
410	85.89	10.41	0.65	2.21	0.85	1.454
430	86.01	10.11	0.46	2.57	0.85	1.411

The data in Table 15 demonstrate that with raising the temperature the substitution of heteroelements with hydrogen is accelerated. The content of oxygen and nitrogen has decreased threefold. The content of sulfur has been decreased from 4.9 in dry pyrolysis TBO down to 1.65 – 2.57%. It seems that the content of sulfur in hydrogenate increases with increasing the temperature, not *vice versa* as it expected, but in fact relatively to hydrogenate yield decreasing also the content of sulfur decreases.

The results of the TLC analysis of the hydrogenates are represented in Fig. 17.

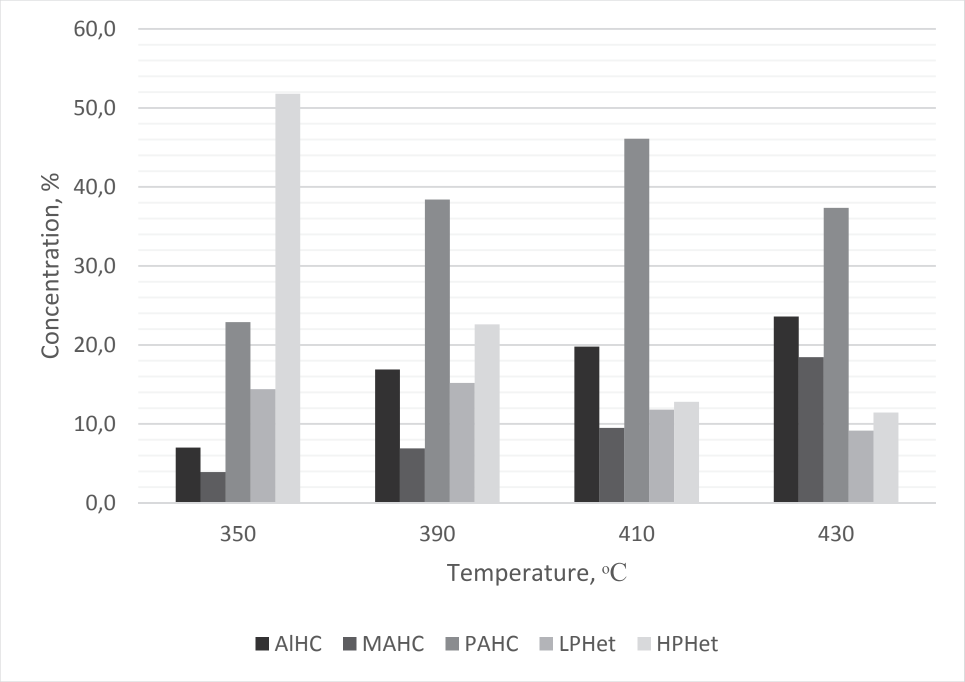

Figure 17. The group composition of hydrogenates obtained at different temperatures.

It can be seen, that the yield of heteroatomic compounds decreases with increasing the hydrogenation temperature more than three times with respective increase in total hydrocarbons yield (AlHC from 7.0 to 23.6%, MAHC from 3.9 to 18.5%, PAHC from 22.9 to 46.1%).

3.6 The comparison of TBO from different thermochemical methods

Table 16 represents results of the ultimate analysis and the group composition of the benzene soluble TBO obtained using different thermochemical destruction methods used in this work. For comparison, the data of Kukersite semi-coking oil are represented.

Table 16 Ultimate analysis and group composition of TBO obtained in optimum conditions using different thermochemical destruction methods

	Dry pyrolysis in autoclave at 400°C	**Thermochemical dissolution with ethanol**	**Water conversion with addition of HCOONa**	**MFAP at 490°C**	**Hydrogenation at 390°C**	**Kukersite semi-coking oil**
Ultimate analysis:						
C	79.7	84.3	82.3	82.3	85.0	81.7
H	9.0	8.5	9.5	9.8	10.7	9.8
N	0.7	0.4	1.9	0.3	0.9	0.6
S	4.9	-	0.9	4.4	2.3	1.1
O	5.7	-	5.4	3.3	1.2	6.8
H/C	1.355	1.210	1.385	1.426	1.512	1.485
Group composition:						
AlHC	10.5	2.6	3.3	14.9	16.9	10.9
MAHC	14.3	2.3	2.1	9.3	6.9	6.8
PAHC	30.5	16.8	12.2	42.3	38.4	14.7
LPHet	16.2	23.9	11.3	14.1	15.2	25.6
HPHet	28.5	54.4	71.7	19.4	22.6	42.0

In comparison with other thermochemical destruction methods, in case of hydrogenation the yield of TBO as well as saturation of hydrocarbons is higher and this method is preferable for further study.

As it can be seen from the Table 16, the high concentration of HPHet and minimum that of AlHC were produced in water conversion with addition of HCOONa. This result can be explained by the reactive role of the carbon monoxide formed as a result of HCOONa decomposition.

Hydrocarbons prevail in the TBO obtained in MFAP and hydrogenation (66.5% and 62.5%, respectively), the yield of TBO differing three times. Kukersite semi-coking oil is characterised by higher content of heteroatomic compounds and lower that of PAHC.

3.7 Technological consideration

The comparison of yields of liquid and gaseous products obtained from different thermochemical destruction methods are represented in Fig. 18.

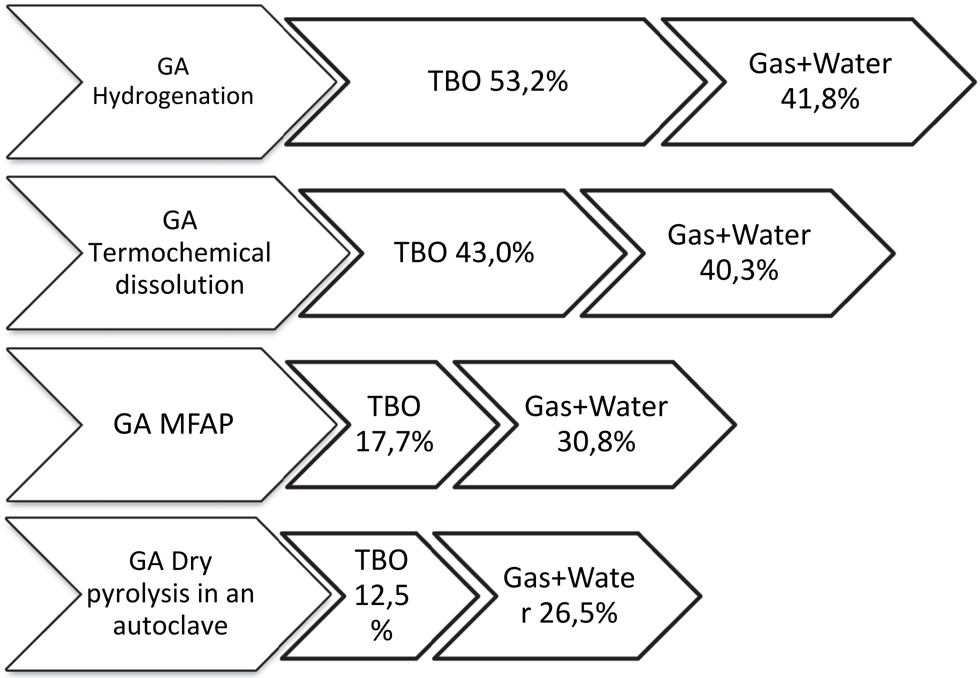

Figure 18. Comparison of the yields of liquid and gaseous products obtained using different methods of thermochemical destruction.

One can see that hydrogenation yields maximum TBO and this method is preferable for the further development.

4 CONCLUSIONS

The main results of the present work include obtaining new data on the composition of graptolite argillite and proposing the effective method for its decomposition.

Graptolite argillite sample represents another Estonian oil shale significantly differing from Kukersite. Just new and alternative method for characterisation of oil shales, was developed basing on thermal dissolution with supercritical carbon dioxide in low-temperature region 50-150 °C and novel homologous series of carboxylic acids, esters, n-alkanones-3, n-alkanones-4, n-alkanones-5, n-alkanones-6 and n-alkanones-7 were found at first time in the composition of bitumoids dissoluted from Estonian oil shales with supercritical fluid.

It has been demonstrated that semi-coking as traditional and the only one industrial technology today does not work on graptolite argillite, giving in both conventional and modified Fischer assay conditions low yield of oil and that is why new technologies basing in use of solvent and hydrogen have been worked out to elevate the liquefaction efficiency of graptolite argillite and to modify the chemical composition of the products.

Liquefaction efficiencies of oil shale in autoclave compared with Fischer assay are differing. In dry pyrolysis of oil shales from Estonian, Jordanian and American deposits the maximum differences were shown by Kukersite and graptolite argillite, the first showing increase in 30% and the other one the same decrease respectively.

As a result of thermal dissolution with using sub- and supercritical water, C6-hydrocarbons and methanol the yield of oil from graptolite argillite was demonstrated to be varying in-between 12-34 % on OM basis. As high as 84-90 % oil yields can be obtained with using ethanol and iso-propanol as supercritical solvents contributed by incorporation of alcohol decomposition fragments into oil structure. $NaHCO_3$, KOH ja NaOH additions increase oil yield 2-3 times and HCOONa 5 times compared with water conversion without any additive.

Hydrogenation of graptolite-argillite with molecular hydrogen in temperature region 350-400°C results in 51-53% oil yield, the latter containing 34-62% various aliphatic, mono- and polycyclic aromatic hydrocarbons. The maximum values of oil yield and hydrocarbons content were obtained as a result of 2 hours hydrogenation at 390 °C in an autoclave.

Oils obtained in semi-coking, thermal dissolution and hydrogenation of graptolite-argillite are similar by chemical group composition and differing by individual compounds in groups. Semi-coking oil contains more hydrocarbons (56 %) and less polar heteroatomic compounds (44 %) compared with thermal dissolution oils (24-40 and 60-75, respectively).

Oil obtained in graptolite-argillite hydrogenation differs from Kukersite semi-coking oil by higher hydrocarbons content and lower polar heteroatomic compounds content. Notably high is the content of polyaromatic hydrocarbons, 46 versus 17 %.

Solid residue of graptolite argillite obtained in optimized conditions of hydrogenation contains only less than 5 % of organic matter and can further utilised as valuable ore for leaching many metals [7, 10, 26].

Hydrogenation method worked out for the effective processing of graptolite argillite can be successful in utilisation of oil shales in their majority characterised by low organic matter and high that of heteroatomic elements.

REFERENCES

1. Soesoo, A., *More out from oil shale?* Oil Shale, 2014, 31(3), 207-210.
2. Urov, K., Sumberg, A., *Characteristics of oil shales and shale-like rocks of known deposits and outcrops. Monograph.* Oil Shale, 1999, 16(3), 1-64.
3. Oja, V., Suuberg E. M., *Oil Shale Processing, Chemistry and Technology* Ripudaman Malhotra. Fossil Energy. Selected Entries from the Encyclopedia of Sustainability Science and Technology, New York, 2013
4. World Energy Council, 2010 Survey Of Energy Resources, 93-122
5. Aarna, A., Põlevkivi. Tallinn, „Valgus“ 1989
6. Veski, R., Palu, V. *Investigation of Dictyonema oil shale and its natural and artificial transformation products by a vankrevelenogram.* Oil Shale, 2003, 20(3), 265-281
7. Vyalova, V. I., Balakhonova, A. S., Laricheva, A. I., and Bogomolov A. K., *Rhenium in the Dictyonema Shale of the Baltic Basin*, Moscow University Geology Bulletin, 2013, 68(2), 123–128.
8. Hade, S., Soesoo, A., *Estonian Graptolite Argillites Revisited: A Future Resourse?* Oil Shale, 2014, 31(1), 4–18.
9. Siirde, A., Diktüoneema kiltkivi termiline lagundamine: Dissertatsioonitöö. Tallinn, Tallinna Polütehniline Instituut, 1957
10. Lippmaa, E., Maremäe, E., Pihlak, A.-T., Aguraiuja, R. *Estonian graptolitic argillites – ancient ores or future fuels?* Oil Shale, 2009, 25(4), 530/539
11. Dyni, J. R. *Geology and resources of some world oil-shale deposits*. Oil Shale, 2003, 20(3), 193-252
12. Krenkel, H., Bromley-Challenor, M., Snäll, S. *Evaluation of liquid hydrocarbon recovery potential from Swedish alum shale.* In: Book of abstracts: International Oil Shale Symposium, Tallinn, Estonia, June 8-11, 2009, 71
13. Koch, R., Kiis, K. *Peculiarities of thermolysis of organic matter in alum shale (argillite),* Proc. Acad. Sci. Estonian SSR. Chem., 1983, 32 (1), 8-18 [in Russian]
14. Koch, R., Kiis, K. *Peculiarities of thermolysis of organic matter in alum shale (argillite)*, Proc. Acad. Sci. Estonian SSR. Chem., 1984, 33 (1), 9-14 [in Russian]
15. Koch, R., Kiis, K. *Peculiarities of thermolysis of organic matter in Maardu argillites (alum shale).* 3. *Compositional elements of organic matter and thermolysis,* Proc. Acad. Sci. Estonian SSR. Chem., 1984, 33 (2), 110-116 [in Russian]
16. Vysotskaja,V., Urov, K. *Mineral matter dependence of the yield and composition of Dictyonema shale thermal thermal decomposition products.* Proc. Acad. Sci. Estonian SSR. Chem., 1983, 32 (4), 246-251 [in Russian]

17. Vysotskaja, V., Urov, K., Ter-Oganesjan, G. *High-rate pyrolysis of Estonian dictyonema shale concentrate and the clay residues of its enrichment.* Proc. Acad. Sci. Estonian SSR. Chem., 1987, 36 (1), 17-23 [in Russian]
18. Urov, K., Vysotskaja, *Effect of Carbonate rock on the yield and composition of dictyonema shale semi-coking products*. Oil Shale, 1985, 2(2), 170-180 [in Russian]
19. Vysotskaja, V., Urov, K. *The effect of pyrite on the yield and composition of oil shale semi-coking products. 1. Dictyonema shale of the Estonian SSR.* Proc. Acad. Sci. Estonian SSR. Chem., 1988, 37 (4), 241-247 [in Russian]
20. Müürisepp, A.-M., Urov, K., Liiv, M., Sumberg, A. *A comparative study of non-aromatic hydrocarbons from kukersite and dictyonema shale semi-coking oils.* Oil Shale, 1994, 11(3), 211-216
21. Blyakhina, I., Urov, K. *Formation of decomposition products from dictyonema shale during the last stages of semi-coking.* Oil Shale, 1996, 13(3), 185-192
22. Ivanov, A., Rang, S., Eisen, O., Styopin, S. *Composition of the low-boiling fractions of dictyonema oil shale.* Proc. Acad. Sci. Estonian SSR. Chem. Geol., 1973, 22 (4), 301-305 [in Russian]
23. Rang. S., Orav, A.,Ivanov, A., Eisen, O., Styopin, S. *Composition of the Toolse Dictyonema shale oil fraction 120-190^{o}C.* Proc. Acad. Sci. Estonian SSR. Chem. Geol., 1974, 23(1), 27-30 [in Russian]
24. Rang, S., Orav, A., Eisen, O. *Composition of the Dictyonema shale oil fraction 190-270^{o}C* Proc. Acad. Sci. Estonian SSR. Chem. Geol., 1975, 24(1), 10-14 [in Russian]
25. Urov, K., Vyssotskaya, V. *About oil secretion of buried burning Dictyonema oil shale. 2. The chemical composition of the oil.* Proc. Acad. Sci. Estonian SSR. Chem., 1981, 30 (2), 101-105 [in Russian]
26. Lippmaa. E., Maremäe, E., Pihlak, A.-T. *Resoures, production and processing of Baltoscandian multimetal black shales.* Oil Shale, 2011, 28(1), 68-77
27. Lunch, P.A., Janka, J.C., Lau, F.S., Feldkirchner, H.L., Dirksen, H.A. *The hydroretorting assay – a new technique for oil shale assessment.* Paper presented at the Joint Fuel/Petroleum Division Meeting of the American Society, St. Louis, April 8-13, 1984.
28. Nappa, L., Klesment, I., Vink, N., Kailas, K. *Low temperature decomposition of organic matter of oil shales by solvent extraction. 2. Dictyonema shales.* Proc. Acad.. Sci. Estonian SSR. Chem., 1982, 31(2), 103-108 [in Russian]
29. Nappa, L., Klesment, I., Vink, N., Kailas, K. *Destructive hydrogenation of Dictyonema oil shale.* Proc. Acad.. Sci. Estonian SSR. Chem., 1980, 29(2), 84-91 [in Russian]

30. Klesment, I., *On the Genesis of the Baltic Oil Shales,* Oil Shale, 1985, 2(1), 12-22.
31. Klesment, I., *Investigation of Aliphatic Structures of Oil Shales by Pyrolysis and Chromatographic Methods,* Journal of Analytical and Applied Pyrolysis, 1980, 2(1), 63-77.
32. Oja, V. *Vaporization parameters of primary pyrolysis oil from kukersite oil shale.* Oil Shale, 2015, 32 (2), 124–133.
33. Lille, Ü. *Behavior of Estonian kukersite kerogen in molecular mechanical force field.* Oil Shale, 2004, 21(2), 99–114.
34. 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.
35. 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.
36. 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.
37. Ots, A. Oil Shale Fuel Combustion. – Eesti Energia AS, Tallinn, 2006
38. Bruner, G. Gas Extraction: An Introduction to Fundamentals of Supercritical Fluids and the Application to Separation Process; Steinkopff Darmstadt, Springer New York, 1994
39. Allawzi, M., Al-Otoom, A., Allaboun, H., Ajlouni. A., Al Nseirat, F., *CO2 supercritical fluid extraction of Jordanian oil shale utilizing different co-solvents*, Fuel Processing Technology, 2011, 92, 2016–2023
40. Tiikma, L., Johannes, I., Luik. H., Zaidensal, A., Vink, N., *Thermal dissolution of Estonian oil shale.* J. Anal. Appl. Pyrolysis, 2009, 85, 502–507
41. Baldwin, R.M., Manley, J.A., *Pyrolysis and hydropyrolysis of Kentucky oil shale in supercritical toluene under rapid heating conditions*, Fuel Processing Technology, 1988, 17(3), 201-207.
42. Baldwin, R.M., Chen, K.W., *Pyrolysis and hydropyrolysis of two carbonaceous Australian oil shales in supercritical toluene and tetralin*, Fuel, 1987, 66, 353.
43. Luik, H., Palu, V., Bityukov, M., Luik, L., Kruusement, K., Tamvelius, H., Pryadka, N. *Liquefaction of Estonian kukersite oil shale kerogen with selected superheated solvents in satic conditions.* Oil Shale, 2005, 22(1), 25-36.
44. Luik, H., Klesment, I. *Liquefaction of kukersite concentrate at 330-370°C in supercritical solvents*. Oil Shale, 1997, 14(3), 419-432.
45. R. Kramer, M. Levy, *Extraction of oil shales under supercritical conditions*, Fuel, 1989, 68(6), 702-709.

46. El harfi, K., Bennouna, C., Mokhlisse, A., Ben chanaa, M., Lemee, L., Joffre, J., Ambles, A., *Supercritical fluid extraction of Moroccan (Timahdit) oil shale with water*, J. Anal. Appl. Pyrol. 1999, 50(2) 163–174.
47. Funazukuri, T., Yokoi, S., Wakao, N., *Characterization of the oil extracted from Chinese Maoming oil shale*, Fuel, 1988, 67(8), 875-877
48. Yanik, J., Yüksel, M., Saglam, M., Olukcu, N., Bartle, K., Frere, B., *Characterization of the oil fractions of shale oil obtained by pyrolysis and supercritical water extraction*, Fuel, 1995, 74(1), 46-50.
49. Gorlov. E., *Thermal dissolution of solid fossil fuels*. Solid Fuel Chemistry, 2007, 41(5), 290-298
50. Smith, W. M., Landrum, T. C., Phillips, G. E., *Hydrogenation of shale oil*. Eng. Chem., 1952, 44 (3), 586-589.
51. Lynch, P. A., Janka, J. C., Lau, F. S., Feldkirchner, H. L., Dirksen, H. A. *The Hydroretorting Assay – a new technique for oil shale assessment.* Symposium on Characterization and Chemistry of Oil Shales, 1985, 71-75.
52. Johannes, I., Tiikma, L., Zaidentsal, A., *Comparison of the thermobituminization kinetics of Baltic oil shale in open retorts and autoclaves*. Oil Shale, 2010, 27, 17-25.
53. Kruusement, K., *Water conversion of oil shales and biomass*: Thesis on chemistry and chemical engineering, Tallinn, Tallinn University of Technology Press, 2007
54. Meisel, T., Halmos, Z., Seybold. K., Pungor, E., *The thermal decomposition of alkali metal formates*, Journal of Thermal Analysis, 1975, 7, 73-80
55. Перильман, В., Краткий справочник химика, Москва, 1954

ACKNOWLEDGMENTS

This work was supported by Estonian Research Council (ESF grant N^{o} 9331), EU Structural Funds (3.2.0501.11-0023) and Estonian Ministry of Education and Research (SF0140028s09).

This research was carried out at the Department of Polymer Materials at Tallinn University of Technology in Laboratory of Oil Shale and Renewables Research.

The author is deeply indebted to the supervisor of her thesis Dr. Hans Luik for introducing her into the field of oil shale, for giving her the necessary knowledge about chemical engineering and for encouraging her during doctoral study.

The special appreciation belongs to author’s colleagues from the Laboratory of Oil Shale and Renewables Research at Tallinn University of Technology for their valuable assistance and consultations. Finally, I owe great gratitude to my family, whose support and encouragement has helped me greatly throughout my studies.

ABSTRACT

Thermochemical destruction of graptolite argillite

Graptolite argillite (GA) belongs to Estonian oil shale resources not found industrial utilisation yet. To obtain shale oil from oil shale thermochemical processing is used. There are several thermochemical processing methods, resulting in disproportion of the organic matter of oil shales into oil, gas and solid residue. Products yields and chemical composition depend on conditions (method) of thermochemical destruction and chemical composition of the initial oil shale. Up to now the only one industrial technology in Estonia and in other countries is the semi-coking realised in retorts of different configuration. Using semi-coking for GA liquefaction is not prospective because of extremely low yield of oil in Fischer retort compared with Kukersite, 1-2% and 23% respectively.

The main goals of this work include working out technological and physical-chemical fundamentals for GA upgrading to obtain higher shale oil yield compared with traditional semi-coking, investigation of shale oil composition formed using different conditions and various methods of thermochemical destruction and comparison the composition of shale oils from GA and Kukersite.

Results of laboratory experiments are represented and analysed, elucidating the effect of temperature, time sub- and supercritical solvents and hydrogen on the yield and composition of the products obtained in GA thermochemical destruction, also the effect of alkali and hydrogen donor compounds was studied. Carried out for the first time complex study demonstrated that thermochemical dissolution and hydrogenation increase oil yield in times at lower temperature than FAP.

Investigation of qualitative and quantitative compositions with using updated methods of chromatographic, spectroscopic and elemental analysis demonstrated that oils formed resulting from pyrolysis, thermal dissolution and hydrogenation of GA are similar to the Kukersite semi-coking oil by the group composition, but the individual composition of groups and their proportions differ significantly.

Thermochemical destruction data of oil shales from Estonian, Jordanian and American deposits confirmed that semi-coking cannot be considered an universal oil shale liquefaction technology applicable to all types of oil shales represented in Earth’s surface in their multitude and variety. Implementation of alternative technologies is inevitable achieving efficient liquefaction of oil shales poor in OM and hydrogen content.

As a result of this work, conditions were worked out to GA effective processing, group and individual composition of the oils obtained in pyrolysis, thermal dissolution and hydrogenation were represented and compared with those of Kukersite semi-coking oil.

KOKKUVÕTE

Graptoliit-argilliidi termokeemiline destruktsioon

Graptoliit-argilliit (GA) on Eestimaa looduslike ressursside hulka kuuluv põlevkivi, mida seni veel tööstuslikult ei kasutata. Õli saamiseks põlevkivist kasutatakse termokeemilise destruktsiooni meetodeid, mille tulemusena põlevkivis sisalduv orgaaniline aine - kerogeen disproportsioneeritakse vedelate, gaasiliste ja tahkete produktide koostisesse. Produktide saagis ja keemiline koostis sõltuvad termokeemilise destruktsiooni tingimustest (meetodist) ja lähtepõlevkivi keemilisest koostisest. Ainsaks tööstuslikuks tehnoloogiaks põlevkiviõli saamiseks nii Eestis kui mujal maailmas on tänaseni poolkoksistamine erinevat tüüpi retortides. GA poolkoksistamine ei ole perspektiivne, kuna laboratoorses Fischeri retordis saadava õli saagis võrreldes Kukersiitpõlevkiviga on äärmiselt väike, vastavalt 1-2% ja 23%.

Käesoleva töö eesmärkideks oli füüsikalis-keemiliste ja tehnoloogiliste aluste väljatöötamine GA senisest efektiivsemaks vedeldamiseks, õli keemilise koostise kindlaksmääramine ja selle võrdlus kukersiidi poolkoksistamise õliga.

Esitatakse ja analüüsitakse laboratoorsete eksperimentide tulemused, kus selgitati temperatuuri, aja, sub- ja superkriitiliste lahustite ja vesiniku mõju produktide saagisele ja koostisele GA termokeemilisel destruktsioonil Fischeri retordis ja autoklaavis, samuti leeliste ja doonorühendite efekt vesikonversioonil. Esmakordselt teostatud GA kompleksse uuringuga on näidatud, et termilise lahustamisel ja hüdrogenisatsioonil on võimalik saada õli kordades rohkem ja oluliselt madalamal temperatuuril võrreldes pürolüüsiga Fischeri retordis.

Õlide kvalitatiivse ja kvantitatiivse koostise uurimine kaasaegsete kromatograafiliste, spektroskoopiliste ja elementanalüüsi meetoditega näitas, et GA pürolüüsil, termilisel lahustamisel ja hüdrogenisatsioonil moodustunud õlid on sarnased Kukersiidi poolkoksistamise õlile keemiliste ühendite grupikoostise poolest, kuid nii gruppide individuaalne koostis kui ka proportsioonid erinevad oluliselt.

Eesti, Jordaania ja Ameerika leiukohtade termokeemilise destruktsiooni tulemused käesolevas töös kinnitavad, et poolkoksistamist ei saa lugeda universaalseks põlevkivide termokeemilise vedeldamise tehnoloogiaks, mis oleks rakendatav kõikidele põlevkividele nende paljususes ja erinevustes. GA, ja enamiku teiste planeedil Maa leiduvate orgaanilise aine ja vesiniku sisalduselt vaeste põlevkivide efektiivseks vedeldamiseks on möödapääsmatu alternatiivsete tehnoloogiate juurutamine.

On töötatud välja tingimused Eesti GA efektiivseks töötlemiseks, esitatud pürolüüsil, termilisel lahustamisel ja hüdrogenisatsioonil saadud õlide grupi- ja individuaalkoostis ning võrreldud seda Kukersiidi poolkoksistamise õliga.

APPENDIX I. GS-MS chromatograms

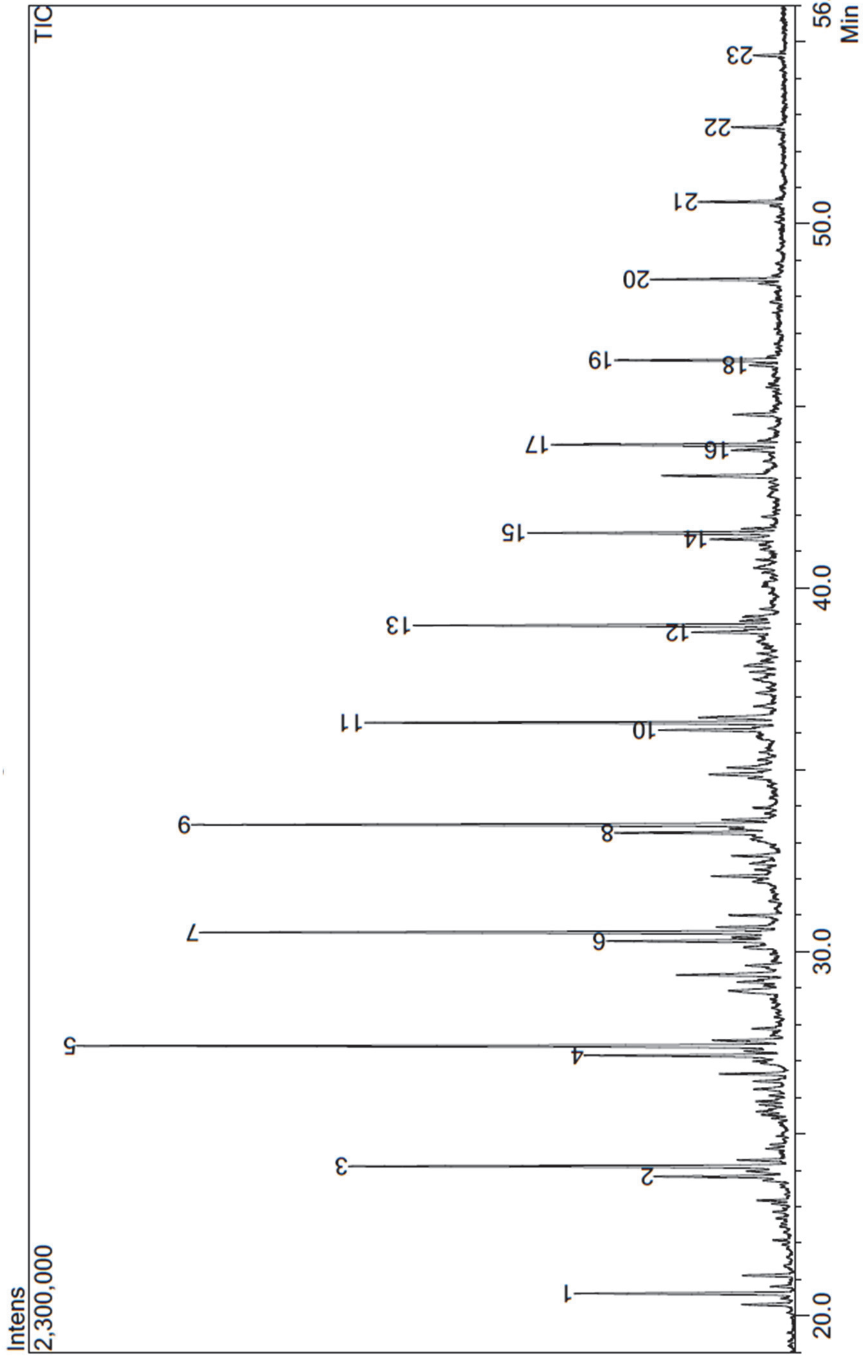

Figure 19. GC-MS chromatogram of the AlHC obtained during FAP

Table 17 Compounds identified in TBO fractions of AlHC obtained during FAP

peak	Name	R.Time	Area%
1	Dodecane	20.6	4.1
2	1-Tridecene	23.8	2.4
3	Tridecane	24.1	8.4
4	1-Tetradecene	27.1	3.6
5	Tetradecane	27.4	13.4
6	1-Pentadecene	30.3	3.1
7	Pentadecane	30.5	11.1
8	1-Hexadecene	33.3	2.8
9	Hexadecane	33.5	11.1
10	1-Heptadecene	36.1	2.0
11	Heptadecane	36.3	8.3
12	1-Octadecene	38.8	1.2
13	Octadecane	39.0	7.0
14	1-Nonadecene	41.3	1.1
15	Nonadecane	41.5	4.9
16	1-Eicosene	43.8	1.0
17	Eicosane	43.9	4.5
18	1-Heneicosene	46.1	0.6
19	Heneicosane	46.3	3.3
20	Docosane	48.5	2.6
21	Tricosane	50.6	1.7
22	Tetracosane	52.7	1.0
23	Pentacosane	54.6	0.7

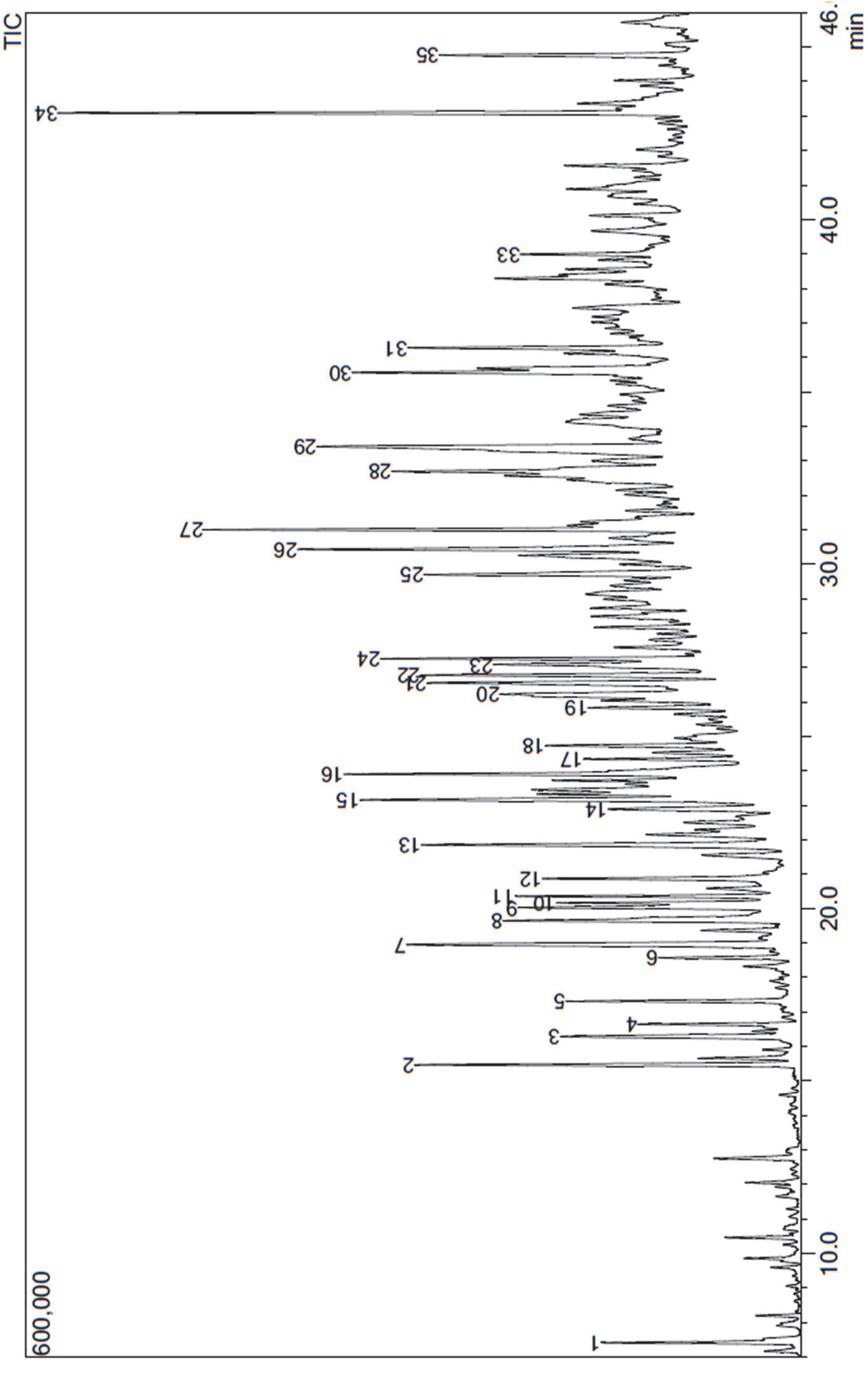

Figure 20. GC-MS chromatogram of the PAHC obtained during FAP

Table 18 Compounds identified in TBO fractions of LPhet obtained during FAP

peak	Name	R.Time	Area%
1	2-Pentanone, 4-hydroxy-4-methyl-	7.4	1.6
2	o-Cresol	15.5	3.9
3	p-Cresol	16.3	2.8
4	2-Nonanone	16.6	1.2
5	Phenol, 3,4-dimethyl-	17.3	2.1
6	Phenol, 4-ethyl-	18.6	1.2
7	Phenol, 3,5-dimethyl-	18.9	5.3
8	Acetophenone, 2'-methyl-	19.6	3.4
9	Phenol, 2,3-dimethyl-	20.0	3.2
10	3-Decanone	20.2	2.2
11	2-Decanone	20.4	2.5
12	Phenol, 3,4,5-trimethyl-	20.9	2.3
13	Phenol, 2,3,5-trimethyl-	21.9	4.7
14	Mixt di-Alkyl-Phenole	22.9	2.2
15	4-Undecanone	23.2	4.5
16	2-Undecanone	23.9	2.6
17	Phenol, 2,5-diethyl-	24.3	1.5
18	Phenol, 3,5-diethyl-	24.7	1.8
19	7-Methylindan-1-one	25.8	1.4
20	Phenol, 2,3,5,6-tetramethyl-	26.2	2.9
21	6-Dodecanone	26.6	3.8
22	Biphenyl	26.8	3.5
23	3-Dodecanone	27.1	2.4
24	2-Dodecanone	27.3	3.1
25	6-Tridecanone	29.7	3.8
26	2-Tridecanone	30.4	4.8
27	impurity -Butylated Hydroxytoluene	31.0	4.0
28	6-Tetradecanone	32.7	1.4
29	impurity -Phthalic acid Derivative	33.4	3.2
30	6-Pentadecanone	35.6	3.1
31	2-Pentadecanone	36.3	2.4
32		38.3	1.0
33	2-Hexadecanone	39.0	1.3
34	impurity-Dibutyl phthalate	43.1	6.0
35	Cyclic octaatomic SULFUR	44.8	2.7

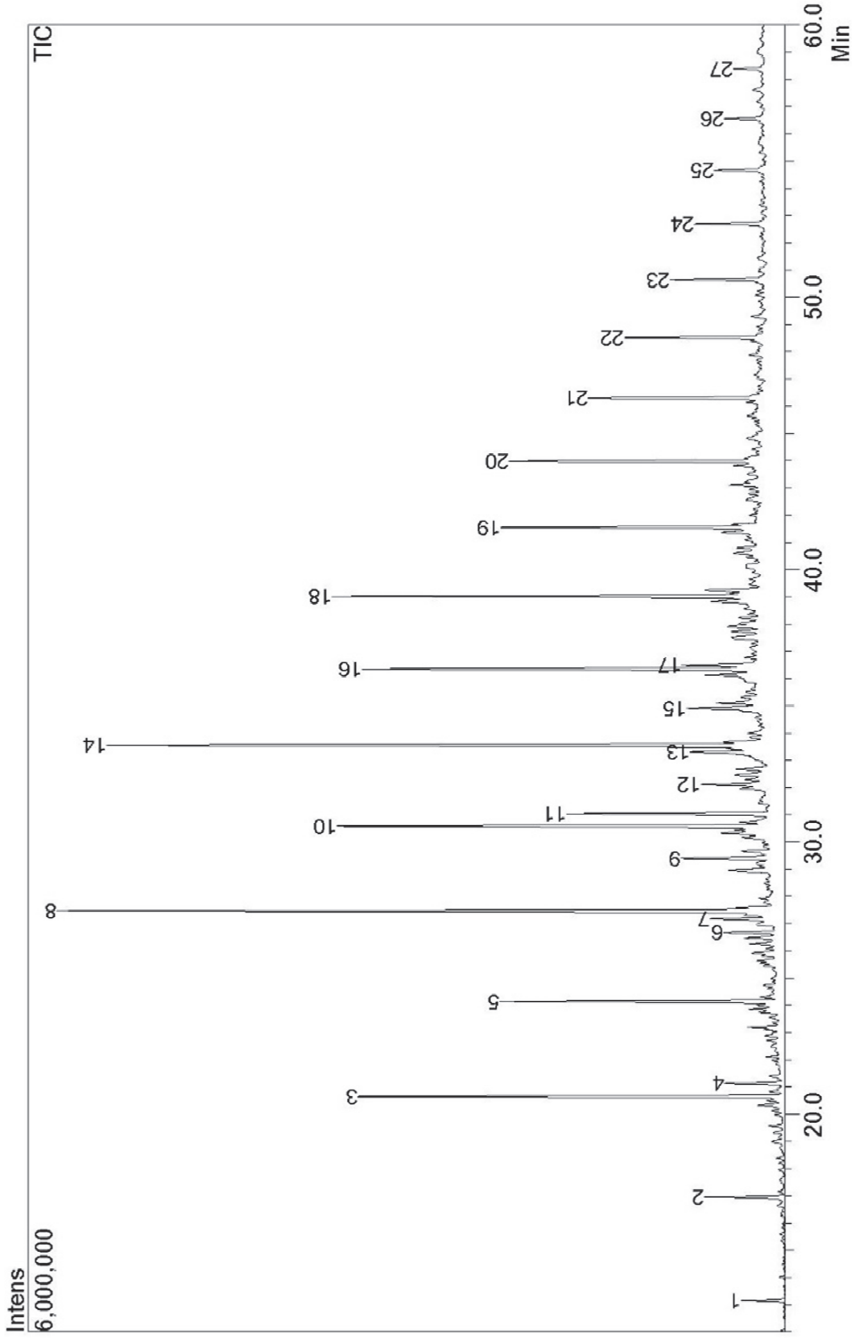

Figure 21. GC-MS chromatogram of the AlHC obtained during thermal dissolution with benzene

Table 19 Compounds identified in TBO fractions of AlHC obtained during thermal dissolution with benzene

Peak	Name	R. Time	Area %
1	Decane	13.1	0.7
2	Undecane	16.9	1.4
3	Dodecane	20.6	8.3
4	Dodecane, 6-methyl-	21.1	1.1
5	Tridecane	24.1	5.3
6	Tridecane, 2,5-dimethyl-	26.7	0.9
7	1-Tetradecene	27.2	0.9
8	Tetradecane	27.4	14.6
9	Tetradecane, 2,5-dimethyl-	29.3	2.1
10	Pentadecane	30.6	8.3
11	p-Cresol, 2,6-di-tert-butyl-	31.0	4.0
12	Cyclopentane, decyl-	32.1	1.0
13	1-Hexadecene	33.2	0.8
14	Hexadecane	33.5	12.8
15	Pristane	34.9	1.3
16	Heptadecane	36.3	8.1
17	Phytane	36.4	1.6
18	Octadecane	39.0	8.0
19	Nonadecane	41.5	4.7
20	Eicosane	43.9	4.6
21	Heneicosane	46.2	3.2
22	Docosane	48.5	2.5
23	Tricosane	50.6	1.6
24	Tetracosane	52.6	1.2
25	Pentacosane	54.6	0.8
26	Hexacosane		
27	Heptacosane		

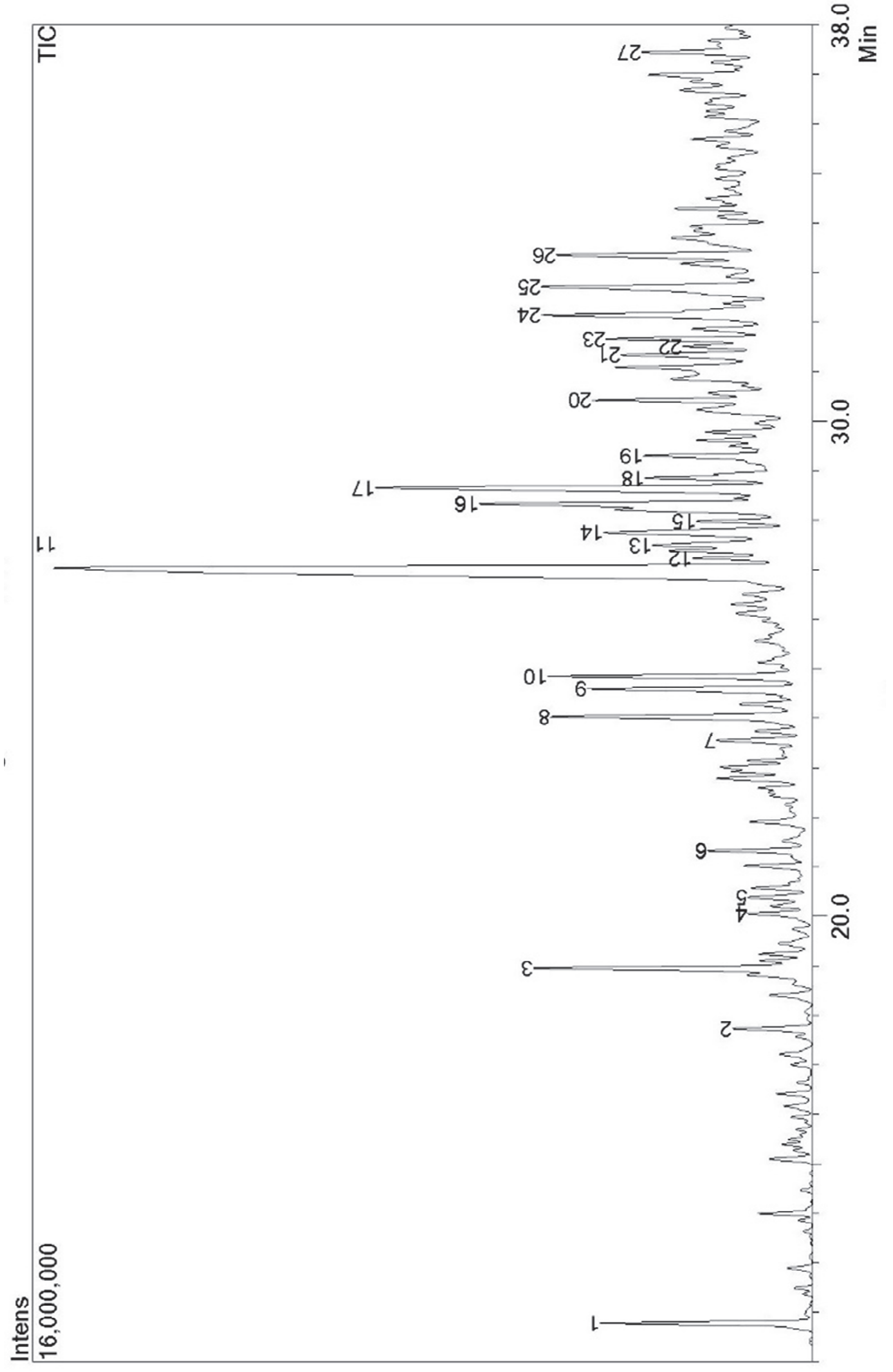

Figure 22. GC-MS chromatogram of the PAHC obtained during thermal dissolution with benzene

Table 20 Compounds identified in TBO fractions of PAHC obtained during thermal dissolution with benzene

Peak	Name	R. Time	Area, %
1	Benzenethiol	11.8	2.9
2	Benzene, 1,2,3,5-tetramethyl-	17.7	1.0
3	Benzene, 1-ethyl-3,5-dimethyl-	18.9	4.0
4	Naphthalene	20.1	0.7
5	Benzothiophen	20.4	0.8
6	Benzene, pentamethyl-	21.3	1.1
7	4,7-Dimethylindan	23.6	1.2
8	Naphthalene, 1-methyl-	24.0	4.2
9	Naphthalene, 2-methyl-	24.6	3.3
10	Benzene, cyclohexyl-	24.8	3.6
11	Biphenyl	27.0	26.4
12	Dimethyl-Benzothiophene Derivative	27.2	1.3
13	Dimethylnaphthalene Derivative	27.5	2.6
14	Dimethylnaphthalene Derivative	27.7	4.0
15	Dimethyl-Benzothiophene Derivative	28.0	1.1
16	Dimethylnaphthalene Derivative	28.3	5.0
17	Diphenylmethane	28.7	7.8
18	Dimethylnaphthalene Derivative	28.8	1.9
19	Dimethylnaphthalene Derivative	29.3	1.5
20	1,1-Diphenylethane	30.4	2.8
21	x,y,z-Trimethylnaphthalene	31.3	3.2
22	x,y,z-Trimethylnaphthalene	31.5	1.4
23	x,y,z-Trimethylnaphthalene	31.7	2.5
24	x,y,z-Trimethylnaphthalene	32.1	5.2
25	x,y,z-Trimethylnaphthalene	32.7	5.3
26	x,y,z-Trimethylnaphthalene	33.4	3.4
27	Camazulene	37.5	1.3
28	Phenanthrene, 2,3,5-trimethyl-	49.5	0.6

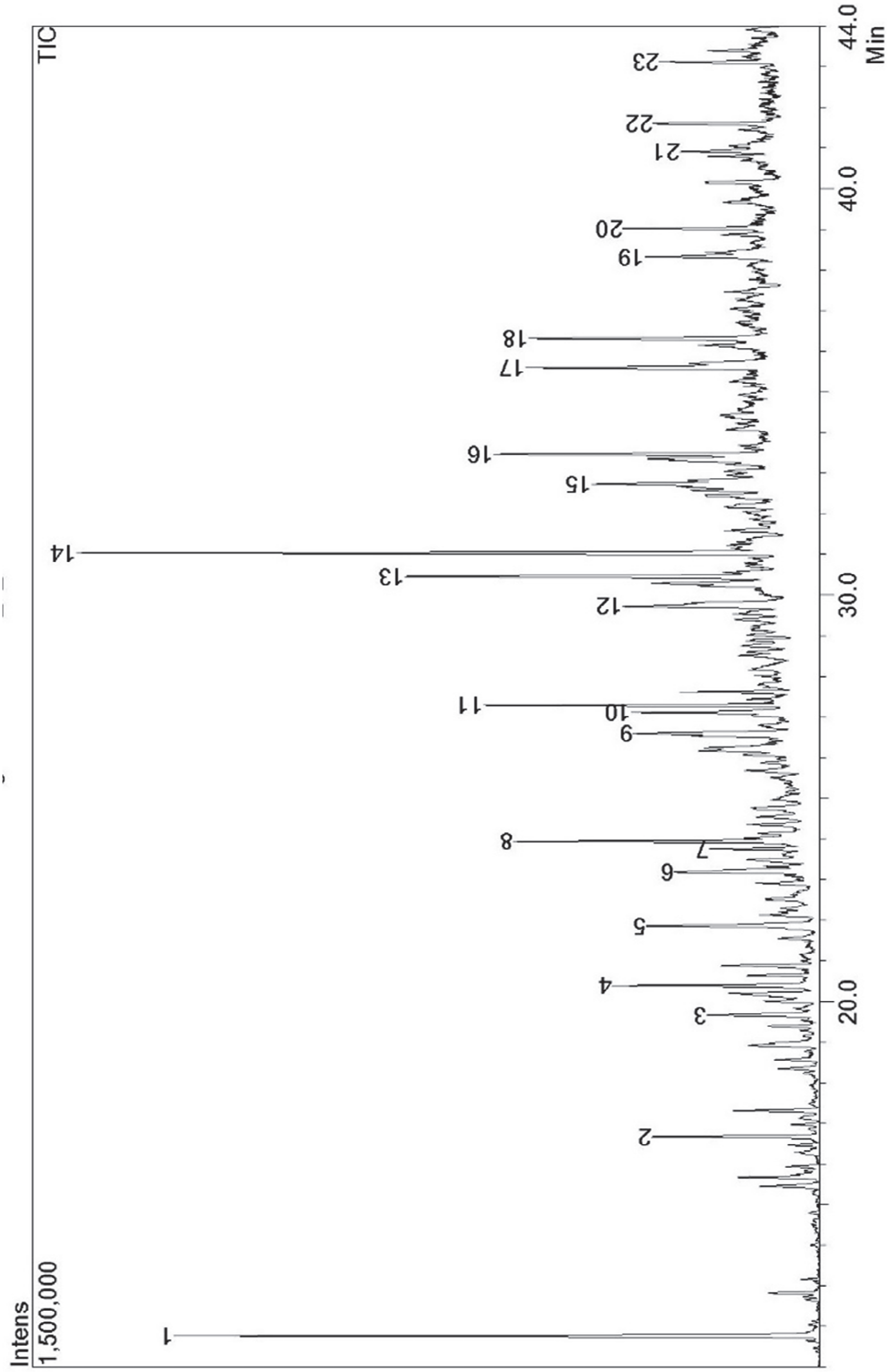

Figure 23. GC-MS chromatogram of the LPHet obtained during thermal dissolution with benzene

Table 21 Compounds identified in TBO fractions of LPHet obtained during thermal dissolution with benzene

Peak	Name	R.Time	Area, %
1	Benzenethiol	11.8	13.1
2	2-Nonanone	16.7	3.0
3	Acetophenone, 2'-methyl-	19.7	2.3
4	2-Decanone	20.4	3.6
5	x-y-z-trimethyl-Phenole	21.9	3.7
6	6-Undecanone	23.2	1.5
7	3-Undecanone	23.7	1.7
8	2-Undecanone	23.9	4.9
9	6-Dodecanone	26.6	5.7
10	3-Dodecanone	27.1	3.0
11	2-Dodecanone	27.3	5.3
12	6-Tridecanone	29.7	1.9
13	2-Tridecanone	30.5	7.9
14	p-Cresol, 2,6-di-tert-butyl-	31.0	13.9
15	6-Tetradecanone	32.7	2.1
16	2-Tetradecanone	33.5	5.3
17	6-Pentadecanone	35.6	5.0
18	2-Pentadecanone	36.3	4.7
19	6-Hexadecanone	38.3	2.1
20	2-Hexadecanone	39.0	2.9
21	6-Heptadecanone	40.9	1.8
22	2-Heptadecanone	41.6	2.1
23	Phthalic acid,- Derivative	43.1	2.3

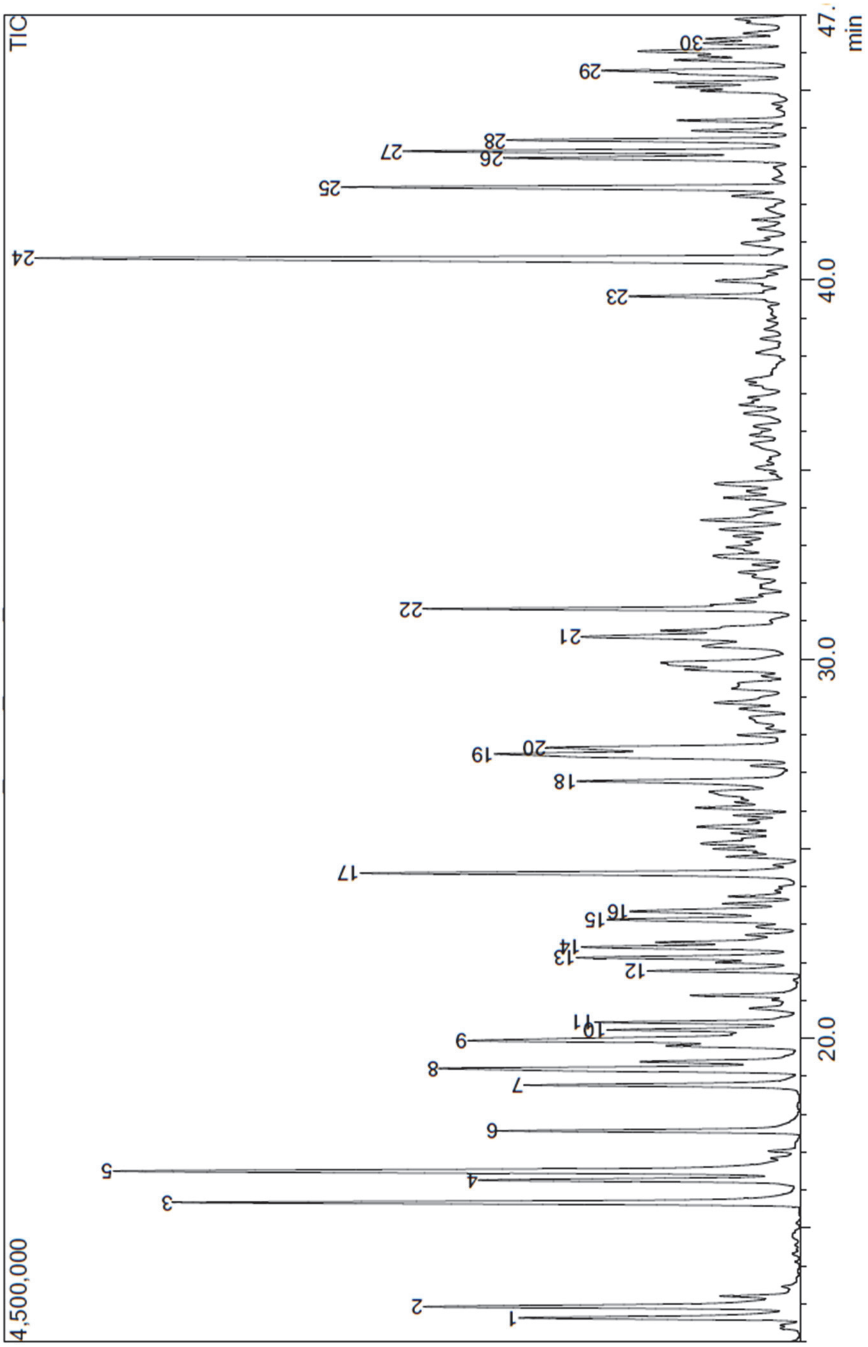

Figure 24. GC-MS chromatogram of the LPHet obtained during hydrogenation at 430°C

Table 22 Compounds identified in TBO fractions of LPhet obtained during hydrogenation at 430°C

Peak	Name	R.Time	Area, %
1	Aniline	12.6	2.7
2	Phenol	12.9	4.1
3	o-Cresol	15.7	5.8
4	p-Aminotoluene	16.3	2.7
5	p-Cresol	16.5	7.1
6	Phenol, 2,6-dimethyl-	17.6	2.4
7	Phenol, 2-ethyl-	18.8	2.2
8	Phenol, 3,5-dimethyl-	19.2	4.5
9	Phenol, 3,4-dimethyl-	19.9	3.6
10	Phenol, 2,4-dimethyl-	20.2	1.1
11	Phenol, 3-(1-methylethyl)-	20.4	1.4
12	Phenol, 2-propyl-	21.8	1.4
13	Phenol, 3,4,5-trimethyl-	22.1	2.0
14	m-Ethylaniline+Phenol,2,3,5-trimethyl	22.4	2.0
15	Phenol, 3-propyl-	23.1	2.0
16	p-Cresol, 2-ethyl-	23.3	2.2
17	Indole	24.4	4.4
18	Methyl-Indole derivative	26.8	2.0
19	Methyl-Indole derivative	27.5	2.7
20	Methyl-Indole derivative	27.7	3.0
21	Dimethyl-Indole derivative	30.6	2.2
22	impurity	31.3	2.8
23	Carbazole, 1,2,3,4-tetrahydro-	39.6	1.2
24	Carbazole	40.6	9.3
25	Methyl-carbazole derivative	42.5	4.3
26	Methyl-carbazole derivative	43.2	2.7
27	Methyl-carbazole derivative	43.4	3.8
28	Methyl-carbazole derivative	43.7	2.4
29	Dimethyl-carbazole derivative	45.5	1.4
30	Dimethyl-carbazole derivative	46.2	0.7

APPENDIX II. Articles

ARTICLE I

Luik, H., Luik, L., Palu, V., **Sharayeva, G.**, Gregor, A. Applicability of Static Supercritical Carbon Dioxide Extraction in Biogeochemical Characterization of Oil Shales. American Journal of Analytical Chemistry, 2014, 5, 173-180

American Journal of Analytical Chemistry, **2014, 5, 173-180**

http://dx.doi.org/10.4236/ajac.2014.53021

Applicability of Static Supercritical Carbon Dioxide Extraction in Biogeochemical Characterization of Oil Shales

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Received November 24, 2013; revised December 27, 2013; accepted January 5, 2014

ABSTRACT

This study aimed at the assessment of applicability of static supercritical carbon dioxide extraction method (SFE) in biogeochemical characterization of oil shales as an alternative to the standard Soxhlet extration. A comparative investigation on yields and compositions of the solvent soluble bitumoids and their constituents extracted from Estonian Kukersite and Dictyonema oil shales by using Soxhlet extraction method (SEM) and static CO_2 supercritical fluid extraction in an autoclave at varied subpyrolysis temperatures was carried out. Resulting from TLC- and GC-MS-analyses, aliphatic and aromatic hydrocarbons and neutral oxygen compounds were separated and identified. For the first time, in the composition of the Kukersite bitumoid, homologous series of *n*-alkanones-3 to *n*-alkanones-7 were detected. The extracts obtained were similar in both group and individual composition, and geochemical parametres calculated on the basis of aliphatic hydrocarbons including that made static SFE applicable to geochemical investigation of oil shales.

KEYWORDS

Oil Shale; Bitumoid; Supercritical Extraction; Soxhlet Extraction; Geochemical Parametres

1. Introduction

Oil shales in their variety have formed as a result of fossilization and sedimentation of marine and terrestrial biomass during millions of years. Maintained to a certain extent, their biogeochemical memory from time immemorial, oil shales in their variety consist of the fragments of ancient relic material in polymerized steric structure formed during fossilization, recognizable and investigable by analytical techniques. Oil shales are characterised by varied contents of the fossilized organic matter (OM) disproportionated between insoluble and soluble portions. Kerogen, making up the bulk of dispersed organic matter, is characterised as insoluble in organic solvents OM. Another part of the OM is not incorporated to the structure of kerogen and can be separated from oil shale matrix by using low-boiling solvents as extractables (bitumoid). The latter can be observed as a mobile phase inside a macromolecular network containing various biomarkers for elucidating the genesis of the OM in oil shale and the degree of its maturity. The composition of both insoluble kerogen and soluble bitumoid represents the source of geochemical information on the biogenic precursors of OM and transformation of the latter in the Earth's crust. Structural constituents of the kerogen are attainable to the analytical investigation only after thermochemical destruction and oil formation occurring usually at the temperatures of 350˚C - 500˚C. Besides, pyrolysis is applicable for obtaining adequate feedback with initial matter via splinters formed from it during pyrolysis and provides reliable data on kerogen structure if the reaction mechanism is known. Fischer assay pyrolysis, hydrous pyrolysis and hydropyrolysis most often have been used [1-4]. At the same time, characteristic fragments of the OM of oil shales are readily transferable to

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the bitumoid composition as compounds of different chemical classes using solid-liquid Soxhlet extraction (SEM) with low-boiling solvents and their mixtures at boiling temperatures and that is why it is used as a classic method for extraction of analytes from solid materials [5,6]. SEM still remains a standard technique to which the performance of modern extraction techniques is compared. The most serious disadvantages of SEM are long extraction time required and a large amount of toxic solvents wasted. These drawbacks support the development for better and efficient techniques, and an intensive research on different modifications has been carried out in order to overcome the main disadvantages of conventional SEM. Available modifications include automated SEM, focused microwave-assisted SEM, high pressure SEM and fluidized bed extraction [7]. Rather little effects than essential advantages were observed. In [8], solvents of different polarities as methanol, acetonitrile, acetone, methylene chloride, tetrahydrofuran, toluene and hexane were used, and the authors became convinced that the yields of extractables from different oil shales at room temperature were in time lower compared with SEM depending differently on the nature of the solvent. In the same work, dynamic SFE was demonstrated as effective for the isolation of substances of medium molecular weight and relatively low polarity. This method was tested for the geochemical investigation of sapropelites in [9].

Introducing supercritical carbon dioxideas fluid offers several advantages over conventional solvent extraction. CO_2 is noncombustible, nontoxic and inexpensive as a solvent having low polarity. Its critical parameters (t_{cr} = 31.1˚C, p_{cr} = 7.38 MPa) are easily accessible. Due to the capacity of supercritical carbon dioxide to penetrate into porous media, the method seems to be prospective for the recovery of the soluble components in oil shale. Due to the low critical temperature of CO_2, SFE like SEM leaves the most of kerogen matrix untouched and brings out the soluble matter trapped in the shale matrix. Carbon dioxide has a higher diffusivity and lower viscosity compared to liquid solvents, which should result in improved mass transfer properties during extraction. The solvent strength of SFE is dependent on its temperature and pressure, which can easily be manipulated to extract certain classes of compounds [10]. In [11], SFE for the extraction of polychlorinated biphenyls from algae samples was used.

It has been reported that, in oil shales, dynamic extractions with pure supercritical carbon dioxide in a flow reactor, mainly *n*-alkanes, were extracted while addition of modifiers as methanol or ionic liquids slightly increased extract yield and enriched its composition with other compounds [8,12].

Estonian Kukersite and Dictyonema oil shales formed in Lower Paleozoic belong to the most ancient ones in the world. The source material of both kerogens is of marine origin. Kukersite is characterised by an extremely low bitumoid content arising from its allochthonous origin and sedimentation under conditions of oxidizing atmosphere. Dictyonema oil shale which proceeded formation under the influence of sulfate-reducing microbes, contains less kerogen and yields considerably more extractables in SEM [13]. Main structural units of OM of sapropelites and their pyrolysis oils are straight and, in less measure, branched carbon chains, precursors of which were fatty acids and isoprenoid structures, respectively, being transformed to bitumoid and kerogen pyrolysis oil composition as paraffins, olefins and ketones [14, 15]. The corresponding structures of oil shale have been formed by fossilization of the most stable components (fatty acids) of biological source material. The hydrocarbon chains in ancient oil shale kerogens have mainly odd carbon numbers [9,14]. Dictyonema oil shale is a brown lithified clay belonging to the formation of black shales of sapropelic origin, whose OM is rich in heteroatoms [16,17].

The aim of the present work is to determine and compare the extraction yields and compositions resulting from static SFE and SEM of oil shales, and on the basis of geochemical parametres calculated estimate the applicability of the SEF as an alternative method to the biogeochemical studies of oil shales.

2. Samples

Air-dry, finely powdered (0.04 - 0.1 mm) and homogenised Kukersite and Dictyonema oil shale samples characterised in **Table 1** were used as initial feedstocks.

One can see that the oil shales under investigation largely differ by OM^d content, kerogen chemical composition and pyrolysis oil yield.

3. Experimental: Methods and Analysis

Oil shale samples were submitted to the static SFE at three different temperatures in a rocking 500 cm^3 stainless steel batch autoclave supplied with a manometer and gas valves. Starting with 100 g, the same portion of oil shale was extracted consequtively at 40, 100, and 150˚C and initial carbon dioxide pressure 9 MPa during 2 hours. At the end of heating, the system was cooled down to the ambient temperature. Then the gas amount was released from the autoclave via gas valve and the autoclave was opened. The extractables formed were diluted with diethyl ether and separated after each step. Diethyl ether was evaporated and the extract yields were determined by weight analysis.

Also, exhaustive SEM using chloroform and benzene-methanol mixture was carried out with obtaining bitu-

Table 1. Characterization of oil shales (%).

Characteristic	Kukersite	Dictyonema
Age, million years	460	480
Mineral matter	Carbonates	Aluminosilicates
Analytical moisture, W^a	0.6	1.4
Ash (per dry mass), A^d	37.2	81.2
CO_2 of carbonates (per dry mass), $(CO_2)^d$	12.3	2.8
Dry organic matte, OM^d	50.5	16.0
Elemental composition of OM^d:		
C	79.32	73.02
H	9.50	9.19
N + S	0.30	2.66
O	10.88	15.12
H/C molar ratio	1.437	1.510
O/C molar ratio	0.103	0.155
Fischer Assay oil yield	61.0	15.1

moids A and C, respectively.

Chemical composition of extracts was investigated by using thin-layer chromatography (TLC) and gas-chromatographic-mass-spectroscopic (GC-MS) methods.

Extracts were separated into groups of compounds by preparative TLC. Plates, 24 × 24 cm coated with a 2 mm silica gel (60 µm, Fluka) were used and 500 mg samples were analysed. *n*-Hexane as the eluent was used. As a result the fractions of aliphatic hydrocarbons, monocyclic aromatic hydrocarbons, polycyclic aromatic hydrocarbons, neutral heteroatomic compounds and high polar heteroatomic compounds were separated. The individual composition of compounds separated was analysed by GC-MS in 30 m capillary columns ZB-5 and HP-5MS. Identification was performed by the monitoring of the key ions.

4. Results and Discussion

4.1. Extraction Yields and Group Composition of the Extracts

Yields of extractables (bitumoids) eluated from oil shales by SEM and stepwise static SFE as well as their group composition separated by TLC are represented in Tables 2 and 3. Kukersite gives in both processes lower extract yields compared with Dictyonema oil shale.

One can see that total bitumoid yields obtained as summarized yields of bitumoids A and C from SEM of Kukersite and Dictyonema oil shales using chloroform and benzene-methanol mixture consequtively were recovered as 0.79% and 4.88%. Stepwise SFE of Kukersite triplicated the yield of extractables while that of Dictyonema oil shale gave extractables less by 30% compared with SEM. It is noteworthy that SFE of Kukersite resulted in higher yields of extractables than those of bitumoids A and C summarized at every process temperature, *i.e.* 40, 100 and 150˚C. SFE of the Dictyonema oil shale at 40˚C resulted roughly in the same extractables yield as that of bitumoid A. So, the extractables obtained at 100 and 150˚C can represent an additional source of geochemical information in Kukersite case and observed as an alternative to the bitumoid C in Dictyonema case.

Group compositition data in Tables 2 and 3 show that all extracts were represented by the same groups of hydrocarbons and heteroatomic compounds despite originated from different oil shales and produced resulting from solvent or fluid processes. Heteroatomic compounds are prevailing over hydrocarbons, particularly in Soxhlet extracts where the content of those amounts to 88% - 92%. Among heteroatomic compounds the polar ones, and in the composition of hydrocarbons the aliphatic ones are prevailing over neutral and aromatic ones, respectively. It can be seen that SFE compared with SEM produces considerably more hydrocarbons and less high polar heteroatomic compounds.

4.2. Extraction Efficiency and Selectivity

Extraction efficiency of SEM and SFE with regard to different compound groups determined is represented in Tables 4 and 5. Extraction efficiency depends on both process variables as temperature, pressure, duration, solvent type and chemical composition of the source matter.

Higher in times efficiencies were obtained on account of certain compounds groups transformed to the extractables composition resulting from SFE. One can see that SFE performed already at 40˚C, *i.e.* the lowest temperature used results in considerably higher production of aliphatic, mono- and polycyclic aromatic hydrocarbons and neutral heteroatomic compounds from both Kukersite and Dictyonema oil shales than SEM with liquid chloroform. Distinction between SFE and SEM efficiences becomes particularly evident when those compounds in extracts yielded from oil shales at 40˚C are compared with their yields in summarized bitumoids A and C. Further extraction at the temperatures 100˚C and 150˚C yielded additive portions of hydrocarbons and neutral heteroatomic compounds and that is why efficiency of different compound classes on the bases of summarized extract (∑150) with that in total bitumoid (bitumoids A + C) would be compared to obtain comparable and reliable data. Such comparison can be seen in Tables 4 and 5 demonstrating amplified regularities described above. Extraction efficiency of the same com-

Table 2. **Yields (1—mg/g, 2—% per OM) and group composition (relative %) of SEM extracts.**

SEM	Yield		Aliphatic hydro-carbons	Mono-cyclic aromatic hydro-carbons	Poly-cyclic aromatic hydro-carbons	Neutral hetero-atomic com-pounds	High polar hetero-atomic com-pounds
	1	2					
				Kukersite			
Bitumoid A	1.63	0.48	19.9	7.6	2.8	14.6	55.1
Bitumoid C	1.03	0.31	10.1	1.6	0.7	1.2	86.4
∑A + C[*]	2.66	0.79	16.2	5.3	2.0	9.3	67.2
				Dictyonema			
Bitumoid A	2.80	1.75	7.5	1.5	3.0	5.5	82.5
Bitumoid C	5.00	3.13	5.6	0.6	0.9	1.3	91.6
∑A + C[*]	7.80	4.88	6.3	0.7	1.9	2.8	88.3

[*] After extraction with chloroform and treatment of the extraction residue with 10% HCl.

Table 3. **Yields (1—mg/g, 2—% per OM) and group composition (relative %) of SFE extracts.**

SFE temperature, ˚C	Yield		Aliphatic hydro-carbons	Mono-cyclic aromatic hydro-carbons	Poly-cyclic aromatic hydro-carbons	Neutral hetero-atomic com-pounds	High polar hetero-atomic com-pounds
	1	2					
				Kukersite			
40	4.21	0.82	20.1	9.7	18.2	14.2	37.8
100	2.94	0.57	17.6	10.9	13.2	21.5	36.8
150	5.00	0.97	18.9	2.6	10.6	8.6	59.3
∑150	12.15	2.36	19.1	7.0	13.9	13.6	46.4
				Dictyonema			
40	2.34	1.47	26.4	6.2	9.6	20.6	37.2
100	2.40	1.51	20.2	4.1	11.8	23.9	40.0
150	1.06	0.67	30.8	2.2	20.1	22.8	24.1
∑150	5.80	3.65	25.3	4.6	12.2	22.2	35.7

Table 4. **Extraction efficiency of different compound groups resulting from SEM (mass ‰).**

SEM	Aliphatic hydro-carbons	Mono-cyclic aromatic hydro-carbons	Poly-cyclic aromatic hydro-carbons	Neutral hetero-atomic com-pounds	High polar hetero-atomic com-pounds	Total extract
			Kukersite			
Bitumoid A	0.96	0.36	0.13	0.70	2.64	4.79
Bitumoid C	0.31	0.05	0.02	0.04	2.68	3.10
∑A + C	1.27	0.41	0.15	0.74	5.32	7.89
			Dictyonema			
Bitumoid A	1.31	0.29	0.50	0.96	14.44	17.50
Bitumoid C	1.75	0.19	0.28	0.41	28.67	31.30
∑A + C	3.06	0.48	0.78	1.37	43.11	48.80

Table 5. Extraction efficiency of different compound groups resulting from SFE (mass ‰).

SFE temperature, ˚C	Aliphatic hydro-carbons	Mono-cyclic aromatic hydro-carbons	Poly-cyclic aromatic hydro-carbons	Neutral hetero-atomic com-pounds	High polar hetero-atomic com-pounds	Total extract
			Kukersite			
40	1.65	0.80	1.49	1.16	3.10	8.20
100	1.00	0.62	0.75	1.22	2.10	5.69
150	1.85	0.25	1.03	0.83	5.75	9.71
Σ 150	4.50	1.67	3.27	3.21	10.95	23.60
			Dictyonema			
40	3.88	0.91	1.41	3.03	5.47	14.70
100	3.05	0.62	1.78	3.61	6.04	15.10
150	2.06	0.15	1.35	1.53	1.61	6.70
Σ 150	8.90	1.68	4.54	8.17	13.12	36.41

pound groups from Dictyonema oil shale surpasses that of Kukersite.

Generalizing, SFE yields from both oil shales mainly various hydrocarbons and neutral heteroaromic compounds while SEM produces lots of high polar heteroatomic compounds the efficiencies of extraction always being higher for Dictyonema oil shale. Productivities of Soxhlet extractor and batch autoclave in case of Dictyonema and Kukersite oil shale were 10 - 50 and 120 - 200 mg/h, respectively. SFE leads to higher productivities at lower temperature and shorter process duration.

4.3. Composition of the Extracts

According to the GC-MS data the compounds having long straight alkyl chains, are the most common in all extracts. In Figure 1 the composition of aliphatic hydrocarbons is depicted and one can see that *n*-alkanes distinctly prevail over isoalkanes. Among monoaromatic hydrocarbons homologoues *n*-alkyl benzenes with maximum 10 carbon atoms in side chain were identified (see Figure 2). Homologous *n*-alkanes C_{11}-C_{25} and regular isoprenoids (m/z 71), alkylcyclohexanes (m/z 83), alkylbenzenes (m/z 92), naphthalene (m/z 128), methyl-, dimethyl-, trimethyl- and tetramethylnaphthalenes (m/z 142, m/z 156, m/z 170 and m/z 184, respectively), *n*-alkanones-2 and symmetric *n*-alkanones (m/z 58), containing maximum 17 carbon atoms in the Kukersite extracts were found. The regularities of distribution and maximum length of hydrocarbonaceous chains was found differing depending on the extract origin.

For the first time, in the composition of Kukersite oil shale extraction products homologous series of *n*-alkanones-3, *n*-alkanones-4 and *n*-alkanones-5, *n*-alkanones-6 and *n*-alkanones-7 were detected. As it can be seen in Figure 3, identification of the latters is complicated because those are characterized with the same m/z values as joint peak.

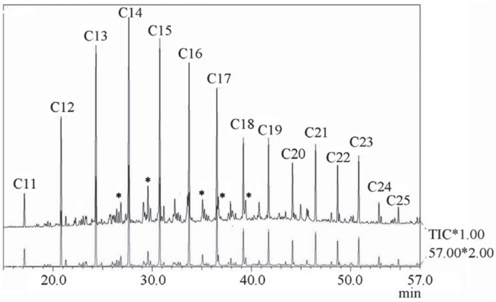

Figure 1. TIC of the *n*-alkanes C_{11}-C_{25} and regular isoprenoids (*) farnesane, 2,6,10-trimethyltridecane, norpristane, pristane, phytane originated from Kukersite bitomoid A.

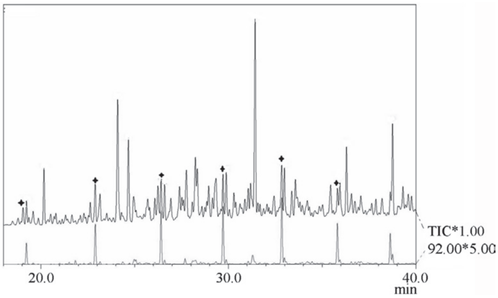

Figure 2. TIC of *n*-alkyl benzenes (✦, m/z 92) in the monoaromatic hydrocarbons fraction of Kukersite SEM extract.

Dictyonema extracts were characterized by the same homologous series of compounds having, in most instances, longer alkyl chains amounting as an absolute

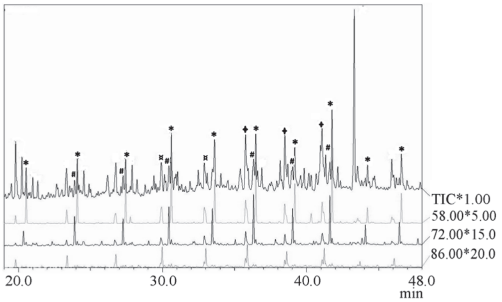

Figure 3. TIC of *n*-alcanones in the neutral heteroatomic fraction of the Kukersite SFE extract: *n*-alcanones-2 (*, m/z 58); *n*-alcanones-3 (#, m/z 72); *n*-alcanones-4 and *n*- alcanones-5 (¤, m/z 86); *n*-alcanones-6 and *n*-alcanones-7 (✦, m/z 71).

maximum to 31 in *n*-alkanes. In addition to those in Kukersite extracts, besides phenantrene and its alkyl derivatives, carboxylic acids and esters were identified in Figure 4. The latter were found when bitumoid C as a whole, characterized by as high as 91.6% content of high polar heteroatomic compounds, was subjected to the GS-MS analysis.

4.4. Geochemical Parametres

Below, in Tables 6 and 7 organic geochemical data of the extracts are represented.

Although there are some diver gencies in the values of parametres often used in geochemical investigation of oil shales and other caustobioliths depending on extraction conditions, the main tendencies and specific features of the oil shale under investigation can be described in like manner. *n*-Alkanes from Kukersite are characterized by odd ones predominance in their relative distribution, characaterized by carbon predominance index (CPI) that being higher than 1 what is characteristic for biogenic *n*-alkanes being preserved in immature OM. Predominance of the odd homologouesare characteristic in side chains of *n*-alkylbenzenes, *n*-alkylcyclohexanes and *n*-alcanones series as well. According to the CPI values of hydrocarbons originated from Dictyonema oil shale originated the content of odd carbon homologoues is equal to those of even numbered. Pristane-to-phytane ratio is higher than 1 for structures originated from Kukersite while in Dictyonema shale this value is near to 1. The extracts obtained at higher SFE temperature are rich in high-molecular *n*-alkanes and some parallels with the bitomoid C can be drawn.

Juxtaposing the respective parametres, one can find similar regularities between bitumoid A and SFE 40˚C extract and bitumoid C and SFE at 150˚C. At the same time one can see in Tables 6 and 7 that summarized extracts from SFE at 40˚C, 100˚C and 150˚C can be characte- rized as less different than bitumoid A and C between themselves. In dilemma, either anyone of the selected extracts or summarised SFE and SEM extracts should be used to characterize oil shale composition more ade- quately total extracts would be recommended.

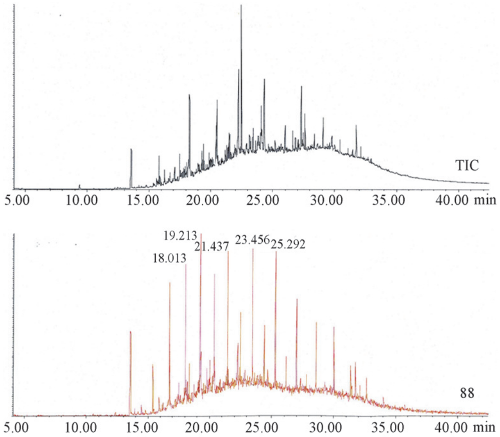

Figure 4. TIC of bitumoid C from SEM of Dictyonema oil shale: carboxylic acids and esters (m/z 60 and m/z 88).

These results lead to the consequence that the composition and relative distribution of *n*-alkanes do not change significantly when SFE of oil shale is used instead of SEM.

5. Conclusions

Stepwise SFE of the Kukersite and Dictyonema oil shales in static autoclaving conditions, representing thermal dissolution at subpyrolysis temperatures, was applied alternatively to conventional Soxhlet extraction (SEM).

Investigation on both group and individual composition and comparison of the geochemical parametres calculated on the basis of SEM and SFE extracts of the oil shales showed similarity, thus indicating the applicability of SFE to more effective separation of bitumoid components compared with laborious SEM.

Homologous *n*-alkanes, alkylmonoarenes, alkylpolyarenes and alkylalkanones easily extracted by SFE were identified, and new compounds as *n*-alkanones-3, *n*-alkanones-4, *n*-alkanones-5, *n*-alkanones-6 and *n*-alkanones-7 were found in SFE extracts.

This process can be observed as supercritical thermal dissolution performed stepwise.

Acknowledgements

The study was supported by the Estonian Research Council: project SF0140028s09, grant No.9331 and EU

Table 6. Geochemical parameters calculated on the basis of GC-MS data for Kukersite extracts.

Parameter	SFE				SEM		
	40˚C	100˚C	150˚C	∑150[a]	Chloroform	Benzene and methanol mixture	Bitumoid A + C[a]
CPI of *n*-alkanes	1.13	1.14	0.97	1.12	1.18	1.28	1.20
$<C_{17}/\geq C_{17}$	0.21	0.28	0.40	0.30	0.46	0.27	0.30
Pristane/phytane	1.01	1.10	1.10	1.10	1.50	1.20	1.25
Pristane + phytane/n-C_{17} + n-C_{18}	0.17	0.14	0.21	0.18	0.40	0.44	0.41
Pristane/n-C_{17}	0.13	0.09	0.20	0.15	0.36	0.47	0.39
Phytane/n-C_{18}	0.25	0.22	0.22	0.23	0.50	0.30	0.38

[a] Calculated weighted average values.

Table 7. Geochemical parameters calculated on the basis of GC-MS data for Dictyonema extracts.

Parameter	SFE				SEM		
	40˚C	100˚C	150˚C	∑150[a]	Chloroform	Benzene and methanol mixture	Bitumoid A + C[a]
CPI of *n*-alkanes	0.96	1.05	0.92	0.98	1.03	0.98	1.00
$<C_{17}/\geq C_{17}$	0.38	0.47	0.40	0.40	0.26	0.21	0.23
Pristane/phytane	0.84	0.91	1.15	1.01	1.00	1.02	1.01
Pristane + phytane/n-C_{17} + n-C_{18}	0.42	0.40	0.81	0.50	0.46	0.52	0.49
Pristane/n-C_{17}	0.38	0.37	0.94	0.51	0.50	0.62	0.57
Phytane/n-C_{18}	0.54	0.43	0.70	0.54	0.43	0.44	0.44

[a] Calculated weighted average values.

Structural Funds: project 3.2.0501.1-0023.

REFERENCES

[1] I. Klesment, "Aliphatic Carbon Chains of Oil Shale Kerogen," *Proceedings of the Academy of Sciences of the Estonian SSR*, Vol. 24, No. 2, 1975, pp. 123-129.

[2] T. L. Robl, A. E. Bland, D. W. Koppenaal and L. S. Barron, "Geochemistry of Oil Shales in Eastern Kentucky," In: F. P. Miknis and J. F. McKay, Eds., *Geochemistry and Chemistry of Oil Shales*, *ACS Symposium Series* 230, American Chemical Society, Washington DC, 1983, pp. 159-180.

[3] T. Barth, "Similarities and Differences in Hydrous Pyrolysis of Biomass and Source Rocks," *Organic Geochemistry*, Vol. 30, No. 12, 1999, pp. 1495-1507. http://dx.doi.org/10.1016/S0146-6380(99)00121-7

[4] J. D. Rocha, S. D. Brown, G. D. Love and C. E. Snape, "Hydropyrolysis: A Versatile Technique for Solid Fuel Liquefaction, Sulphur Speciation and Biomarker Release," *Journal of Analytical and Applied Pyrolysis*, Vol. 40-41, 1997, pp. 91-103. http://dx.doi.org/10.1016/S0165-2370(97)00041-7

[5] M. D. Luque de Castro and F. Priego-Capote, "Soxhlet Extraction: Past and Present Panacea," *Journal of Chromatography A*, Vol. 1217, No. 16, 2010, pp. 2388-2389. http://dx.doi.org/10.1016/j.chroma.2009.11.027

[6] K. Urov and A. Sumberg, "Characteristics of Oil Shales and Shale-Like Rocks of Known Deposits and Outcrops. Monograph," *Oil Shale*, Vol. 16, No. 3, 1999, pp. 1-64.

[7] A. Zygler, M. Słomińska and J. Namieśnik, "Soxhlet Extraction and New Developments such as Soxtec," In: J.Pawliszyn, Ed., *Comprehensive Sampling and Sample Preparation*. Analytical Techniques for Scientists, Vol. 2, Theory of Extraction Techniques, 2012, pp. 65-82.

[8] M. Koel, S. Ljovin, K. Hollis and J. Rubin, "Using Neoteric Solvents in Oil Shale Studies," *Pure and Applied Chemistry*, Vol. 73, No. 1, 2001, pp. 153-159. http://dx.doi.org/10.1351/pac200173010153

[9] I. Klesment and E. Bondar, "Biogeochemical Aspects of Evolution of Sapropelites According to Data of Molecular Paleontology," *Oil Shale*, Vol. 14, No. 1, 1997, pp. 19-40.

[10] M. Allawzi, A. Al-Otoom, H. Allaboun, A. Ajlouni and F. Al Nseirat, "CO_2 Supercritical Fluid Extraction of Jordanian Oil Shale Utilizing Different Co-Solvents," *Fuel Processing Technology*, Vol. 92, No. 10, 2011, pp. 2016-2023. http://dx.doi.org/10.1016/j.fuproc.2011.06.001

[11] M. O. Punin Crespo and M. A. Lage Yusty, "Comparison of Supercritical Fluid Extraction and Soxhlet Extraction for the Determination of PCBs in Seaweed Samples," *Chemosphere*, Vol. 59, No. 10, 2005, pp. 1407-1413. http://dx.doi.org/10.1016/j.chemosphere.2004.12.025

[12] E. Bondar and M. Koel, "Application of Supercritical Fluid Extraction to Organic Geochemical Studies of Oil Shales," *Fuel*, Vol. 77, No. 3, 1998, pp. 211-213. http://dx.doi.org/10.1016/S0016-2361(97)00188-9

[13] I. Klesment, "On the Genesis of the Baltic Oil Shales," *Oil Shale*, Vol. 2, No. 1, 1985, pp. 12-22.

[14] I. Klesment, "Investigation of Aliphatic Structures of Oil Shales by Pyrolysis and Chromatographic Methods," *Journal of Analytical and Applied Pyrolysis*, Vol. 2, No. 1, 1980, pp. 63-77. http://dx.doi.org/10.1016/0165-2370(80)80046-5

[15] J. S. Sinninghe Damste and J. W. De Leeuw, "Analysis, Structure and Geochemical Significance of Organically-Bound Sulphur in the Geosphere: State of the Art and Future Research," *Organic Geochemistry*, Vol. 16, No. 4-6, 1990, pp. 1077-1101. http://dx.doi.org/10.1016/0146-6380(90)90145-P

[16] A. Loog, V. Petersell, J. Aruväli and M. Kalm, "Methods for the Determination of the Texture and Mineral Composition of the Dictyonema Shale," *Bulletin of the Geological Survey of Estonia*, Vol. 8, 1998, pp. 32-36.

[17] R. Veski and V. Palu, "Investigation of Dictyonema Oil Shale and Its Natural and Artificial Transformation Products by a Vankrevelenogram," *Oil Shale*, Vol. 20, No. 3, 2003, pp. 265-281.

ARTICLE II

Sharayeva, G.; Luik, H.; Luik, L. Effect of of Different Temperature-Time Combinations in Kerogen Pyrolysis to Thermobitumen and Oil. International Journal of Environmental Engineering, 2015, 2 (1), 174−181

International Journal of Environmental Engineering– IJEE
Volume 2 : Issue 1 [ISSN : 2374-1724]
Publication Date: 30 April, 2015

Effect of Different Temperature-Time Combinations in Kerogen Pyrolysis to Thermobitumen and Oil

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***Abstract*—Liquefaction of Kukersite and Dictyonema oil shales originating from Baltic deposits and varying by kerogen content and chemical composition were pyrolysed in a Fischer assay with the aim to maximize liquid product yield being determined as a sum of volatiles (oil) and solubles (thermobitumen). The effect of temperature in the range of 320–490 °C during 20 and 60 min residence time on the yield of thermobitumen, oil, gas, solid residue and water was studied. The chemical group and individual composition of the compounds in the liquid product such as aliphatic hydrocarbons, monoaromatic hydrocarbons, polyaromatic hydrocarbons, low-polar heteroatomic compounds and high-polar heteroatomic compounds were estimated by using TLC and GC/MS-methods. Varied temperature-time regimes used in modified Fischer assay analysis yield thermobitumen and oil in different proportions the sum of those being considerably higher compared with standard Fischer assay pyrolysis. Up to 90% of Kukersite kerogen was decomposed to the summary liquid product of thermobitumen and oil at 400 °C, 20 min or 390 °C, 60 min in a Fischer assay.**

***Keywords*—modified Fischer assay pyrolysis, kerogen, thermobitumen, shale oil, yield**

Abbreviations

TB_{SS} – thermobitumen recovered as solvent soluble
O_{CV} – oil recovered as condensable volatiles
TBO – recovered as a sum of TB_{SS} and O_{CV}
SR – solid residue
OM – organic matter
FAP – Fischer assay pyrolysis
MFAP – modified Fischer assay pyrolysis
TLC – adsorption thin-layer chromatography
GC/MS – gas chromatography / mass-spectroscopy
AlHC – aliphatic hydrocarbons
MAHC – monoaromatic hydrocarbons
PAHC – polyaromatic hydrocarbons
LPHet – low-polar heteroatomic compounds
HPHet – high-polar heteroatomic compounds

I. Introduction

World reserves of conventional petroleum are finite and the oil shale in its varieties is observed as alternative source for liquid fuels and chemicals. Deposits of oil shale occur in many parts of the world. Oil shales of different deposits differ by kerogen content and chemical composition. Oil shale is commonly known as a sedimentary rock, which contains varied amounts of kerogen bound dispersedly in a mineral matrix. A complex macromolecular structure of the kerogen was formed as a result of its fossilization during hundreds millions of years. Unlike the bitumen in oil sands, the kerogen in oil shale is insoluble in conventional organic solvents [1]. However, the durable steric structure of kerogen can be pyrolytically cracked above 350 °C in special retorts. Fischer assay pyrolysis (FAP) is the standard method for evaluating the potential oil yield of an oil shale [2–4]. Total world resources of shale oil are estimated by Word Energy Council conservatively at 4.8 trillion barrels that surpassing several times the amount of crude petroleum in the world [5]. Fischer assay models industrial retorts. There are two types of retorts in industrial use. Gas heated vertical retort processes produce a large amount of harmful semicoking waste. Horizontal solid heat carrier retorts have a complicated multi-stage technological scheme. [6]. Upon heating oil shale in the retort the kerogen is initially converted to what is termed thermobitumen [7–11]. The latter being not volatile but soluble in usual solvents thermally degrades to shale oil, gas, carbonaceous residue and pyrolytic water, among which shale oil, gas and water leave (vaporize) from the shale particle matrix. Carbonaceous residue remain mixed in with the minerals, forming solid residues called semicoke. Shale oil, gas and solid residue as final products are of secondary origin being formed only after thermal decomposition of the primary thermobitumen as an intermediate.

Yields and compositions depend on pyrolysis processing conditions and diagenetic history of oil shale [12–14]. A range of pyrolysis conditions have been investigated in the pyrolysis of different oil shales to obtain maximum yield of oil. These parametres include pyrolysis temperature, time, heating rate, pyrolysis atmosphere, particle grain size, reactor type and bed geometry [15–19]. Pyrolysis temperature and heating rate were shown to have the most influence on yield and composition of the derived oil [19–22]. The pyrolysis products distribution depends on the abundance, type, distribution and size of both the mineral and organic matter contents [13]. On the basis of pyrolytic behavior of Spanish, Turkish Göynük and US Green River oil shales it was found that pyrolysis reactions can be adsorbed, catalyzed or inhibited by the mineral matrixe present in oil shale [22–28]. In [29] and [30] variations in gas and oil evolution from shales of different

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organic contents of various Colorado oil shales were monitored and variations registered. Effect of the pressure on pyrolysis was investigated in [13,31,32] and it was shown that vacuum pyrolysis limits the secondary decomposition reactions while oil yield was reduced as the pressure was increased in Green River oil shale. In [32] and [33] considerable differences were registered in the yields and compositions of shale oil obtained from Turkish Göynük oil shale as a result of slow pyrolysis, flash pyrolysis and extractions with super and subcritical water.

In [1] was implied that there exists an optimal retorting temperature for the maximum yield of liquid oil. The review above shows that Fischer assay yields and compositions can be modified by varying standard regime of pyrolysis. In [34–36] the modified Fischer assay pyrolysis was used for evaluating the potential liquid fuel. In [37] modified Fischer is represented as a quick and simple screening method requiring only 100 mg of sample. The same was noticed in modified Gray-King assay method (the same as Fischer but operating with 10 g of shale per assay only [38]. In [23] three kerogen types were pyrolyzed by material balance modified Fischer assay.

The yield of shale oil determined as volatiles in Fischer assay standard pyrolysis is always much lower than that of non-volatile but soluble high-molecular thermobitumen.

The goal of this work is to maximize the liquid product yield separated as a sum of volatiles and solubles from two different kerogens by modifying temperature-time conditions in Fischer assay pyrolysis.

II. Material and methods

Kukersite and Dictyonema oil shales characterized in Table 1 were crushed to less than 1 mm and homogenized for use in the Fischer assay.

TABLE I. CHARACTERISATION OF THE INITIAL OIL SHALES

Characteristic	Kukersite	Dictyonema
Age	Middle Ordovician	Lower Ordovician
Analytical moisture, W^a	0.6	1.4
Ash (per dry mass), A^d	49.5	81.2
CO_2 of carbonates (per dry mass), $(CO_2)^d$	18.2	2.8
Dry organic matter OM^d	32.3	16.0
Elemental analysis of organic part:		
C	79.32	73.02
H	9.50	9.19
N + S	0.30	2.66
O (by difference)	10.88	15.13

The samples were submitted to the pyrolysis in a Fischer assay following standard and modified regimes. Fischer assay pyrolysis (FAP) in standard conditions followed ISO 647-74: heating 50 g of oil shale in aluminium retort up to 525 °C during 90 min. Modified Fischer assay pyrolysis (MFAP) was conducted at varied temperatures in-between 320–525 °C with residence times 20 and 60 min.

As a result of pyrolysis series solvent soluble thermobitumen (TB_{SS}), oil as condensable volatiles (O_{CV}), solid residue (SR), non-condensable gas and water were quantitatively yielded. Upon cooling of the volatile matter, condensable material was collected in a round-bottomed flask. The condensate contained all the O_{CV} as well as water. The water fraction was removed by azeotropic distilliation using Dean and Stark distillation method with the use of toluene as solvent [39]. Condensable distillate at a given temperature and solubles in benzene-methanol mixture from Fischer assay dry distillation residue as O_{CV} and TB_{SS} were summarized and calculated as total liquid product (TBO).

Chemical group composition of TBO was estimated by adsorption thin-layer chromatography (TLC). For this aim, 0.5 g of the sample was taken and fractionated on the 2 mm silica gel (Fluka, 60 µm) layer on a plate 24x24 cm. n-Hexane as eluting solvent was used. The following fractions of hydrocarbons and heteroatomic compounds were separated: aliphatic hydrocarbons (AlHC), monoaromatic hydrocarbons (MAHC), polyaromatic hydrocarbons (PAHC), low-polar heteroatomic compounds (LPHet) and high-polar heteroatomic compounds (HPHet). The fractions were weighted after desorption with diethyl ether and desiccation.

The individual composition of TLC fractions was determined by GC-MS-analysis (Shimadzu QP 2010 Plus) using 30 m capillary columns ZB-5 and HP-5MS.

III. Results and discussion

As a result of conventional FAP O_{CV} in yields 65.6 and 9.8% on OM bases from Kukersite and Dictyonema oil shales, respectively, were produced as condensable volatiles. The yield of TB_{SS} separated as solubles in benzene-ethanol mixture was negligible. Recoverable O_{CV} and TB_{SS} yields as well as those of SR, gas and water obtained from both kerogens as a result of MFAP at constant residence time (20 or 60 min) and varied temperatures are represented in Fig. 1.

In the Fig. 1 one can see common features and dissimilarities between two oil shales mentioned above. The former ones are visible in SR and gas yields while the latter ones in the yields of TBO liquids. With increasing the temperature the yield of SR proportionally decreases and that of gas increases up to twice. Exception is Kukersite MFAP during 60 min where gas yield practically was not changed with temperature rise from 370 to 410 °C. Concerning regularities of TB_{SS}, O_{CV} and water formation one can notice significant differences.

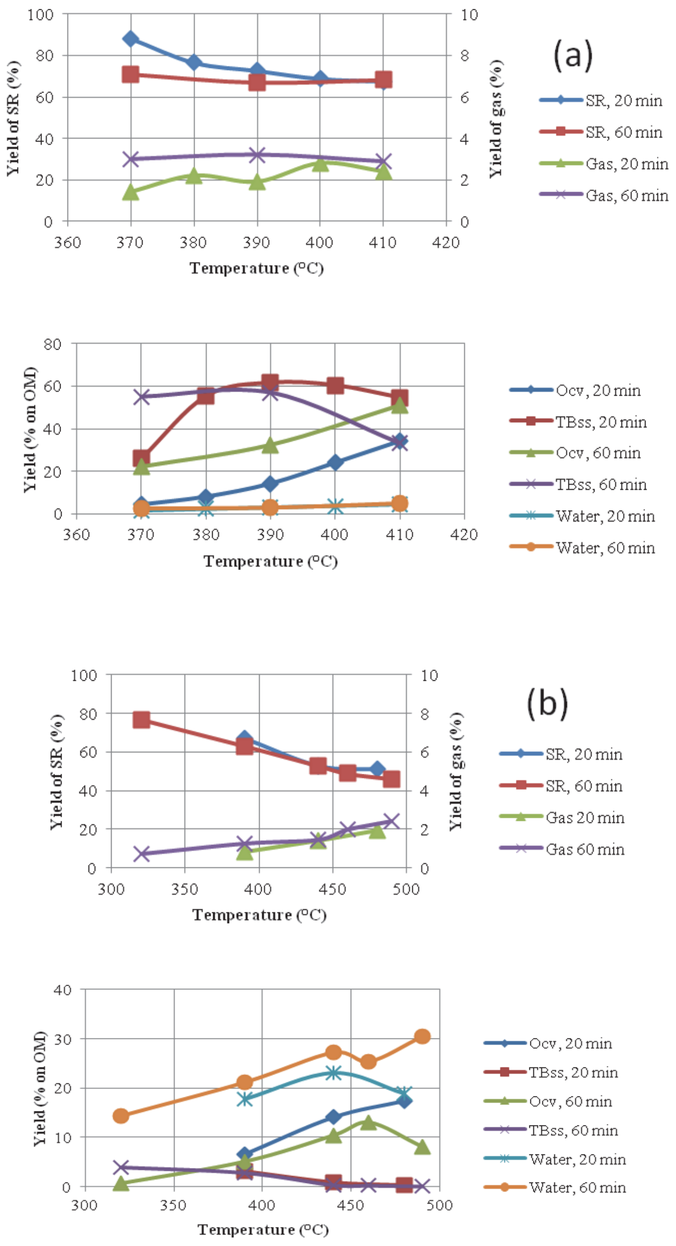

Figure 1. Yield of pyrolysis products from Kukersite (a) and Dictyonema (b) oil shales *versus* temperature.

Kukersite curves demonstrate that TB_{SS} yield abruptly increases from 25.9 to 54.7% with temperature increasing from 370 to 390 °C and then decreases with further increase of the temperature up to 410 °C (20 min). When the residence time was prolonged to 60 min, the yield of TB_{SS} was almost the same (55–57%) in the range 370–390 °C but abruptly decreases down to 33.4% with temperature reaching to 410 °C. The tendency of O_{CV} and gas formation as a result of TB_{SS} decomposition leading to decrease of TBO is observable with increasing the temperature.

Regularities of TB_{SS} formation from Dictyonema oil shale at residence times 20 and 60 min are described similarly. TB_{SS} maximum has been formed below 350 °C and at 450 °C all the TB_{SS} is decomposed to O_{CV}, gas and water. The maximum O_{CV} yield obtained in parallel with the minimum that of TB_{SS} (0.2%) was 17.67% (at 20 min and 480 °C). Dictyonema oil shale pyrolysis was accompanied with significant water formation compared with Kukersite (3–5 and 0.6–1.6% per oil shale, respectively). Water of crystallization in Dictyonema mineral part can have its role in larger water release. Twice lower kerogen content and higher that of mineral matter in Dictyonema oil shale compared with Kukersite led to considerably lower TB_{SS}, O_{CV} and finally to lower TBO as the sum.

Group composition of TBO is displayed in Fig.2 and one can see that it is different for Kukersite and Dictyonema. 60–75% of Kukersite TBO make HPHet. The content of hydrocarbons is low. In the composition of Dictyonema TBO prevail PAHC their yield amounting to 40%. HPHet, dominating in Kukersite TBO make only 20%. Among hydrocarbons PAHC are dominating in Kukersite TBO as well. It seems that the temperature has only small effect on TBO composition. With increasing the temperature slightly decreases the content of HPHet and increases that of hydrocarbons (in Dictyonema case, particularly PAHC content).

The individual composition of TLC fractions analyzed by using GC/MS-methods is represented in the Figures 3 and 4 and Table 2.

One can see that the TBO of Kukersite oil shale differs from that of Dictyonema mainly by the composition of AlHC and LPHet. Kukersite pyrolysis yielded both alkenes and alkanes C_9–C_{19} and alkanones. Longer alkanes (C_{12}–C_{31}), no alkenes and sulfur compounds in parallel to alkanones were produced in pyrolysis of Dictyonema oil shale.

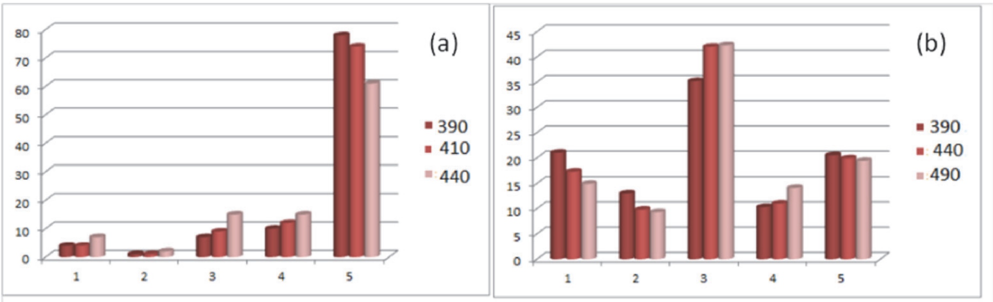

Figure 2. Group composition of TBO of Kukersite (a) and Dictyonema (b) oil shales, %. Fractions separated by TLC as follows: 1 – aliphatic hydrocarbons (AlHC), 2 – monoaromatic hydrocarbons (MAHC), 3 – polyaromatic hydrocarbons (PAHC), 4 – low-polar heteroatomic compounds (LPHet), 5 – high-polar heteroatomic compounds (HPHet).

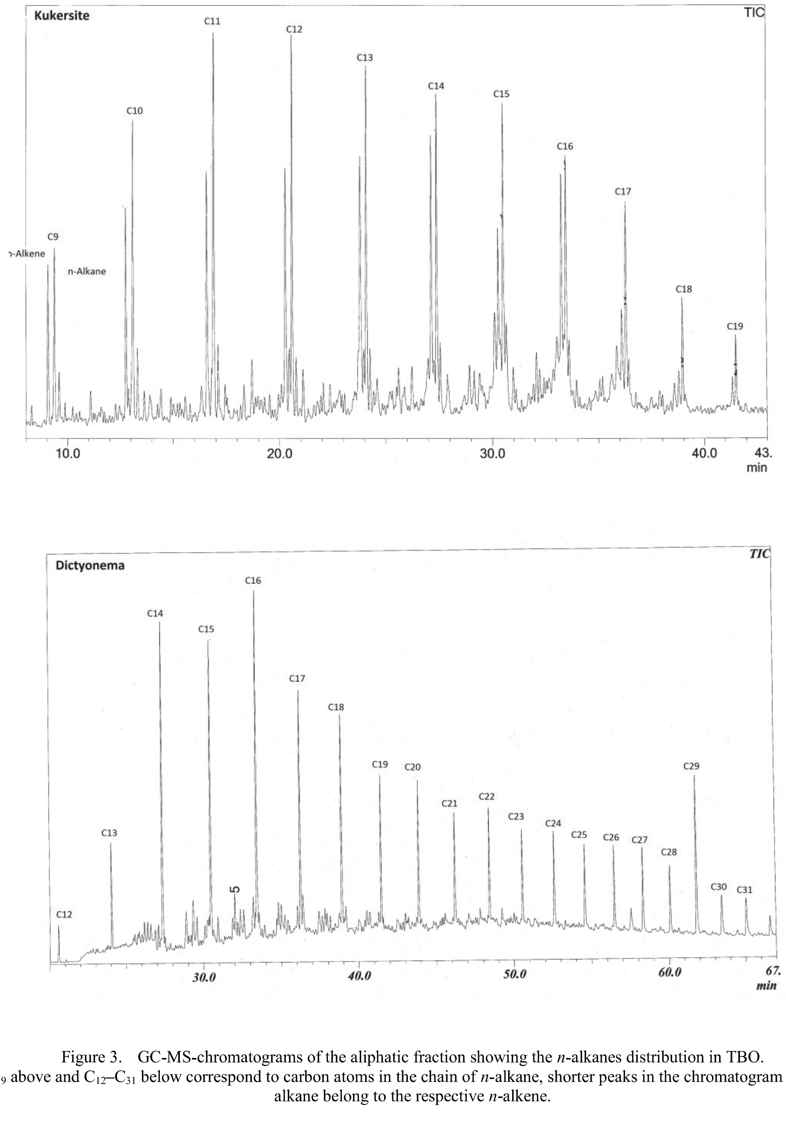

Figure 3. GC-MS-chromatograms of the aliphatic fraction showing the *n*-alkanes distribution in TBO.
The numbers C_9–C_{19} above and C_{12}–C_{31} below correspond to carbon atoms in the chain of *n*-alkane, shorter peaks in the chromatogram above preceding to the *n*-alkane belong to the respective *n*-alkene.

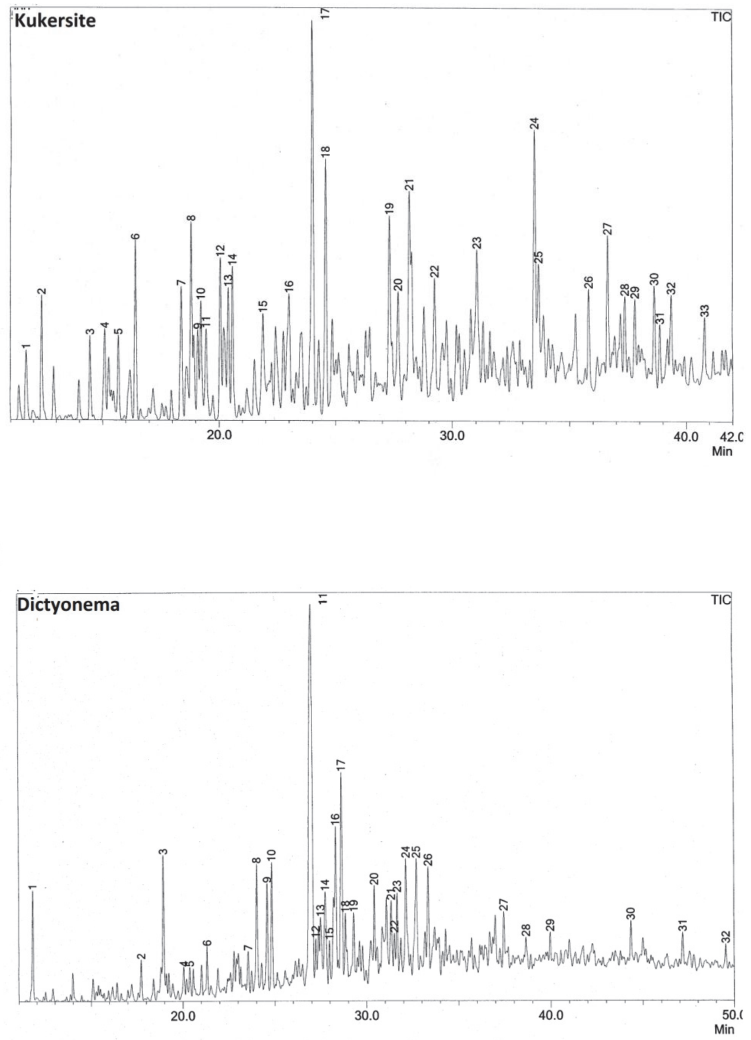

Figure 4. GC-MS-chromatograms of the polyaromatic hydrocarbons and low-polar heteroatomic compounds. The identification of the peaks marked by numbers is shown in Table 2.

TABLE II. COMPOUNDS IDENTIFIED IN TBO FRACTIONS

Peak number	Kukersite	Dictyonema
1	Isopropylbenzene	Benzenethiol
2	o-;m-;p-Ethyltoluene	1,2,3,5-tetramethylbenzene
3	Indane	1-ethyl-3,5-dimethylbenzene
4	Sec-Butylbenzene	Naphtalene
5	o-;m-;p-Propyltoluene	Benzothiophene
6	1-metylindane	Pentamethylbenzene
7	Methylindane, isomere	4,7-dimethylindane
8	Methylindane, isomere	1-methylnaphtalene
9	Pentylbenzene	2-methylnaphtalene
10	Tetralin	Cyclohexylbenzene
11	p-isobutyltoluene	Biphenyl
12	Naphtalene	Dimethylbenzothiophene
13	2-ethylindane	Dimethylnaphtalene
14	Dimethylindane, isomere	Dimethylnaphtalene
15	Etylindane, isomere	Dimethylbenzothiophene
16	Methyltetralin	Dimethylnaphtalene
17	Methyl-Naphtalene, isomere	Diphenylmetane
18	Methyl-Naphtalene, isomere	Dimethylnaphtalene
19	Ethyl-Naphtalene	
20	Dimehtyl-Naphtalene, isomere	1,1-Diphenylethane
21	Dimethyl-Naphtalene, isomere	X,y,z-trimethylnaphtalene
22	Dimethyl-Naphtalene, isomere	X,y,z-trimethylnaphtalene
23		X,y,z-trimethylnaphtalene
24	Allylnaphtalene	
25	Allylnaphtalene	
26		
27	Antracene, phenantrene derivate	1,4,5,8- tetramehylnaphtalene
28	Antracene, phenantrene derivate	Antracene, phenantrene derivate
29		Diphenyldisulphide
30		Triphenylmethane
31		Antracene, phenantrene derivate
32	Pyrene	Antracene, phenantrene derivate
33	Benz(de)antracene derivate	

IV. Conclusions

- The pyrolysis results indicate that high liquid yield can be achieved as the sum of condensable volatiles and solvent soluble with proper process conditions.
- The liquid yield and bitumen-to-oil ratio in it depend strongly on the chemical composition of the initial kerogen and pyrolysis variables in a Fischer assay.
- The maximum liquid yield from Kukersite and Dictyonema oil shales amounted at varied temperature-time regimes to 90.2 and 17.7%, respectively, surpassing those in Fischer assay by 1.4 times.
- Kukersite liquid is rich in high-polar heteroatomic compounds (60–75%) while that of the Dictyonema oil shale is characacterized by as high content as 42% of polyaromatics.
- Varying with pyrolysis temperature and time in Fischer assay it is possible to obtain higher liquefaction degree of kerogen and to modify liquid product chemical composition.

This work was financed by Estonian Research Council (SF 0140028s09, G9331) and EU Structural Funds.

References

[1] J. G. Na, C. H. Im, S. H. Chung, and K. B. Lee, “Effect of oil shale retorting temperature on shale oil yield and properties,” Fuel, vol. 95, pp. 131–135, May 2012.
[2] F. Fischer, The Conversion of Coal into Oil. New York: Van Nostrand, 1925.
[3] ISO 647. Brown Coals and Lignites - Determination of Yields of Tar, Water, Gas and Coke Residue by Low Temperature Distillation, 1st ed., 1974.
[4] P. F. V. Williams, “Oil shales and their analysis,” Fuel, vol. 62, pp. 756–771, July 1983.
[5] World Energy Council, 2010 Survey of Energy Resources, pp. 93–122. http://www.worldenergy.org/documents/ser_2010_report_1.pdf. (accessed 30.07.2014).
[6] M. Niu, S. Wang, X. Han, and X. Jiang, “Yield and characteristics of shale oil from the retorting of oil shale and fine oil-shale ash mixtures,” Appl. Energ., vol. 111, pp. 234–239, November 2013.
[7] F. P. Miknis, T. F. Turner, G. L. Berdan, and P. J. Conn, “Formation of soluble products from thermal decomposition of Colorado and Kentucky oil shales,” Energ. Fuel., vol. 1, pp. 477–483, November 1987.
[8] K. Rajeshwar, “The kinetics of the thermal decomposition of Green River oil shale kerogen by non-isothermal thermogravimetry,” Thermochim. Acta, vol. 45, pp. 253–263, May 1981.
[9] D. S. Thakur, and H. E. Jr. Nuttall, “Kinetics of pyrolysis of Moroccan oil shale by thermogravimetry,” Ind. Eng. Chem. Res., vol. 26, pp. 1351–1356, July 1987.
[10] B. Horsfield, and S. J. Dueppenbecker, “The decomposition of Posidonia shale and Green River shale kerogens using microscale sealed vessel (MSSV) pyrolysis,” J. Anal. Appl. Pyrol., vol. 20, pp. 107–123, July 1991.
[11] J. W. Larsen and K. Kidena, “The sudden release of oil and bitumen from Bakken shale on heating in water,” Energ. Fuel., vol. 16, pp. 1004–1005, June 2002.
[12] A. Ekstrom, C. J. R. Fookes, H. J. Loeh, C. H. Randall, C. Rovere, J. Ellis, and P. T. Crisp, “Chemical and pyrolysis characteristics of two types of oil shale from the Condor deposit in Queensland, Australia,” Fuel, vol. 66, pp. 1133–1138, August 1987.
[13] H. Pakdel, C. Roy, and W. Kalkreuth, “Oil production by vacuum pyrolysis of Canadian oil shales and fate of the biological markers,” Fuel, vol. 78, pp. 365–375, February 1999.
[14] Y. H. Khraisha, N. A. Irqsousi, I. M. Shabig, “Spectroscopic and chromatographic analysis of oil from an oil shale flash pyrolysis unit,” Energ. Convers. Manage., vol. 44, pp. 125–134, January 2003.
[15] P. R. Solomon, R. M. Carangelo, and E. Horn, “The effects of pyrolysis conditions on Israeli oil shale properties,” Fuel, vol. 65, pp. 650–662, May 1986.
[16] H. Bar, R. Ikan, and Z. Aizenshtat, **“**Kinetic study of isothermal oil shale pyrolysis: 2. Evaluation of the organic pyroproducts distribution,” J. Anal. Appl. Pyrol., vol. 10, pp. 167–179, January 1987.
[17] D. Skala, M. Bastić, J. Jovanović, and I. Rahimian, “Pyrolysis of oil shale in a microretorting unit,” Fuel, vol. 72, pp. 829–835, June 1993.
[18] N. Salhi, C. Bennouna, H. Bitar, M. Sergent, and R. P. T. Luu, “An experimental design to optimize pyrolysis conditions of Timahdit (Morocco) oil shale,” Fuel, vol. 75, pp. 633–640, April 1996.
[19] M. Kılıç, A. E. Pütün, B. B. Uzun, and E. Pütün, “Converting of oil shale and biomass into liquid hydrocarbons via pyrolysis,” Energ. Convers. Manage., vol. 78, pp. 461–467, February 2014.
[20] P. T. Williams, and N. Ahmad, “Influence of process conditions on the pyrolysis of Pakistani oil shales**,”** Fuel, vol. 78, pp. 653–662, May 1999.
[21] P. T. Williams, and N. Ahmad, “Investigation of oil-shale pyrolysis processing conditions using thermogravimetric analysis,” Appl. Energ., vol. 66, pp. 113–133, June 2000.
[22] B. Janković, “The kinetic modeling of the non-isothermal pyrolysis of Brazilian oil shale: Application of the Weibull probability mixture model,” J. Petrol. Sci. Eng., vol. 111, pp. 25–36, November 2013.
[23] A. J. Gannon, and D. A. Henstridge, “Pyrolysis stoichiometry for three kerogen types,” Fuel, vol. 66, pp. 350–352, March 1987.
[24] A. G. Borrego, J. G. Prado, E. Fuente, M. D. Guillén, and C. G. Blanco, “Pyrolytic behaviour of Spanish oil shales and their kerogens,” J. Anal. Appl. Pyrol., vol. 56, pp. 1–21, September 2000.
[25] M. Al-Harahsheh, O. Al-Ayed, J. Robinson, S. Kingman, A. Al-Harahsheh, K. Tarawneh, A. Saeid, and R. Barranco, “Effect of demineralization and heating rate on the pyrolysis kinetics of Jordanian oil shales**,”** Fuel Process. Technol., vol. 92, pp. 1805–1811, September 2011.
[26] A. Karabakan, and Y. Yürüm, “Effect of the mineral matrix in the reactions of oil shales: 1. Pyrolysis reactions of Turkish Göynük and US Green River oil shales,” Fuel, vol. 77, pp. 1303–1309, October 1998.
[27] P. T. Williams, and H. M. Chishti, “Influence of residence time and catalyst regeneration on the pyrolysis–zeolite catalysis of oil shale,” J. Anal. Appl. Pyrol., vol. 60, pp. 187–203, August 2001.
[28] M. Sert, L. Ballice, M. Yüksel, and M. Sağlam, “Effect of mineral matter on the isothermal pyrolysis product of Şırnak asphaltite (Turkey),” Fuel, vol. 90, pp. 2767–2772, August 2011.
[29] E. W. Cook, “Green River shale-oil yields: correlation with elemental analysis,” Fuel, vol. 53, pp. 16–20, January 1974.
[30] E. B. Huss, and A. K. Burnham, “Gas evolution during pyrolysis of various Colorado oil shales,” Fuel, vol. 61, pp. 1188–1196, December 1982.
[31] R. D. Noble, W. F. Tucker, and H. G. Harris, “Isothermal oil shale pyrolysis. 1. Oil generation and composition at various pressures,” Fuel, vol. 61, pp. 482–484, May 1982.
[32] E. M. Suuberg, J. Sherman, and W. D. Lilly, “Product evolution during rapid pyrolysis of Green River Formation oil shale,” Fuel, vol. 66, pp. 1176–1184, September 1987.
[33] J. Yanik, M. Yüksel, M. Sağlam, N. Olukçu, K. Bartle, and B. Frere,”Characterization of the oil fractions of shale oil obtained by pyrolysis and supercritical water extraction,” Fuel, vol. 74, pp. 46–50, January 1995.
[34] T. T. Coburn, and A. M. Rubel, “Comments on the modified Fischer assay of Eastern oil shales of Kentucky,” Fuel Process. Technol., vol. 8, pp. 1–12, September 1983.
[35] N. V. Dung, “Pyrolysis behaviour of Australian oil shales in a fluidized bed reactor and in a material balance modified Fischer assay retort,” Fuel, vol. 68, pp. 1570–1579, December 1989.
[36] L. Roets, J. R. Bunt, H. W. J. P. Neomagus, and D. van Niekerk, “An evaluation of a new automated duplicate-sample Fischer Assay setup according to ISO/ASTM standards and analysis of the tar fraction,” J. Anal. Appl. Pyrol., vol. 106, pp. 190–196, March 2014.
[37] S. Sato, and A. Matsumura, “Screening method for oil shale samples for Fischer assay,” J. Jpn. Petrol. Inst., vol. 46, pp. 210–213, May 2003.
[38] N. C. Watson, “A modified Gray-King assay method for small oil shale samples,” Fuel, vol. 63, pp. 1455–1458, October 1984.
[39] ISO 1897-2, Phenol, o-Cresol, p-Cresol, Cresolic Acid and Xylenols for Indutrial Use Methods of Test. Part II. Determination of Water - Dean and Stark Method, 1st ed., 1977.

ARTICLE III

Sharayeva, G., Tiikma, L., Luik, H., Johannes, I. Low Temperature Pyrolysis of Graptolite Argillite (Dictyonema Shale) in Autoclaves Int. Journal of Engineering Research and Applications, 2015, 5 (11), 16-22

RESEARCH ARTICLE OPEN ACCESS

Low Temperature Pyrolysis of Graptolite Argillite (Dictyonema Shale) in Autoclaves

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ABSTRACT

The results of the systematic experimental study obtained in this work on the effects of temperature (340–420 °C) and exposure time (0–8h) at nominal temperature on the yield of pyrolysis products from Estonian graptolite argillite (GA) generated in autoclaves without any solvent are described. The yields of solid residue (SR), gas, pyrogenetic water (W) and extractable with benzenemix ofthermobitumen and oil (TBO) were estimated. The compound groups of TBO were assessed. The highest yield of TBO, 2.18% on dry GA basis and 13.2% of organic matter (OM) was obtained at temperature of 420 °C and duration 0.5 h. The main compound groups in TBO obtained at 400 ^{o}C are polar hetero-atomic compounds and polycyclic hydrocarbons surpassing 45% and 30% of TBO. The shares of aliphatic and monocyclic hydrocarbons are below 15% of TBO. The yield of W from GA is – about 10-15% of OM. The quantity of OM left in SR after pyrolysis is high, about 65% of OM. The yield of pyrolysis products from GA and the composition of its TBO are compared with those obtained under similar conditions from different oil shales: Estonian Kukersite, US Utah Green River, and Jordanian Attarat.

Keywords-Graptolite argillite, Dictyonema shale, Low temperature pyrolysis, Autoclaves

I. INTRODUCTION

The Lower Ordovician organic-rich marine metalliferous black shale – graptolite argillite (GA) lies beneath most of Northern Estonia. Earlier it was called „Dictyonema shale“, „Dictyonema argillite“ or „alum shale“. Alum shale, as well as graptolite argillite, are distinguished by remarkably high concentrations of trace metals such as U, Mo, V and Ni, but may also be locally enriched with rare earth elements, Cd, Au, Sb, As, Pt [1].

In the study [2] all the published data concerning GA OM elemental composition and its changes during natural and artificial processes by employing vankrevelenogram were cited. The probably elemental composition of native GA OM elucidated from the study [2] is: C 75.7, H 7.8, N 2.3, O 14.2%, atomic ratios H/C 1.24 and O/C 0.16. The calorific value of GA ranges from 4.2 to 6.7 MJ/kg [1].

Pyrolysis of GA was studied in Fischer assay [2-6]. Varied temperature-time regimes used in modified Fischer assay pyrolysis yield thermobitumen and oil in different proportions, the sum of those being considerably higher compared with standard Fischer assay pyrolysis [6]. GA pyrolysis was accompanied with significant water formation (3–5 % per oil shale) whereas water of crystallization in GA mineral part could have its role in larger water release [6].

In our previous works, a systematic experimental study of slow pyrolysis in autoclaves of different shales was conducted, and the kinetics of kerogen decomposition into TBO was calculated for Estonian Kukersite [7], US Green River [8] and Jordanian Attarat[9] oil shales.

Oil yield per unit of OM can vary widely between oil shales from different deposits. On the basis of solvent swelling experiments Oja concluded [10] that oil yield is usually higher for oil shales with organic matter consisting of Type I kerogen than for those with Type II kerogen. Kerogen, which makes up most of oil shale’s organic matter, is a highly cross-linked, organic, macromolecular material [11]. Depending on the oil shale kerogen type, loosening or tightening of the kerogen structure can occur in the temperature region before an active pyrolytic volatilization of oil. Solvent swelling experiments [12] 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 [13]. The characteristic is qualitatively similar to that of high tar yield softening coals. On the other hand, the low oil yield kerogen (Type II) of GA, which possesses non-softening pyrolysis behavior, shows a tendency for pre-pyrolysis structural tightening [14].

The goal of this study was to elucidate conditions for obtaining the maximum yield of liquid product, TBO, from GA and to compare with those from previously studied oil shales (Estonian Kukersite,US Green River and Jordanian Attarat). For this purpose, a systematic experimental study of the effects of temperature and time on the yield of pyrolysis products from GA in autoclaves without any solvent was conducted.

II. EXPERIMENTAL

A. *Characterization of the initial sample*

The conditional OM (weight loss in incineration at 550 °C) of the sample was 16.00%, ash content (weight loss in incineration at 825 °C) 80.80% and moisture 1.38%.

The elemental analysis gave: C 73.02%, H 9.19%, N+S 2.66%, O (by difference) 15.13 of OM. The yields of the pyrolysis products in Fischer assay were as follows: oil 2.96%, semicoke 91.32%, pyrogenetic water 2.61% and gas + losses 3.11% of the dry shale.

B. *Liquefaction procedure*

Pyrolysis of GA was carried out in glass test tubes placed in 58 cm3 autoclaves. In each experiment about 12 g of the air dried GA powdered to 0.04–0.1 mm were used. The samples were placed into a cold muffle oven. The constant nominal temperature varying from 340 to 420 °C was attained for the period of 60 minutes. The pyrolysis duration was measured from the time when the muffle oven reached the nominal temperature prescribed. Efficiency of the liquefaction process was evaluated by the yield of pyrolysis products: gas, total benzene solubles - bitumen, thermobitumen and oil (TBO), solid residue (SR) and pyrogenetic water (W).

C. *Analysis*

The mass of gas formed was determined by the weight loss of glass test tubes with the sample after discharging gaseous products from the open autoclave at room temperature. The liquid products consisting of TBO, W and moisture were extracted exhaustively with boiling benzene in a Soxhlet extractor. The water phase was gathered and weighted as drops on the walls of the test tube, and condenser of Soxhlet extractor after the azeotropic mixture of water and benzene was decomposed. The mass of moisture in the initial samples and SRwere weighted by drying at 105–110 °C during 2 h. The content of OM in SR was measured as weight loss in incineration at 550°Cduring 4 h.The solvents applied were removed from TBO solutions in a vacuum rotation evaporator at 60–70 °C.

The distillation residues of the TBO extracts obtained in the rotation evaporatorwere left in the open flask for evolution of the solvent traces remained. Like in the authors' earlier works, removing traces of benzene from TBO was a problematic procedure. The quantity of TBO can be underestimated due to evaporation of low-boiling destruction products or overestimated when part of the solvent, having a higher boiling temperature than the lighter fractions or being incorporated into destruction products is not removed. So, the mass of TBO was preferred to determine by subtracting the mass of gas, W and SR from the initial mass of the shale.

The compound groups of TBO were estimated by preparative thin-layer chromatography separating 500 mg samples on 24 × 24 cm plates coated with a 2 mm silica gel layer (60 mm, Fluka), and using n-hexane as the eluent. Five groups of compounds were separated and extracted from silica gel with ethyl ether: aliphatic hydrocarbons (AlHC), monocyclic hydrocarbons (MCHC), polycyclic hydrocarbons and some sulfur compounds (PCHC), neutral hetero-atomic (Nhet) and polar hetero-atomic (Phet) compounds.

III. RESULTS AND DISCUSSION

Yields of the pyrolysis products from the dry GA obtained in the test series conducted at various nominal temperatures and isothermal durations are presented in Tables 1 and 2.

The results in Table 1 show that at any temperature series the gas yield increases with time whereas the yield of TBO has a maximum and that of SR a minimum shifting with increasing temperature to shorter durations. The maximum yield of gas achieved is only 2.7%, and the maximum transformation degree of the OM is 7.4% of the dry initial shale.

The better characterization of the process can be obtained when the yields are depicted on the basis of OM. Effect of pyrolysis duration at various nominal temperatures on the yields of the main decomposition products – gas, TBO, W, and SR of OM, are presented in Table 2 and Fig. 1

The experimental data in Table 2, and in Figs. 1 and 2 prove the tendencies in Table 1. The decomposition of OM starts in the heating stage already before the nominal temperature has been achieved. The yields of gas, SR and W change with increasing both nominal temperature and pyrolysis time up to a characteristic steady state whereas the yield of TBO passes a maximum at several optimal combinations of temperature and time. The yields on OM basis achieve close values: for gas about 16%, for TBO 13.2%, and for W 15%. OM in SR after pyrolysis at most expedient pyrolysis conditions can be reduced not lower than to 58 %. Yield of the target product, TBO, obtained using the low-temperature pyrolysis procedure, s.c. TBO-technology, is not good enough.

TABLE 1.Effect of nominal temperature and isothermal duration on the yield of pyrolysis products from GA in autoclaves, % on dry GA basis

Pyrolysis conditions		**Gas**	**W**	**TBO**	**TBO+W**	**OM in SR**	**SR**
Temp. °C	**Time h**						
340	0.00	0.06	0.05	0.38	0.43	15.98	99.51
340	1.00	0.89	0.82	0.74	1.56	14.02	97.55
340	2.00	1.25	1.81	0.96	2.77	12.44	95.97
340	4.00	1.37	2.30	1.10	3.41	11.70	95.23
340	6.00	1.55	2.37	1.52	3.89	11.02	94.55
340	8.00	1.65	2.23	1.68	3.90	10.92	94.45
360	0.00	0.37	0.05	0.40	0.45	15.65	99.18
360	0.50	0.99	0.65	1.19	1.84	13.64	97.17
360	0.75	1.17	0.96	1.51	2.47	12.83	96.36
360	1.00	1.38	1.26	1.72	2.98	12.11	95.64
360	1.50	1.62	1.64	1.60	3.24	11.60	95.13
360	2.00	1.76	2.08	1.58	3.66	11.05	94.58
360	3.00	1.84	2.34	1.55	3.89	10.74	94.27
360	4.00	1.89	2.44	1.53	3.96	10.61	94.14
360	6.00	1.98	2.50	1.55	3.99	10.44	93.97
380	0.00	0.41	0.13	0.30	0.43	15.63	99.16
380	0.50	1.28	1.46	1.48	2.94	12.26	95.79
380	0.75	1.49	1.83	1.79	3.62	11.36	94.89
380	1.00	1.74	2.00	1.91	3.92	10.81	94.34
380	1.50	1.90	2.25	1.91	4.16	10.41	93.94
380	2.00	1.99	2.31	1.87	4.18	10.30	93.83
380	3.00	2.09	2.44	1.74	4.18	10.21	93.74
380	4.00	2.29	2.47	1.80	4.27	9.91	93.44
380	6.00	2.38	2.49	1.86	4.35	9.74	93.27
400	0.00	0.54	0.20	0.31	0.51	15.42	98.95
400	0.50	1.45	1.63	1.89	3.51	11.50	95.03
400	1.00	2.06	2.08	1.98	4.06	10.36	93.89
400	1.50	2.16	2.22	2.05	4.27	10.04	93.57
400	2.00	2.27	2.42	1.86	4.28	9.93	93.46
400	4.00	2.27	2.40	1.93	4.33	9.87	93.40
420	0.00	0.64	0.36	0.20	0.57	15.26	98.79
420	0.50	1.97	2.18	2.18	4.36	10.14	93.67
420	1.00	2.34	2.42	1.90	4.32	9.81	93.34
420	1.50	2.53	2.49	1.82	4.31	9.63	93.16
420	2.00	2.55	2.55	1.75	4.30	9.61	93.14
420	3.00	2.66	2.56	1.66	4.22	9.59	93.12

TABLE 2. Effect of nominal temperature and isothermal duration on the yield of pyrolysis products from GA in autoclaves, % on OM basis

Pyrolysis conditions		**Gas**	**W**	**TBO**	**TBO+ W**	**OM in SR**	**Conversion degree**
Temp °C	**Time h**						
340	0.00	0.38	0.29	2.31	2.60	97.02	2.98
340	1.00	5.39	5.00	4.50	9.50	85.11	14.89
340	2.00	7.60	11.00	5.84	16.84	75.56	24.44
340	4.00	8.29	13.99	6.71	20.69	71.02	28.98
340	6.00	9.44	14.41	9.22	23.64	66.93	33.07
340	8.00	10.01	13.52	10.18	23.70	66.30	33.70
360	0.00	2.24	0.31	2.45	2.75	95.00	5.00
360	0.50	6.00	3.94	7.22	11.16	82.84	17.16
360	0.75	7.13	5.80	9.18	14.98	77.89	22.11
360	1.00	8.38	7.64	10.47	18.11	73.51	26.49
360	1.50	9.84	9.97	9.73	19.70	70.46	29.54
360	2.00	10.70	12.65	9.58	22.23	67.07	32.93
360	3.00	11.19	14.20	9.39	23.59	65.22	34.78
360	4.00	11.49	14.80	9.26	24.06	64.45	35.55
360	6.00	12.04	15.15	9.40	24.20	63.41	36.59
380	0.00	2.48	0.78	1.82	2.60	94.92	5.08
380	0.50	7.75	8.85	8.99	17.84	74.41	25.59
380	0.75	9.05	11.12	10.87	21.99	68.96	31.04
380	1.00	10.55	12.17	11.63	23.80	65.66	34.34
380	1.50	11.51	13.67	11.60	25.27	63.22	36.78
380	2.00	12.09	14.03	11.33	25.36	62.55	37.45
380	3.00	12.67	14.80	10.57	25.37	61.96	38.04
380	4.00	13.90	14.99	10.96	25.94	60.16	39.84
380	6.00	14.44	15.12	11.32	26.44	59.12	40.88
400	0.00	3.27	1.22	1.86	3.08	93.65	6.35
400	0.50	8.83	9.88	11.45	21.33	69.84	30.16
400	1.00	12.48	12.61	12.02	24.63	62.89	37.11
400	1.50	13.11	13.47	12.45	25.92	60.97	39.03
400	2.00	13.76	14.67	11.30	25.97	60.27	39.73
400	4.00	13.79	14.60	11.70	26.30	59.91	40.09
420	0.00	3.90	2.21	1.24	3.45	92.65	7.35
420	0.50	11.98	13.25	13.21	26.46	61.56	38.44
420	1.00	14.21	14.70	11.55	26.25	59.54	40.46
420	1.50	15.34	15.10	11.08	26.18	58.48	41.52
420	2.00	15.51	15.48	10.65	26.13	58.36	41.64
420	3.00	16.16	15.55	10.08	25.63	58.21	41.79

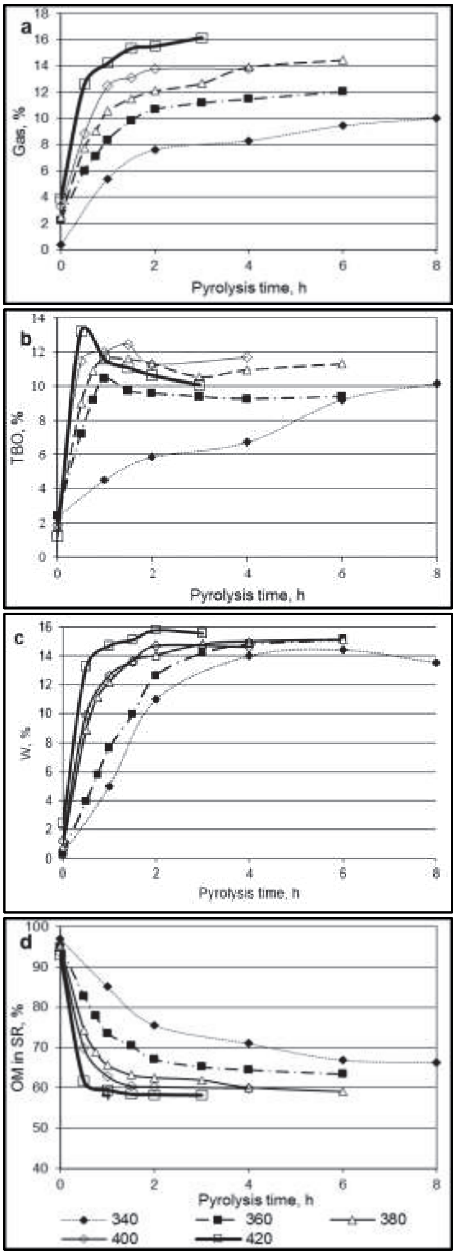

Fig. 1. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of gas (a), TBO (b), pyrogenetic water (c) and solid residue (d), % on OM basis at different pyrolysis temperature: 340, 360, 380, 400, 420°C.

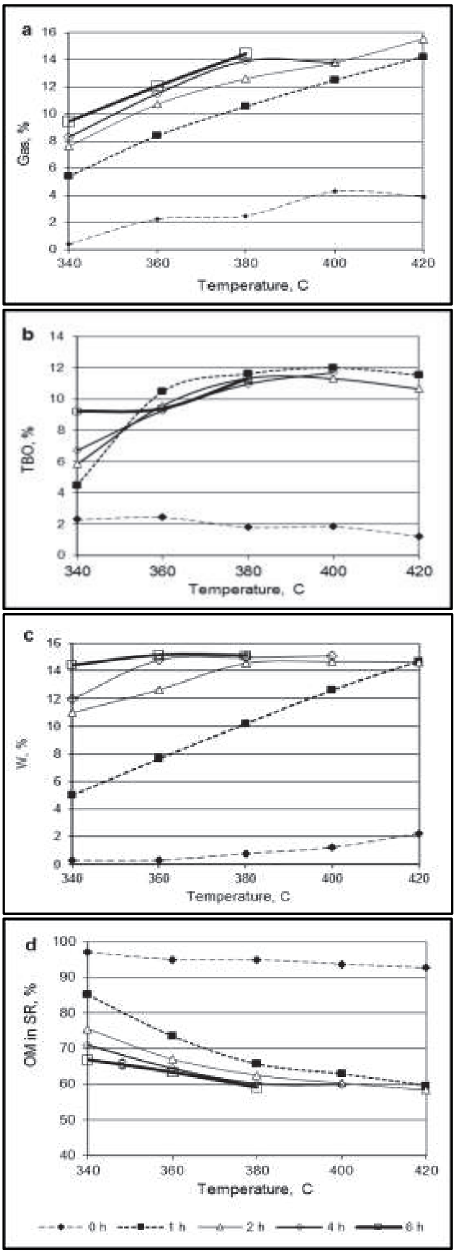

Fig. 2. Effect of nominal temperature in autoclavic pyrolysis on the yield of gas (a), TBO (b), pyrogenetic water (c) and solid residue (d), % on OM basis at different isothermal duration: nominal temperature achieving, 1h, 2h, 4h, 6h.

IV. COMPARISON OF YIELDS AND GROUP COMPOSITIONS OF THE PYROLYSIS PRODUCTS FROM DIFFERENT OIL SHALES

The yields of pyrolysis products from GA obtained in this work for the first time, were compared with our earlier results obtained using the TBO-technology on oil shales from different deposits: Estonian Kukersite (31% OM) [7], US Utah Green River (13.6% OM) [8], and Jordanian Attarat (21.4% OM) [9]. Also, the group composition of their TBO were compared.

The yields of pyrolysis products from the oil shales obtained in autoclaves at the identical conditions are given in Fig. 3.

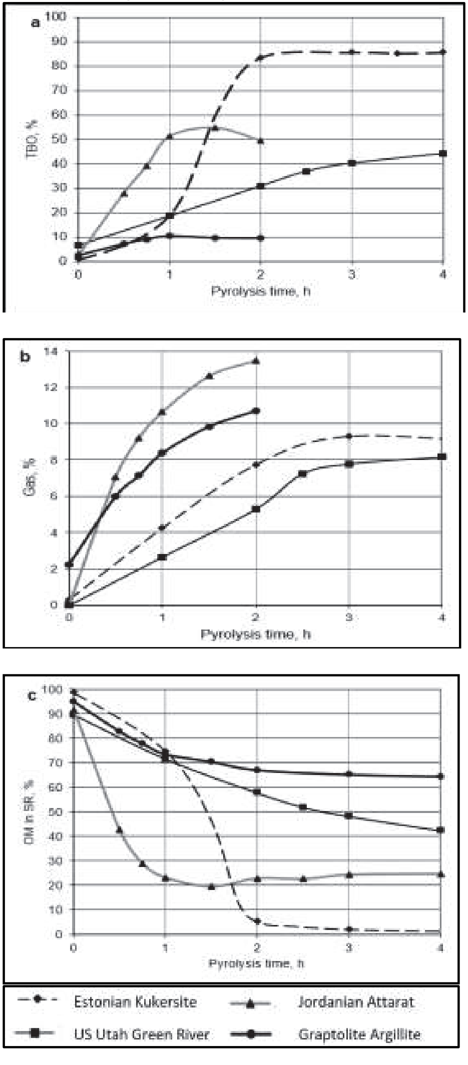

Fig. 3. Comparison yieldsof pyrolysis products (360°C) from different oil shales.

The optimum durations at 360 °C and maximum yields of TBO in their OM basis depicted in Fig. 3a are very different: for Estonian Kukersite about 2 h, 85%, for Jordanian oil shale 1.5 h, 55%, for US Utah Green River 4h and 45%, and for Estonian GA –1h and 10-12% only.At higher temperature the maximum is achieved at shorter time. The angle of inclination gives the possibility to compare the speed of TBO formation. Kinetics of destruction of Estonian Kukersite, US and Jordanian oil shales was described in [7,8,9].

The yield of gas from different oil shales (Fig. 3b) increases steadily with temperature and time increasing. The gas yield is higher for Jordanian oil shale and GA (more than 11-13%) and compared withKukersite and US shales (8-9%).

The pyrolysis time for minimum quantity of OM left in SR after pyrolysis using TBO technology (Fig. 3c) corresponds with the conditions for the maximum yield of TBO. About 65% of OM is left in the residue of GA, 40% of US, and 20-25% of Jordanian oil shale. The organic residue of Kukersite oil shale is 2-5% of OM only.

TABLE 3. Group composition of TBO, % of TBO

Compound group	Estonian		US Green River 380°C, 2h	Jordanian Attarat 380°C, 1h
	GA 400°C,1.5 h	Kukersite 360°C, 3h		
AlHC	10.5	14.4	24.4	8.2
MCHC	14.3	2.3	5.5	8.4
PCHC	30.5	20.9	11.6	32.9
Nhet	16.2	14.3	10.0	13.2
Phet	28.5	48.1	48.5	37.3

The group composition of TBO obtained at pyrolysis conditions with maximum TBO yield from compared shales is given in Table 3. According to Table 3, the main compound groups in TBO obtained in the slow pyrolysis from GA in an autoclave without any solvent are polycyclic hydrocarbons (about 30%) and polar hetero-atomic compounds making totally 59% of TBO. The quantity of latter is close of that from in Green River oil shale and less than in Jordanian and Kukersite oil shales (69-70%). The yields of desired aliphatic and monocyclic hydrocarbons in TBO of GA is below 25%, what is less than in US shale and exceeding that of Kukersite and Jordanian shales.

V. CONCLUSIONS

A systematic experimental study of the effects of temperature and time on the yield of pyrolysis products from Estonian graptolite argillite (GA) in autoclaves was conducted.

In the low-temperature (340–420 °C) pyrolysis of GA in autoclaves during the exposure time of 0–8 h at nominal temperature, the gas yield increases with time and temperature. In the optimum combinations of temperature and duration the yield of benzene extract, consisting of natural bitumen, a pyrolysis intermediate product thermobitumen and oil (TBO), passes a maximum, and the yield of solid residue (SR) a minimum.

The highest yield of TBO, 2.18% of dry GA and 13.2% of organic matter (OM),was obtained at the temperature of 420 °C and duration 0.5 h. The yields of pyrogenetic water from GA is high – about 10-15% of OM. At optimal pyrolysis conditions not less than 58.5% of OM was left in SR.

The main compound groups in TBO obtained from GA in pyrolysis at 400 °C are polycyclic hydrocarbons (about 30%) and polar hetero-atomic compounds surpassing totally 45% of TBO.

The yield of pyrolysis products from GA and group composition of their TBO were compared with those from different deposits of oil shales (Estonian Kukersite, US Utah Green River, Jordanian Attarat). The share of desired aliphatic and monocyclic hydrocarbons in TBO of GA was below 25%, what is less than in US Green River oil shale and exceeding that of Kukersite and Jordanian shales.

VI. ACKNOWLEDGEMENTS

This work was financed by Estonian Research Council (SF 0140028s09, G9331) and EU Structural Funds.

REFERENCES

[1] Hade, S., Soesoo, A. Estonian graptolite argillites revisited: A future resource? *Oil Shale* 31 (1), 2014, 4-18.

[2] Veski, R., Palu, V. Investigation of Dictyonema oil shale and its natural and artificial transformation products by a vankrevelenogram. *Oil Shale*, 20(3), 2003, 265–281.

[3] Oil Shale Formations.- Tallinn, 1973 [in Russian]

[4] Lippmaa, E., Maremäe, E. Uranium production from the local Dictyonema shale in North-East Estonia. *Oil Shale*, 17(4), 2000, 387–394.

[5] Siirde, A. Some new data about Dictyonemashale.*Proc. Tallinn Polytech. Inst.* 1956. Vol. A, No. 73. 3-22 [in Russian].

[6] Sharayeva, G.; Luik, H.; Luik, L. (2015). Effect of Different Temperature-Time Combinations in Kerogen Pyrolysis to Thermobitumen and Oil. *International Journal of Environmental Engineering*, 2(1), 174 - 181.

[7] Johannes, I., Tiikma, L., Zaidentsal, A., Comparison of the thermobituminizationkinetics of Baltic oil shale in open retorts and autoclaves. *Oil Shale*, 27, 2010, 17-25.

[8] Johannes, I., Tiikma, L., Luik, H., Sharajeva, G. Thermal extraction of oil from Utah Green River (USA) oil shale in autoclaves. *International Journal of Engineering and Applied Sciences*, 6 (5), 2015, 23-35.

[9] Tiikma, L., Johannes, I., Luik, H., Lepp. A., Sharayeva, G. Extraction of oil from Jordanian Attarat oil shale. *Oil Shale*, 32 (3), 2015, 218–239.

[10] Oja, V. Vaporization parameters of primary pyrolysis oil from kukersite oil shale. *Oil Shale*, 32 (2), 2015, 124–133.

[11] Lille, Ü. Behavior of Estonian kukersite kerogen in molecular mechanical force field. *Oil Shale*, 21(2), 2004, 99–114.

[12] Savest, N., Oja, V., Kaevand, T., Lille, Ü. Interaction of Estonian kukersite with organic solvents: A volumetric swelling and molecular simulation study. *Fuel*, 86(1–2), 2007, 17–21.

[13] Savest, N., Hruljova, J., Oja, V. Characterization of thermally pretreatedkukersite oil shale using the solvent-swelling technique. *Energ. Fuel*, 23(12), 2009, 5972–5977.

[14] 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.*, 89(2), 2010, 261–264.

ARTICLE IV

Tiikma, L.; Johannes, I.; Luik, H.; Lepp, A.; **Sharayeva, G**. Extraction of Oil from Jordanian Attarat Oil Shale. Oil Shale, 2015, 32 (3), 218−239

Oil Shale, 2015, Vol. 32, No. 3, pp. 218–239
doi: 10.3176/oil.2015.3.03

ISSN 0208-189X

EXTRACTION OF OIL FROM JORDANIAN ATTARAT OIL SHALE

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Abstract. *A short overview of the previous works concerning oil extraction from Jordanian oil shale is presented. The results of the systematic experimental study obtained in this work on the effects of temperature (320–420 °C) and exposure time (0–10 h) at nominal temperature on the yield of pyrolysis products from Attarat oil shale generated in autoclaves without any solvent and in the presence of benzene, water and tetralin are described. The yields of solid residue, gas, pyrolytic water and subsequent extracts with benzene (thermobitumen and oil (TBO) including asphaltenes and hexane solubles) and tetrahydrofurane (asphaltols) were estimated. The compound groups of TBO were assessed. The highest yield of TBO, 59.4% of organic matter (OM), was obtained at a temperature of 420 °C and duration 0.25 h. The 20% lower yield of TBO from Jordanian oil shale OM in comparison with that from Estonian Kukersite OM is explained by close values of the apparent kinetic constants estimated for the overall decomposition of the Attarat oil shale OM, and for the secondary decomposition of TBO.*

Keywords: *Jordanian Attarat oil shale, pyrolysis, autoclaves, kinetics.*

1. Introduction

The proven amount of Jordanian oil shales is about 5×10^{10} tons [1]. So, there is interest in attaining a maximum utilization potential of the local energy source reducing Jordan's dependence on imported oil. The eight most important deposits – Juref ed Darawish, Sultani, Wadi Maghar, El-Lajjun, Attarat Um Ghudran, Khan ez Zabib, Sigawa and Wadi Thamad, are located in west-central Jordan. Recovery of liquid fuels from the shales of different deposits amounts to 8–12%. The best-explored deposits are El-Lajjun, Sultani, Juref ed Darawish and to some extent Attarat Um Ghudran [2, 3].

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The oil shales have shown unexpected structural and reactivity differences despite they were deposited at roughly the same time in the same region [4].

Oil shale organic matter (OM) consists of organic solvents soluble bitumen and insoluble kerogen. A special feature of Jordanian oil shale is that there are quite a lot of foraminifera shells (diameter < 20 μm) filled with bitumen or kerogen instead of the usual calcite [1]. Beneficiation of the oil shale by froth flotation has shown a poor recovery of oil-rich components (maximum 3%) just due to the fact that during crushing and milling kerogen and bitumen wet most of the oil shale particles, making it difficult to adjust surface properties [5].

Kerogen can be extracted from the oil shales only after its thermal or chemical decomposition.

1.1. Extraction of bitumen

In Jordanian oil shale the share of OM soluble in organic solvents without thermal decomposition (bitumen) is quite high. Al-Harasheh [6] and Shawaqfeh and Al-Harasheh [7] have studied the extraction of bitumen from El-Lajjun and Sultani oil shales using different types of solvents by continuous contact mixing. The oil yield obtained in the Fischer Assay of the samples was respectively 9.38 and 12.45%. The weight loss of the samples in the extraction without thermal decomposition increased from 2 to 6% in the row of the solvents: diesel, butanol, kerosene, propanol, ethanol, benzene, methanol, ethyl acetate, cyclohexane, solvent mixture (toluene, methanol, and chloroform), toluene, xylene and carbon disulfide, and was 9.5% with high polarity dimethyl sulfoxide. It can be supposed that the weight loss exceeding the oil yield in the Fischer Assay could partly be the result of dissolution of the mineral part of the shale in the polar solvents. The solubility in cyclohexane was found to increase with an increase in mixing time (1–6 h), temperature (25–50 °C) and solvent/shale ratio (2/1, 3/1, 5/1 g/g), and to decrease with an increase in grain size (100–1600 μm). The yield of bitumen depended on the solvent type and deposit and decreased from 3 to 0.5% in the row: chloroform, toluene, hexane and ethanol for the Sultani deposit whereas for the El-Lajjun deposit hexane was the weakest solvent. It was proved in [6] that distribution of aliphatic and aromatic hydrocarbons, hetero-compounds and asphaltenes was affected by polarity of solvents. Guo [8] explained that the solubility in different solvents depended upon their ability to disrupt the non-covalent bond interactions between bitumen and kerogen. The oil yield obtained by continuous mixing at 50 °C was 0.3–1.2% lower than that obtained using a Soxhlet apparatus at a boiling temperature of solvents.

Matouq et al. [9] and Matouq and Alayed [10] reported that the efficiency of various solvents can be substantially increased assisted by low frequency ultrasound or gamma-ray radiation. It was shown that the fraction extracted from El-Lajjun oil shale was 90% of the total extract obtained already after 10 minutes of sonication. Using tetrahydrofurane (THF) as the solvent, the extraction time was decreased four-fold while the fraction extracted was increased thrice at room temperature by using ultrasounds under 20 kHz frequency. After gamma radiation exposure for 72 h at room temperature without any mixing source, the yield of the extract from the Fischer Assay increased from 13 to 71% in the row: water, benzene, acetone, acetone + water and acetone + benzene [10].

1.2. Retorting

Usually solid fuels are liquefied by semicoking in the course of which the thermal decomposition of OM under inert atmosphere in an open retort by heating up the sample to a nominal temperature (450–500 °C), keeping the temperature during a prescribed period, and separation of the liquids (oil and water) and non-condensable gaseous products are conducted. The effect of OM content on the oil yield of Jordanian oil shale from the main five deposits described in [11] is depicted in Figure 1.

The linearity of the dotted trendline ***A*** with a slope of 0.377(±0.013) reveals that the oil yield in the Fischer Assay increases nearly proportionally (correlation coefficient $R^2 = 0.88$) with increasing OM content. Actually, the curve ***B*** depicting the oil yield on the basis of OM shows a practically constant value, 37.9(±0.5)%, being close to the slope of ***A*,** when OM content is 25% or higher only, and decreases for poorer samples with decreasing OM content like for any other oil shale [12]. The decrease can be explained by increasing surface of the mineral matter adsorbing the oil formed and accelerating catalytically the secondary decomposition of the adsorbed oil layer into coke and gas.

Jaber et al. [13] showed, using a fixed bed reactor at a nominal temperature of 500 °C, that the oil yield from El-Lajjun and Sultani oil shales increased from 10 to 15% with an increase in particle size from 0.85

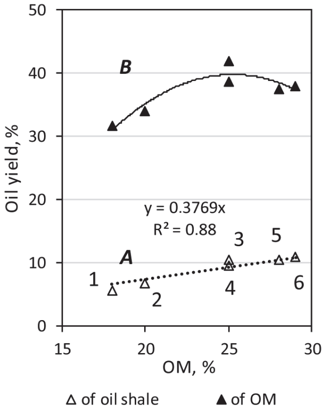

Fig. 1. Effect of organic matter (OM) content on the oil yield on the basis of oil shales (***A***) [11] and of their OM (***B***) in the Fischer Assay from the deposits: 1 – Jure Ed-Darawish, 2 – Wadi Maghar, 3 – El-Thamad, 4 – Sultani, 5 – El-Lajjun, 6 – Attarat Um Ghudran.

up to 5.6 mm whereas the gas yield of the samples decreased respectively from 6.1 to 5.6% and from 5.6 to 5.0%. The phenomenon was explained by the fact that the small particles had a greater surface area per mass unit, favoring the adsorption of oil and its secondary cracking. The yield of water (hygroscopic and pyrogenetic) was invariably about 10%.

Nazzal [14] pyrolized El-Lajjun oil shale in a fixed bed reactor at heating rates of 2–30 °C/min under the atmosphere of N_2 and the mixture of N_2/water steam as sweeping gases. The maximum yields of different products were observed at different flow rates. So, the maximum yield of oil was 8.9% under N_2 and 10.3% under N_2/water steam at the heating rate of 10 °C/min. The corresponding gas yield was 9.64 and 9.9% at 30 °C/min, and of water, 5.7 and 6.6% at 15 °C/min. Thereby, it was not explained how the yield of water was found in the presence of N_2/water steam.

Tucker et al. [15] compared the retorting and supercritical extraction of El-Lajjun oil shale. Retorting in the Fischer Assay (heating rate 10 °C/min, residence time 50 min at a nominal temperature of 500 °C) gave the oil yield of 11.7 L/kg under N_2 and 12.0 L/kg under CO_2. Extraction of the shale in supercritical CO_2 and water gave respectively 8.8 and 17.7 L/kg of oil. A bit more mid-distillate and narrower molecular weight compounds were found using CO_2. The most promising conditions resulting in 61% of oil from OM obtained using supercritical water will be described below in Part 1.4 concerning solvent extraction.

1.3. TGA

The thermogravimetric analysis (TGA) represents an alternative to the retorting process in an open device. In this procedure some milligrams of a sample are decomposed under an inert atmosphere monitoring changes in temperature and weight loss with time. So, the rate of changes in the transformation degree of oil shale expressing evolution of total volatiles (including oil, water and gas) can be tracked, and the corresponding apparent kinetic constants can be estimated.

The total weight loss of El-Lajjun and Sultani oil shales in TGA within the temperature range of 300–500 °C has been 22 and 18%, respectively [13].

Al-Harahsheh et al. [16] reported that the total weight loss of El-Lajjun oil shale between 200 and 550 °C was about 20%, and about 70% of its OM isolated by sequential HCl and HCl/HF digestions. It was concluded that the mineral matter enhanced the catalytic cracking of the oil shale.

TGA in the temperature range of 120–550 °C of Jordanian oil shale from five deposits gave the weight loss as follows, %: Sultani 23.14, El-Lajjun 19.05, Ma’an 17.72, Yarmouk 16.54, and Attarat 13.57 [4, 17]. Subtraction from the total volatiles of gas yields being between 5 and 8% in the Fischer retort would give the oil yields close to the values obtained in the Fischer Assay discussed in Part 1.2.

Increase in the heating rate from 3 to 40 °C/min increased the weight loss in TGA of two another oil shale samples from the Attarat deposit from 23.1 to 24.93% and from 20.61 to 21.11% [18]. So, the pyrolysis behavior of Attarat shale was analogous to that of the more surveyed El-Lajjun and Sultani oil shales described above.

The possibility for an exact monitoring of the transformation rate and temperature in TGA has given a favorable technique to investigate effects of various parameters on the pyrolysis kinetics. The isothermal and non-isothermal integral and differential methods have been developed, approximating the complicated thermal decomposition mostly to a single, but also to parallel or consecutive apparent reactions. Mainly, the simple first order kinetic reactions have been assumed. The values of the apparent activation energy have varied between 7 and 112 kJ/mol [13–19], depending on the degree of transformation, temperature interval, heating rate, particle size and OM content.

1.4. Solvent extraction under sub- and supercritical conditions

As described above, the yield of oil obtained from Jordanian oil shale in laboratory conventional open retorts is below 40–50% of OM, being 10–25 % lower than the corresponding value of Estonian Kukersite OM, 60–66%. So, modification of the thermal liquefaction process has been of interest for a more complete utilization of Jordanian oil shale OM. With the aim to increase the oil yield, liquefaction of Jordanian oil shale has been investigated in the presence of several solvents under sub- and supercritical conditions.

Tucker et al. [15] conducted a 2-hour supercritical (SC) extraction of a 20 g El-Lajjun oil shale sample at 375 °C and 14.3 MPa in SC-CO_2 and at 439 °C and 24.9 MPa in SC-H_2O, giving in both the experiments the same solvent density, 0.119 g/cm^3. It is noteworthy that the reaction temperature in the SC solvents applied was significantly lower than in the Fischer Assay (500 °C). The oil yield obtained in SC-H_2O was higher than that obtained in N_2 retorting and amounted to 177 cm^3/kg of the shale or 61% of OM. In SC-CO_2 the oil yield was only 88 cm^3/kg or 30% of OM. It can be supposed that the 2-hour duration used was insufficient for the thermal decomposition at 375 °C. Unfortunately, the scheme and solvents applied for oil separation from the solid residue and water were not described. So, we cannot be sure that part of water remained in the liquid product in the experiments with SC-H_2O.

Fei et al. [20] treated El-Lajjun oil shale (24.2% OM) in 27 ml autoclaves for 1 and 5 hours at temperatures of 300, 355 and 425 °C without water, and in the medium of water to oil shale ratios of 1:1 and 1:3 in the presence of N_2, CO and H_2 by adding various catalysts. The conversion degree of OM into hydrocarbon gas and products soluble in THF (oil + water + asphaltenes + asphaltol) was 86% at 355 °C (5 h), and close to 100% at 425 °C (1 h). The summary yield of oil and water was respectively 9–12 and 17–18% on the basis of oil shale, corresponding to 37–50 and 70–74% of OM. Thereby it is possible that the sum of oil plus water of OM is overestimated because part of pyrogenetic water could be originated from the crystal water of minerals. The presence of N_2, CO and even H_2 (3 MPa, at room temperature) gave similar conversions of the shale at the same temperature and duration. The yields without water and in the presence of 1 g/g water were close. Increasing the water to oil shale ratio to 3 g/g generally decreased the oil yield and increased the yields of gaseous hydrocarbons and CO_2. Addition of $NaAlO_2$, $Cu(OAc)_2$, $Fe(OAc)_2$, SnO_2 and Ni(OAc) having proved themselves as catalysts in coal conversion gave no significant increase in the yields of useful products from Jordanian oil shale.

Allawzi et al. [21] found that a relatively high oil yield can be obtained in a fixed bed autoclave using CO_2 (12.5 ml/min) supercritical extraction with co-solvents like acetone or hexane. The highest oil yield, 10% of El-Lajjun oil shale, actually not surpassing that in retorting (Fig. 1), was obtained at 450 °C and 22.5 MPa with hexane as a co-solvent.

The effect of temperature between 355 and 425 °C on the pyrolysis during 1 h of Jordanian oil shale from five deposits in autoclaves without solvents under N_2 and H_2 gas (3 MPa at room temperature) was reported in the paper of Amer et al. [4]. The yields of extraction fractions estimated on the basis of OM varied in wide ranges depending on the conditions and decreasing in the row as follows: CH_2Cl_2-solubles + H_2O + gas (39.8–93.6%) including oil + H_2O (31.6–89.7%) and insoluble in hexane asphaltenes (1.7–29.9%), and soluble in THF asphaltols (0.6–5.7%), gaseous hydrocarbons + H_2S (0.0–9.1%), and CO_2 (0.0–3.5%). As an example, the effect of temperature on the yield of CH_2Cl_2 soluble oil + H_2O is depicted in Figure 2 using the data published in Table 4 in [4].

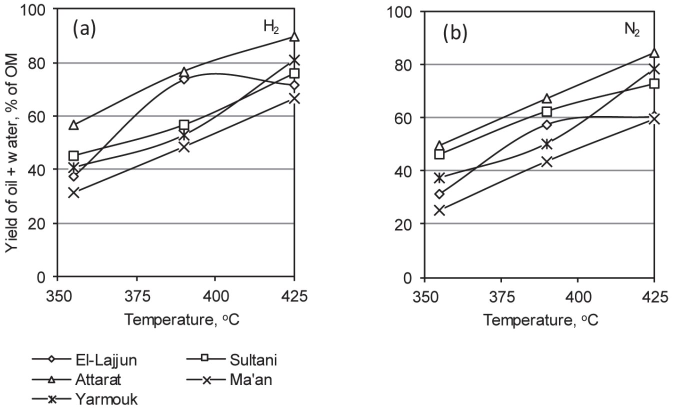

Fig. 2. Effect of temperature on the yield of oil + water in the 1-h pyrolysis in autoclaves in the presence of hydrogen (a) and nitrogen (b). The data are taken from [4].

Figure 2 shows that the yield of oil and water fraction extracted after the 1-h pyrolysis increases proportionally with increasing temperature. Apparently, this effect is amplified with the insufficient reaction time applied. The most reactive is Attarat and the least reactive Ma'an oil shale OM. As an exception, the oil shale from the El-Lajjun deposit attains a steady state already at 390 °C. It can be supposed that the secondary cracking characteristic of the oil formed particularly from El-Lajjun oil shale prevents further increase in oil yield. The atmosphere of H_2 increases the yield of oil + water by 2–16%, in comparison with N_2, however, the curves depicting pyrolysis are similar under both the gases. The yields of oil + water obtained in the work [4] extracting the pyrolysates produced in autoclaves without solvents are close to the oil yields obtained in water medium and without water published earlier [20]. Noteworthy is that the data depicted in Figure 2 are about twice higher than the oil yields presented in Figure 1 where the yield of water was not included.

According to Haddadin [22], the samples of El-Lajjun oil shale undergo softening and molecular rearrangement up to 330 °C. Thereafter, heating up to 500 °C results in evolution of oil and gas corresponding to the weight loss by 23% in the untreated shale and by 42% in the decarbonated shale. It was reported that up to 90% of OM was transformed into decomposition products by dissolution conversion when 2 g/g of tetralin was added as a hydrogen donor solvent at a temperature of 315°C.

1. 5. Flash pyrolysis and pyrolysis in a solid heat carrier unit

Fluidized bed pyrolysis appears to be a promising procedure since a rapid evolution of volatiles due to a fast heating rate can avoid the secondary cracking of the valuable oil formed. Nazzal and William [23] treated the oil shale samples from the Sultani deposit in a semi-continuous fluidized bed reactor under N_2 and N_2/water steam atmosphere in the temperature range of 400–540 °C. The fluidized medium was quartz sand. The residence time of the vapor phase was 30 s and of the shale 45 min. The maximum oil yield obtained at 540 °C was 8.7% of the initial shale under nitrogen, and 9.8% under nitrogen/steam atmosphere. The results are close to the oil yield from the shale under standard conditions in the Fischer Assay, 9.2% (Fig. 1).

Yorudas and Gavrilov [24] processed 15 kg/h of oil shale from the El-Lajjun deposit, containing 21.26% of conditional OM $[100 - A^d - (CO_2)_{mineral}{}^d]$, in a solid heat carrier unit using the Galoter method. The oil yield from the sample was 10.7% (50% of OM), being 81% of the oil yield found in the Fischer Assay.

1.6. Comparison of the thermal liquefaction of Jordanian and Estonian Kukersite oil shales

The yield of pyrolytic oil from an oil shale depends on its OM content and composition of both the organic and mineral parts [12].

The investigations described above have revealed that independently of the liquefaction procedure applied, typically, about 10–13% of oil can be extracted from the initial Jordanian oil shale, corresponding to 40–60% on the basis of OM. Whenever higher yields were reported, like in TGA and solvent extraction, water and/or gases were included.

It was shown in our previous works [12, 25] that the oil yield at a low-temperature pyrolysis of Estonian Kukersite using open retorts at 350–370 °C was also up to 40% of OM. But when the high-molecular thermobitumen (TB) was extracted from the cubic residue after retorting or from the total pyrolysate obtained in autoclaves, the total yield of the liquid product, stating the sum of thermobitumen and oil (TBO), exceeded 80% of OM.

Formation of the thermobitumen intermediate is a common feature in the thermal decomposition of highly aliphatic organic matter of Baltic, Colorado, Green River and Australian oil shales whereas more aromatic oil shales such as Turkish, Kentucky New Albany, and Mississippi are prone to quick condensation of the aromatic rings and formation of insoluble in benzene coke [3]. According to Fei et al. [20], a solid state ^{13}C NMR spectrum of the acid-washed shale showed the atomic ratio of C_{ar} to C_{aliph} of 0.21:0.79, indicating a high aliphatic content with an H/C atomic ratio of 1.44 for the total organic material. So, the formation of TB may be characteristic of Jordanian oil shales.

The goal of this study was to elucidate conditions for obtaining a maximum yield of liquid product, TBO, from Jordanian Attarat oil shale. For this purpose, a systematic experimental study of the effects of temperature and time on the yield of pyrolysis products from Jordanian oil shale in autoclaves without any solvent and in the presence of benzene, water and tetralin was conducted.

2. Experimental

2.1. Characterization of the initial sample

The oil shale sample studied was taken from Jordanian Attarat deposit and delivered by Indrek Aarna, Head of R&D Department, Eesti Energia AS.

The conditional OM (weight loss in incineration at 550 °C) of the sample was 21.44%, ash content (weight loss in incineration at 825 °C) 61.9%, carbon dioxide 20.4% and moisture 0.68%.

The elemental analysis gave: C 20.6%, $C_{organic}$ 15.0%, H 2.1%, N 0.3%, S_{total} 3.11%, $S_{organic}$ 2.67%, and $S_{pyritic}$ 0.28% of the dry shale.

The yields of the pyrolysis products in the Fischer Assay on dry shale were as follows: oil 10.4%, semicoke 84.6%, pyrogenetic water 0.8% and gas + losses 4.2% of the dry shale.

2.2. Liquefaction procedure

Pyrolysis of the oil shale was carried out in glass test tubes placed in 58 cm^3 autoclaves. The tubes facilitating to wash out the pyrolysis products were omitted only in the test series with water medium corroding glass at the temperatures applied.

In each experiment 10 g of the air dried shale powdered to 0.04–0.1 cm or 8, 6 or 5 grams of the shale and 8, 12 or 15 grams of the solvent (to achieve a ratio of the solvents to shale of 1, 2 and 3 g/g) were used. The samples were placed into a cold muffle oven. The constant nominal temperature varying from 320 to 420 °C was attained for the period of 60 minutes. The pyrolysis duration was measured from the time when the muffle oven reached the nominal temperature prescribed.

Efficiency of the liquefaction process was evaluated by the yield of pyrolysis products: gas, subsequent extracts with benzene (TBO) and THF (asphaltols), and solid residue. TBO, representing the total benzene solubles (bitumen, thermobitumen and oil), was divided into hexane soluble maltenes and hexane insoluble asphaltenes. The asphaltols were less soluble and higher molecular hetero-compounds than TB.

2.3. Analysis

The mass of gas formed was determined by the weight loss after discharging the volatiles from the open autoclave at room temperature. The pyrolysis liquid products consisting of TBO and asphaltol were extracted exhaustively with boiling benzene, and subsequently with THF in a Soxhlet extractor. The mass of the solvents insoluble solid residue (SR) was weighted after drying at 105–110 °C during 1–2 h. The solvents applied were removed from the TBO and asphaltol solutions in a vacuum rotation evaporator at 60–70 °C. The distillation residues of the benzene and THF extracts obtained in the rotation evaporator were left in the open flask and weighted after 24 h for evolution of the solvent traces remained. Like in the authors' earlier works, removing traces of benzene from TBO has been a problematic procedure. The quantity of TBO can be underestimated due to evaporation of low-boiling destruction products or overestimated when part of the solvent, having a higher boiling temperature than the lighter fractions or being incorporated into destruction products, is not removed. So, the mass of TBO was preferred to determine by subtracting the mass of gas, water, THF extract and solid residue from the initial mass of the shale.

TBO was divided into two fractions: soluble in hexane maltenes (oil) and insoluble in hexane asphaltenes, the latter being undesirable as a fraction more prone to coke formation. For this purpose, 10 g/g of hexane was added to an aliquot of the incompletely dried benzene extract. After 24 h the precipitate of asphaltenes was filtrated, dried and weighted.

The compound groups of TBO were estimated by preparative thin-layer chromatography separating 500 mg samples on 24 × 24 cm plates coated with a 2 mm silica gel layer (60 mm, Fluka), and using *n*-hexane as the eluent. Five groups of compounds were separated and extracted from silica gel with ethyl ether: aliphatic hydrocarbons (AlHC), monocyclic hydrocarbons (MCHC), polycyclic hydrocarbons and some sulfur compounds (PCHC), neutral hetero-atomic (Nhet) and polar hetero-atomic (Phet) compounds.

3. Experimental results and discussion

3.1. Pyrolysis without solvents in autoclaves

Soxhlet extraction of bitumen from the initial sample without thermal decomposition yielded, % of the dry shale (% of OM): benzene extract 1.09 (5.14), THF extract 0.53 (2.49), and solid residue 98.38 (92.37).

Yields of the pyrolysis products from the dry oil shale obtained in the test series conducted at various temperatures and isothermal durations are presented in Table 1.

The results in Table 1 show that at any temperature series the gas yield increases with time whereas the yield of TBO has a maximum and that of SR a minimum shifting with increasing temperature to shorter durations. The maximum yield of TBO achieved is only 12%, and the maximum transformation degree of the oil shale is 17–18% of the dry shale. The yields are close to those obtained at semicoking of Jordanian oil shales in the Fischer Assay [6, 7, 11, 13, 14] and depicted in Figure 1.

As the products given in Table 1 are generated in the thermal decomposition of OM, the better characterization of the process can be obtained when the yields are depicted on the basis of OM. Effect of pyrolysis duration at various nominal temperatures on the yields of the main decomposition products – gas, TBO, asphaltols, and solid residue of OM, are presented in Figure 3.

The data in Figure 3 prove that increasing the temperature and duration results in a steady increase in gas yield. The yield of TBO has a maximum amounting 55–60% of OM at nominal temperatures of 320, 360, 380, 400 and 420 °C respectively after 10, 1.5, 1.0, 0.75 and 0.25 h. The maximum yield of TBO surpasses the oil yield of Attarat oil shale estimated in the Fischer Assay (Fig. 1) by 17–22% of OM. The optimum duration for obtaining a minimum yield of SR, about 20%, agrees with the duration for attaining a maximum TBO yield. It has been firstly revealed that the time dependence of the yield of asphaltols, the most condensed extract defined as the product being insoluble in benzene but soluble in THF, is complicated and has two maximums. It can be supposed that during the first maximum the kerogen molecules decompose into intermediate products being precursors of TBO, and the second maximum reflects the secondary condensation of TBO into precursors of coke.

Table 1. Effect of nominal temperature and isothermal duration on the yield of pyrolysis products from Attarat oil shale in autoclaves, % of oil shale

Temperature, °C	Time, min	Gas	Benzene extract (TBO)		THF extract (asphaltols)	Pyrogenetic water	Solid residue (SR)
			total	including asphaltenes			
320	0	0.00	0.55	0.28	0.77	0.19	98.49
	60	0.95	6.07	3.50	0.42	0.54	92.03
	90	1.25	7.20	3.81	1.32	0.57	89.66
	120	1.63	8.67	3.91	1.87	0.30	87.53
	150	1.81	9.04	3.98	2.58	0.08	86.48
	240	2.06	10.21	4.69	1.85	0.21	85.67
	300	2.32	11.26	5.35	1.69	0.30	84.44
	360	2.34	11.73	5.72	1.61	0.38	83.95
	420	2.47	11.70	5.87	1.70	0.38	83.75
	480	2.50	11.62	4.21	1.89	0.36	83.64
	600	2.52	12.33	5.40	1.96	0.35	82.85
360	0	0.00	0.80	0.40	0.73	0.22	98.25
	30	1.50	7.69	4.02	2.65	0.35	87.82
	45	1.96	10.17	4.40	2.50	0.46	84.91
	60	2.27	12.53	5.75	0.90	0.62	83.69
	90	2.69	12.1818	5.58	0.77	0.43	83.93
	120	2.86	11.54	3.66	1.81	0.16	83.63
	150	3.05	10.71	3.52	2.49	0.22	83.53
	180	3.78	10.35	3.14	2.14	0.30	83.89
	240	3.55	10.00	2.82	1.75	0.52	84.18
	300	3.82	9.73	2.31	1.14	0.60	84.71
	360	3.92	8.75	1.78	1.29	0.63	85.42
380	0	0.03	1.03	0.68	1.02	0.20	97.72
	15	0.95	6.06	2.71	2.18	0.28	90.54
	30	1.56	11.20	4.60	2.86	0.42	83.97
	45	1.87	12.47	4.49	1.84	0.64	83.18
	60	2.65	12.35	5.79	1.51	0.63	82.86
	90	3.33	10.20	2.48	1.39	0.32	84.77
	120	3.63	10.29	1.87	1.28	0.27	84.54
	240	4.60	8.49	1.10	1.19	0.37	85.35
400	0	0.00	1.67	0.94	0.50	0.32	97.51
	15	1.74	8.39	4.60	1.65	0.42	87.80
	20	1.96	7.15	2.90	2.80	0.55	87.53
	30	2.52	10.44	5.47	2.86	0.81	83.36
	45	3.12	11.52	3.80	0.89	0.59	83.88
	60	3.81	10.40	2.17	0.62	0.43	84.75
	90	4.39	9.13	1.04	0.64	0.27	85.58
	120	4.78	8.75	0.83	0.53	0.19	85.75
	180	5.49	7.87	0.60	0.29	0.15	86.20
	240	5.65	6.98	0.44	0.62	0.22	86.52
420	0	0.00	2.14	1.06	0.59	0.44	96.83
	5	0.59	1.45	0.99	1.58	0.51	95.87
	15	2.18	12.61	6.29	2.10	0.96	82.14
	20	2.46	10.85	3.32	1.57	0.73	84.39
	30	3.35	10.48	2.05	0.99	0.30	84.88
	60	4.72	8.46	0.70	0.09	0.15	86.58
	120	6.33	6.30	0.35	0.37	0.21	86.78

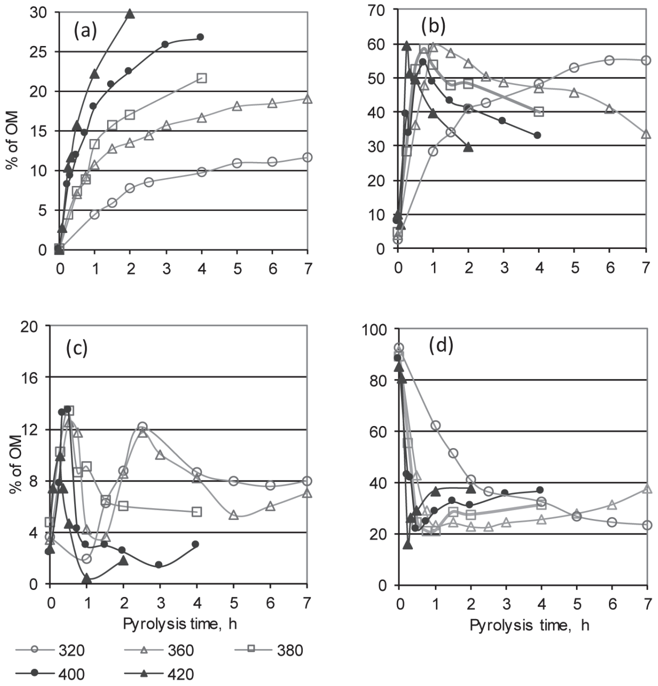

Fig. 3. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of gas (a), TBO (b), asphaltols (c) and solid residue (d).

The maximum total yield of benzene and THF extracts (the sum of TBO and asphaltol) reaches about 65% of OM (Figs. 3 and 4). Nevertheless, the yield of liquid products is 15–20% lower than that obtained from Estonian Kukersite [25].

The effect of pyrolysis duration and temperature on the formation of pyrolytic water has been studied for the first time. The experimental results depicted in Figure 4a evidence that in autoclaves the yield of pyrolytic water passes two maximums like that of asphaltols (Fig. 3c). The first maximum appears at the duration corresponding to the exhaustion of the initial kerogen and attains 2–4.5% of OM. Thereafter, the yield of pyrogenetic water decreases to a minimum, 0.5–1.5% of OM, in the stage of condensation of TBO into asphaltols. After that, a second increase in the yield of water could be explained by the subsequent coke formation from the intermediate product, asphaltol.

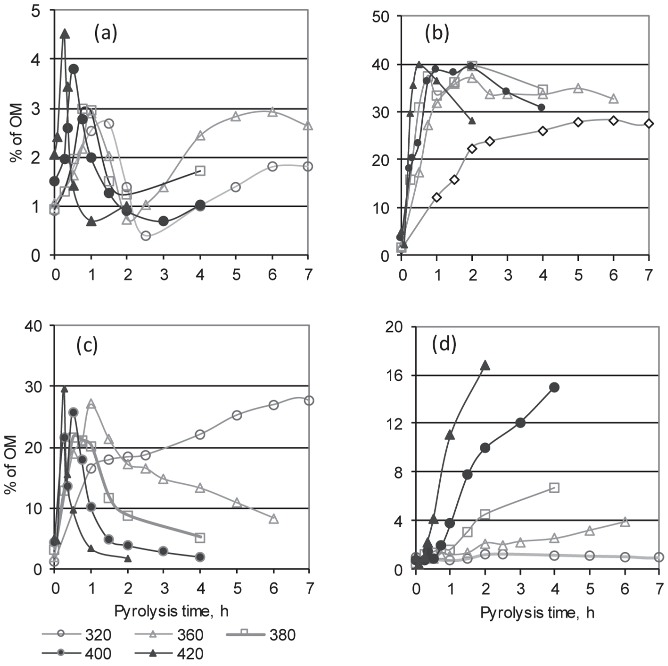

Fig. 4. Effect of nominal temperature and isothermal duration in autoclavic pyrolysis on the yield of pyrolytic water (a), asphaltenes (b) and maltenes (c), and on the ratio of maltenes/asphaltenes (d).

3.2. Pyrolysis in solvent medium

With the aim to increase the yield of liquid products and reduce the coke formation, the liquefaction was tested in the medium of 1–3 g/g of benzene, water or tetralin. The procedure was conducted during 1 h, being the optimal duration at a temperature of 380 °C. The yields of pyrolysis products on the basis of the initial shale are presented in Table 2. The yields of the most characteristic products, TBO and SR, on OM basis, are depicted in Figure 5. It was impossible to estimate directly the yields of gas and pyrogenetic water dissolved partly in the solvents. So, the data were taken from the corresponding results of experiments conducted without any solvent and presented in Table 1.

The data in Table 2 evidence that the addition of solvents increases the yield of TBO of the shale by 1–3% only. The influence of the benzene medium is the smallest. Tetralin, being supposed to act as a potential hydrogen donor, is not much more efficient at 380 °C tested. In this work, the summary yield of liquid products (TBO, asphaltols and water) in tetralin

Table 2. Effect of solvent/shale ratio on the yield of pyrolysis products at various temperatures and durations, % of oil shale

T, °C	Time, min	Solvent/OS, g/g	Gas[1]	Benzene extract (TBO)		THF extract (asphaltols)	Pyrogenetic water[1]	SR
				total	including asphaltenes			
In benzene								
360	180	0	3.32	10.35	3.78	2.14	0.30	83.88
		1	3.32	11.61	3.61	0.51	0.30	84.26
		2	3.32	12.03	5.11	0.55	0.30	83.79
		3	3.32	12.28	3.27	0.62	0.30	83.48
380	60	0	2.65	12.35	5.79	1.51	0.63	82.86
		1	2.65	12.92	2.73	0.35	0.63	83.51
		2	2.65	12.91	3.05	0.28	0.63	83.58
		3	2.65	12.61	3.70	0.94	0.63	83.22
	120	0	3.63	10.29	1.87	1.28	0.27	84.53
		2	3.63	11.73	1.27	0.75	0.27	83.62
In water								
	60	0	2.65	12.35	5.79	1.51	0.63	82.86
		1	2.65	12.50	n. d.	0.46	0.63	83.77
		2	2.65	11.97	n. d.	0.08	0.63	84.68
		3	2.65	13.94	5.28	0.49	0.63	82.30
	120	0	3.63	10.29	1.87	1.83	0.27	82.95
		2	3.63	10.91	2.75	0.94	0.27	84.47
In tetralin								
	60	0	2.65	12.35	5.79	1.51	0.63	82.86
		1	2.65	13.57	n. d.	1.49	0.63	81.67
		2	2.65	14.21	n. d.	0.92	0.63	81.59
		3	2.65	11.57	n. d.	2.91	0.63	82.24

[1] Taken from Table 1; n. d. – not determined.

is 74% of Attarat oil shale OM like in the work of Fei et al. [20] on EL-Lajjun oil shale OM. The yield of TBO remains roughly 60% of OM in various solvents, being characteristic of the maximum yield attained in autoclaves at various nominal temperatures without any solvent (Fig. 3).

The group compositions of TBO extracted from the pyrolysates produced in an optimum combination of temperature and duration, 380 °C and 1 h, without any solvent, and in benzene and water are presented in Table 3, and on the basis of total OM in Figure 6. The analogous data in tetralin are absent because it was impossible to separate the solvent (b. p. 208 °C) from the pyrolysis oil without losses of the lighter fractions. For comparison, the yields of compound groups of Estonian Kukersite oil shale under the same conditions taken from [26] are depicted in the same figure.

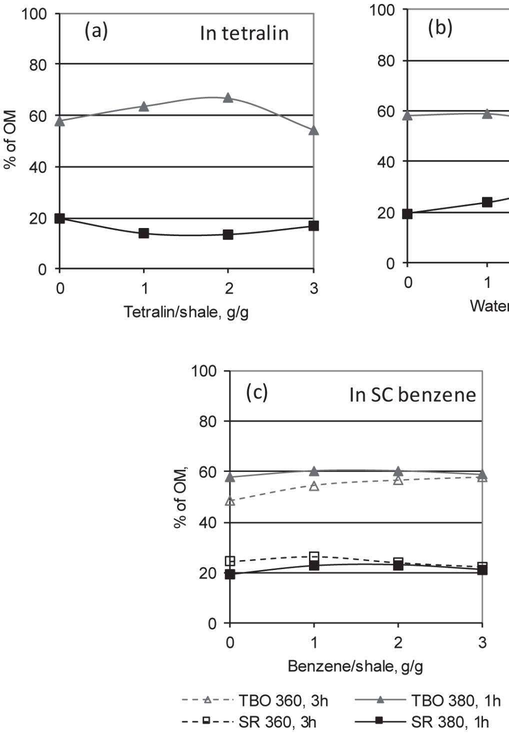

Fig. 5. Effect of solvent/shale ratio on the yield of TBO and solid residue in tetralin (a), SC water (b) and SC benzene (c) on OM basis (SC – supercritical).

Table 3. Group composition of TBO (1 h, 380 °C), %

Compound group	Symbol	Solvent			
		–	Benzene	Water	Tetralin
Aliphatic hydrocarbons	AlHC	8.2	7.5	6.2	8.2
Monocyclic hydrocarbons	MCHC	8.4	5.4	3.4	8.4
Polycyclic hydrocarbons	PCHC	32.9	39	32.8	32.9
Neutral hetero-atomic compounds	Nhet	13.2	10.8	12.1	13.2
Polar hetero-atomic compounds	Phet	37.3	37.3	45.5	37.3

According to Table 3 and Figure 6, the main compound groups in the benzene extract obtained in the pyrolysis of Jordanian oil shale in benzene, water or without any solvent at 380 ^{o}C are polycyclic hetero-atomic compounds and polycyclic hydrocarbons surpassing totally 40–50% of OM. The yields of desired aliphatic and monocyclic hydrocarbons are below 5%. The

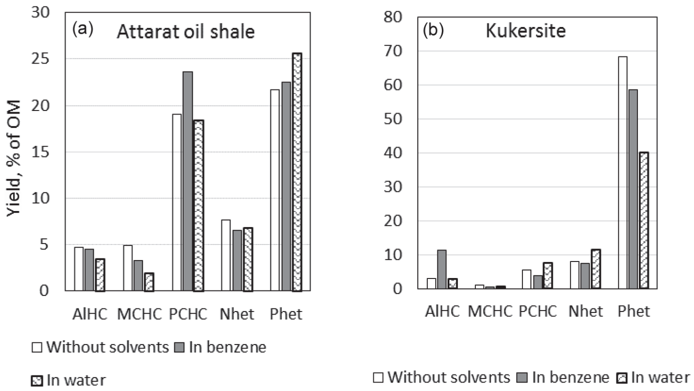

Fig. 6. Yield of compound groups of TBO from pyrolysis of Attarat oil shale (a) and Estonian Kukersite (b).

highest yield of polar hetero-atomic compounds in the water medium suggests that the yield of TBO could be increased due to the incorporation of some water molecules into the liquid product. Differently, in the Kukersite origin benzene extract polar hetero-atomic compounds (mainly oxygen compounds) prevail whereas the yields of the other groups are lower than those from the pyrolysis of Jordanian oil shale.

3.3. Kinetics of OM decomposition

The results of this work agree with published ones establishing that the yields of liquid products on the basis of Attarat oil shale OM in open retorts, in autoclaves without solvents, and in the medium of various solvents are 15–20% lower than those of Estonian Kukersite oil shale under the same conditions.

The time-dependence of the yields depicted in Figure 3 shows that the exhaustion of the initial OM of Jordanian oil shale takes place approximately twice faster than that of Estonian oil shale [25].

In this work, for approximate characterization and comparison purposes, the kinetics of the complicated pyrolysis process consisting of several parallel and consecutive reactions, the time-dependence of changes in the yield of solid residue (Fig. 3d) reflecting the total conversion of kerogen into gas, TBO, asphaltols, pyrolytic water and coke, and the total subsequent decomposition of TBO (Fig. 3b) into gas and coke were discussed only.

The rate factors for the isothermal decomposition of kerogen (k_1) and TBO (k_2) at any nominal temperature tested were estimated presuming a simple first order reaction as follows:

$$\ln(C_0/C) = -k_i(t-t_0), \tag{1}$$

where C_0 is the maximum yield of SR or TBO, t_0 is the corresponding duration, and C is the yield after duration t. The values of k_1 were calculated using only the linear part of the function described by Equation (1) where the coke formation was insignificant and SR represented unreacted kerogen only.

The apparent kinetic constants, frequency factor A and activation energy E, were found from the slope (b) and reciprocal (a) of the linear trendlines of the logarithmic form of the Arrhenius relationship:

$$\ln k = \ln A - E/(\mathrm{R}T). \tag{2}$$

The trendlines obtained introducing into Equation 2 the values of k estimated at various nominal temperatures using experimental data found for the overall decomposition of Attarat oil shale (Fig. 3d) and for the intermediate product TBO (Fig. 3b), and the corresponding total factors deduced from the rate factors of Estonian Kukersite published in [25] are depicted in Figure 7.

The regression coefficients, a and b, of the linear trendlines in Figure 7, and the corresponding apparent kinetic constants (A = exp(a), $E = -b\mathrm{R}$, R = 0.008314 kJ/mol K) are given in Table 4.

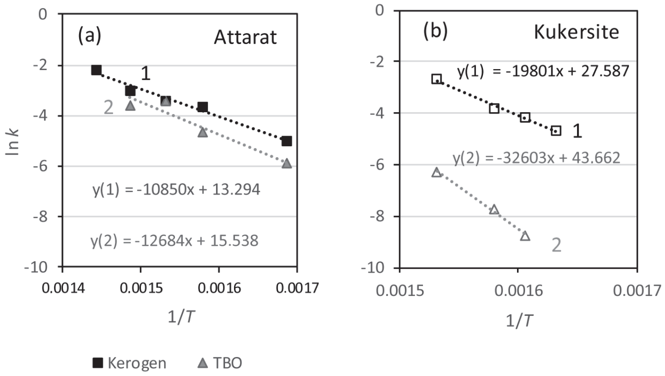

Fig. 7. Arrhenius plot of rate factors for the overall decomposition of initial kerogen and TBO of Attarat oil shale (a) and Estonian Kukersite (b).

Table 4. Apparent kinetic constants for decomposition of kerogen and TBO in autoclaves

Oil shale	Initial object	*a*	–*b*	*A*, 1/min	*E*, kJ/mol
Attarat	Kerogen	13.3	10850	5.91×10^5	90.2
Attarat	TBO	15.6	12684	5.61×10^6	106
Kukersite [25]	Kerogen	27.6	19801	9.69×10^{11}	165
Kukersite [25]	TBO	43.7	32603	9.15×10^{18}	271

The kinetic constants (E_1 and A_1) estimated for decomposition of Attarat oil shale kerogen in this work are comparable with those for decomposition of El-Lajjun oil shale found by Al-Ayed et al. [27], 98–120 kJ/mol and (5.7–7.0) × 10^7 1/min, under non-isothermal conditions (350–550 °C), and with the activation energy, 99.6 kJ/mol, found by Khraisha [28] under isothermal conditions. The kinetic constants E_2 and A_2 for the secondary decomposition of the intermediate product, TBO of Attarat oil shale, have been estimated in this work for the first time.

Noteworthy is that the analogous apparent activation energies, E_1 and E_2 for Estonian Kukersite kerogen and TBO, are respectively 1.8 and 2.6 times higher, and the logarithms of the frequency factors 2.1 and 2.8 times higher than those of Jordanian oil shale.

As a rule, an increase in E occurring with an increase in A follows a linear relationship called the compensation effect. The plot of kinetic constants in Table 4 depicted in Figure 8 indicate that the linear regression

$$\ln A = 0.169(\pm 0.008)E - 1.73(\pm 1.39) \tag{3}$$

is kept (R^2 = 0.9955) between the apparent kinetic constants of Attarat oil shale and Estonian Kukersite.

The co-effect of the kinetic constants having an opposite influence on rate factor is explained by the Arrhenius exponential equation:

$$k = A\exp(-E/RT). \tag{4}$$

The values of k at various temperatures calculated introducing the kinetic constants from Table 4 into Equation (4) are depicted in Figure 9.

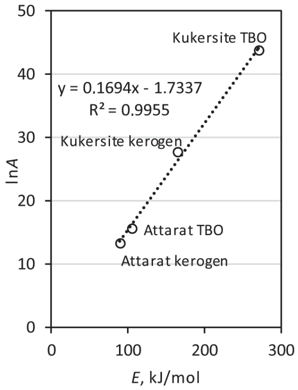

Fig. 8. Kinetic compensation effect (A, 1/min).

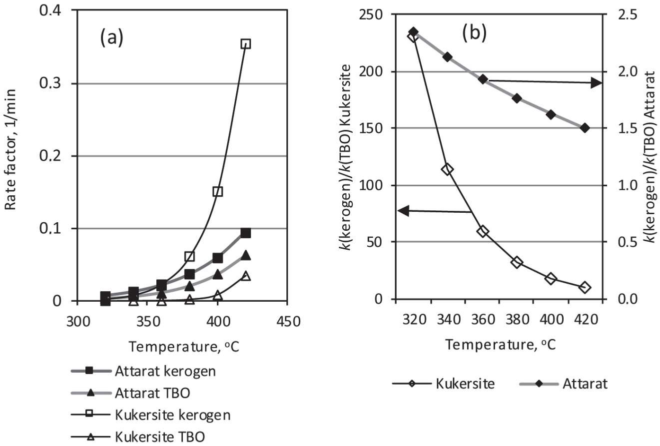

Fig. 9. Effect of temperature on the rate factors for the overall decomposition of Attarat and Estonian Kukersite oil shale kerogen and TBO (a) and on the ratio of the factors (b).

The curves in Figure 9a show that the effect of temperature on the rate factors is vital above 360 °C having a really great influence on the rate of Kukersite decomposition, being a controlling stage before the maximum yield of TBO has been attained. When the temperature increases from 320 to 425 °C, the ratio of the factors (Fig. 9b) of Estonian Kukersite decreases from 230 to 10, while that of Attarat oil shale from 2.4 to 1.5 only. So, the decomposition rate of TBO of Attarat oil shale is comparable with its formation rate from the initial kerogen at any temperature tested. As a result, the maximum yield of liquid products from Attarat oil shale remains essentially lower than that from Estonian Kukersite. The addition of any solvent tested or variation in pyrolysis conditions could not suppress the secondary decomposition of TBO in autoclaves.

Both the oil shales are highly aliphatic: $C_{ar}/(C_{al} + C_{ar})$ of Attarat oil shale is 0.21 [3], and the corresponding ratio of the peak areas in the ^{13}C MAS NMR spectrum of Estonian Kukersite 0.217 [29]. The H/C atomic ratio of Attarat oil shale is 1.69 and of Kukersite 1.50. So, the obviously quicker coke formation from Attarat oil shale than from Estonian Kukersite is surprising and the reasons need further investigation.

4. Conclusions

In the low-temperature (320–420 °C) pyrolysis of Jordanian Attarat oil shale in autoclaves during the exposure time of 0–10 h at nominal temperature, the gas yield and the ratio of maltenes to asphaltenes increase with time and temperature. In the optimum combination of temperature and duration the yield of benzene extract, consisting of bitumen, an intermediate product thermobitumen and oil (TBO), and its components, asphaltenes and maltenes, pass a maximum, and the yield of solid residue a minimum. The yields of pyrogenetic water and THF extract (asphaltols) have two maximums, the first one at the optimum duration of the TBO formation, and the other one in the stage of the secondary decomposition of TBO.

Increase in the nominal temperature from 320 to 420 °C decreases the optimum duration from 10 to 0.25 h.

The maximum yield of TBO extracted under optimum conditions amounts to 55–60% of organic matter (OM) and that of asphaltol to 10–12%. The maximum total yield of the liquid products extracted (TBO + asphaltols) is 65–70% of OM, being 20% lower than that from Estonian Kukersite oil shale, and exceeds the yield of oil from Attarat oil shale OM by 25–30% as estimated in the Fischer Assay.

The addition to Attarat oil shale of 1, 2 and 3 g/g of supercritical benzene or water, or tetralin, known as a hydrogen donor, has an unimportant effect on the yield of the pyrolysis products.

The main compound groups in TBO obtained from Attarat oil shale in pyrolysis without any solvent and in benzene or water are polycyclic hydrocarbons and polar hetero-atomic compounds, making both 30–45% of TBO. Differently, in TBO from Estonian Kukersite where the single polar hetero-atomic compound group prevails attaining 64–80% of TBO, the share of polycyclic hydrocarbons is in the range of 5–12% of TBO only.

The lower yield of TBO from Attarat oil shale than from Estonian Kukersite is explained by their decomposition kinetics. The apparent kinetic constants estimated in this work for the consequent decomposition of Attarat oil shale kerogen and the intermediate TBO in autoclaves are quite close. The activation energy for the overall primary decomposition of kerogen into gas, TBO, asphaltols and coke, E_1, is 90.2(±9.9) kJ/mol, and for the overall secondary transformation of TBO into gas, asphaltols and coke, E_2, 106(±25) kJ/mol. The corresponding frequency factors (A_1 and A_2) are 5.91×10^5 and 5.61×10^6 1/min. So, the yield of liquid products from Attarat oil shale is suppressed due to the intensive transformation of TBO into gas, asphaltols and coke.

The values of E_1 and E_2, and A_1 and A_2 for the decomposition of Estonian Kukersite kerogen and TBO are much higher, essentially differing from each other: 165 and 271 kJ/mol, and 9.69×10^{11} and 9.15×10^{18} 1/min, respectively. The co-effect of the values of E and A on the rate factors results from that the primary reaction of Kukersite kerogen decomposition prevails over the much slower secondary transformation of TBO.

The next challenges to solve would be characterization of the unstable and complicated TBO and asphaltols, and upgrading of the polycyclic and polar hetero-compounds into market-value liquid fuels.

Acknowledgements

This work was financed by the Estonian Research Council (project SF0140028s09), by EU Structural funds National R&D program "Energy technology"(AR12004), and by the Estonian Research Council Grant 9331.

REFERENCES

1. Hrayshat, E. S. Oil shale – an alternative energy source for Jordan. *Energ. Source. Part A,* 2008, **30**(20), 1915–1920.
2. Alali, J. Jordan oil shale, availability, distribution and investment opportunity. *Int. Oil Shale Conf. "Recent Trends in Oil Shale"*, Amman, Jordan, 7–9 Nov. 2006, paper no. rtos-A117.
3. Dyni, J. R. *Geology and Resources of Some World Oil-Shale Deposits*. Scientific Investigations Report 2005–5294. U.S. Department of the Interior, U.S. Geological Survey, 2005, 18–21. http://pubs.usgs.gov/sir/2005/5294/pdf/sir5294_508.pdf. Retrieved 2014-10-14.
4. Amer, M. W., Marshall, M., Fei, Y., Jackson, W. R., Gorbaty, M. L., Cassidy, P. J., Chaffee, A. L. A comparison of the structure and reactivity of five Jordanian oil shales from different locations. *Fuel*, 2014, **119**, 313–322.
5. Al-Otoom, A. Y. An investigation into beneficiation of Jordanian El-Lajjun oil shale by froth flotation. *Oil Shale,* 2008, **25**(2), 247–253.
6. Al-Harasheh, A. M. The effect of a solvent system on the yield and fractional composition of bitumen extracted from the El-lajjun and Sultani oil shale deposits. *Energ. Source. Part A,* 2011, **33**(7), 665–673.
7. Shawaqfeh, A. T., Al-Harasheh, A. Solvation of Jordanian oil shale using different organic solvents by continuous contact mixing. *Energ. Source.,* 2004, **26**(14), 1321–1330.
8. Guo, S. Solvent extraction of Jordanian oil shale kerogen. *Oil Shale,* 2000, **17**(3), 266–270.
9. Matouq, M., Koda, S., Maricela, T., Omar, A., Tagawa, T. Solvent extraction of bitumen from Jordan oil shale assisted by low frequency ultrasound. *J. Jap. Petr. Inst.,* 2009, **52**(5), 265–269.
10. Matouq, M., Alayed, O. Combined process of solvent extraction and gamma-ray radiation for the extraction of oil from oil shale. *Energ. Source. Part A,* 2007, **29**(16), 1471–1476.
11. Bsieso, M. S. Jordan's experience in oil shale studies employing different technologies. *Oil Shale,* 2003, **20**(3S), 360–370.
12. Johannes, I., Luik, H., Bojesen-Koefoed, J. A., Tiikma, L., Vink, N., Luik, L. Effect of organic matter content and type of mineral matter on the oil yield from oil shales. *Oil Shale,* 2012, **29**(3), 206–221.
13. Jaber, J. O., Probert, S. D., Williams, P. T. Evaluation of oil yield from Jordanian oil shales. *Energy,* 1999, **24**(9), 761–781.
14. Nazzal, J. M. Influence of heating rate on the pyrolysis of Jordan oil shale. *J. Anal. Appl. Pyrol.,* 2002, **62**(2), 225–238.

15. Tucker, J. D., Masri, B., Lee, S. A comparison of retorting and supercritical extraction techniques on El-Lajjun oil shale. *Energ. Source.,* 2000, **22**(5), 453–463.
16. Al-Harahsheh, M., Al-Ayed, O., Robinson, J., Kingman, S., Al-Harahsheh. A., Tarawneh, K., Saeid, A., Barranco, R. Effect of demineralization and heating rate on the pyrolysis kinetics of Jordanian oil shales. *Fuel Process. Technol.,* 2011, **92(**9), 1805–1811.
17. Amer, M. W., Marshall, M., Fei., Y., Jackson, W. R., Gorbaty, M. L., Cassidy, P. J., Chaffee, A. L. Comparison of the yields and structure of fuels derived from freshwater algae (torbanite) and marine algae (El-Lajjun oil shale). *Fuel,* 2013, **105**, 83–89.
18. Abu-Qudais, M., Jaber, J. O., Sawalha, S. Kinetics of pyrolysis of Attarat oil shale by thermogravimetry. *Oil Shale,* 2005, **22**(1), 51–63.
19. Jaber, J. O., Probert, S. D. Non-isothermal thermogravimetry and decomposition kinetics of two Jordanian oil shales under different processing conditions. *Fuel Process. Technol.,* 2000, **63**(1), 57–70.
20. Fei, Y., Marshall, M., Jackson, W. R., Gorbaty, M., L., Amer, M. W., Cassidy, P. J., Chaffee, A. L. Evaluation of several methods of extraction of oil from a Jordanian oil shale. *Fuel,* 2012, **92**(1), 281–287.
21. Allawzi, M., Al-Otoom, A., Alloboun, H., Ajlouni, A., Al Nseirat, F. CO_2 supercritical fluid extraction of Jordanian oil shale utilizing different co-solvents. *Fuel Process. Technol.,* 2001, **92**, 2016–2023.
22. Haddadin, R. A. A kinetic and mechanistic comparison for Jordan oil shale pyrolysis and dissolution. *Fuel Process. Technol.,* 1982, **6**(3), 235–243.
23. Nazzal, J. M., Williams, P. T. Influence of temperature and steam on the products from the flash pyrolysis of Jordan oil shale. *Int. J. Energ. Res.,* 2002, **26**(14), 1207–1219.
24. Yorudas, K.-A. A., Gavrilov, A. F. Study of the El-Lajjun (Jordan) oil shale and the products of its processing at the units with solid heat carrier. *Oil Shale,* 1999, **16**(4S), 399–409.
25. Johannes, I., Tiikma, L., Zaidentsal, A. Comparison of the thermobituminization kinetics of Baltic oil shale in open retorts and autoclaves. *Oil Shale,* 2010, **27**(1), 17–25.
26. Tiikma, L., Johannes, I., Luik, H., Zaidentsal, A., Vink, N. Thermal dissolution of Estonian oil shale. *J. Anal. Appl. Pyrol.,* 2009, **85**(1–2), 502–507.
27. Al-Ayed, O. S., Matouq, M., Anbar, Z., Khaleel, A. M., Abu-Nameh, E. Oil shale pyrolysis kinetics and variable activation energy principle. *Appl. Energ.*, 2010, **87**(4), 1269–1272.
28. Khraisha, Y. H. Kinetics of isothermal pyrolysis of Jordan oil shales. *Energ. Convers. Manage.,* 1998, **39**(3–4), 157–165.
29. Lille, Ü., Heinmaa, I., Pehk, T. Molecular model of Estonian kukersite kerogen evaluated by ^{13}C MAS NMR spectra. *Fuel*, 2003, **82**(7), 799–804.

Presented by A. Siirde
Received December 17, 2014

ARTICLE V

Johannes, I.; Tiikma, L.; Luik, H.; **Šarajeva, G**. Thermal Extraction of Oil from a Utah Green River (USA) Oil Shale in Autoclaves. International Journal of Engineering and Applied Sciences (EAAS), 2015, 6 (5), 23−35

May. 2015. Vol. 6. No. 5 ISSN2305-8269
International Journal of Engineering and Applied Sciences

www.eaas-journal.org

THERMAL EXTRACTION OF OIL FROM A UTAH GREEN RIVER (USA) OIL SHALE IN AUTOCLAVES

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ABSTRACT

Pyrolysis in autoclaves of a USA oil shale from Uintah basin of Green River formation in Utah was studied. The influence of temperature (360-425 °C) and exposure time (0-7 h) at nominal temperature on the yield of pyrolysis products was examined. The yields of solid residue, gas, pyrolytic water and the consecutive extracts with benzene (thermobitumen and oil, TBO) including asphaltenes and hexane solubles, and with tetrahydrofurane (asphaltol) were estimated, and the compound groups of TBO under optimum conditions were assessed. The highest yield of TBO, 55% of organic matter (OM), was obtained at temperature 400 °C and duration 1 h. By 30-40% lower yield of TBO of Utah oil shale OM than that of Estonian Kukersite is explained by close rate factors of the Utah oil shale OM decomposition (k_1) and the subsequent decomposition of TBO (k_2) whereas k_1 of Estonian Kukersite OM prevails k_2 scores of times.

Keywords: ***Oil Shale, Green River, Pyrolysis, Autoclaves, TBO, Kinetics.***

1. INTRODUCTION

The largest and most concentrated deposit of oil shale in the world – the Green River formation is located in the states of Colorado, Wyoming, and Utah in the western USA. The Green River oil shale deposits have been well characterized by more than a quarter million assays on core and outcrop samples, and contain approximately 1.2 trillion barrels of oil equivalent with oil yield 100 L/t or higher [1].

The existing industrial technologies for oil extraction from oil shales include aboveground pyrolysis in modifications of vertical gas generators, horizontal retorts, and the most advanced solid heat carrier units. The extensively studied technology is based on the retorting of solid fuels at temperature about 500 °C. The laboratory standard retorting is carried out in a device called Fischer Assay [2] as follows: a 100 gram oil shale sample crushed to <2.38 mm is heated in an aluminum retort under an inert atmosphere to 500 °C at a heating rate of 12 °C/min, and held at that temperature for 40 minutes. The decomposition of organic matter (OM) into gas and coke by parallel and following reactions to oil formation, decreases the oil yield in retorting. So, the oil yield, obtained using several alternatives of oil extraction can be greater or lower than the oil yield estimated in Fischer Assay. For example, the oil yield from Estonian type I oil shale

Kukersite was increased by 20% and overcame 80% of OM in low-temperature (350-420 °C) pyrolysis where the intermediate product, thermobitumen (TB), was extracted before its secondary decomposition into coke and gas [3].

There have been many studies describing the Green River oil shale characteristics. According to Das [4], the typical western USA oil shale was made up to 40% of type I kerogen. Urov and Sumberg [5] published the average content of conditional OM in the Green River Utah basin much lower – 19.4%, with elemental composition in weight %: C 78.3, H 9.9 (atomic ratio H/C 1.52), S 1.6, N 2.1, O 8.1, ash content 61.6%, and CO_2 in carbonates 19.0%. For comparison, the analogous characteristics of Estonian Kukersite oil shale published in [5] were as follows: OM 35.5, ash 46.5, CO_2 18.0, whereas OM consisted of C 77.3, H 9.8 (H/C 1.52), S 1.7, N 0.4 and O 10.8%.

Tiwari and Deo [6] found in the oil shale of the Mahogany zone of Green River C 17.45, H 1.6, N 0.53, S 0.18 and O 15.69%. The main minerals were carbonates, quartz and feldspars. Amount of minerals with a potential to release water on thermal treatment was small – 5.8% illite (looses 12% water at 110-140 °C), and 2.4% of analcime (looses 8% water at 175-375 °C).

1.1 Retorting of Green River Oil Shale

Hillier et al. [7] studied pyrolysis in an open retort of an oil shale sample from Colorado Green River formation consisting 24.39% of OM. The yield of total volatiles from the initial shale was 18.3% (75% of OM), and from the demineralized sample 79%. The yield of oil condensed was about 60% of OM.

Thermogravimetric analysis (TGA) is a modification of the open to air retorting developed for quantitative characterization of the pyrolysis kinetics. According to TGA experiments [6], the total weight loss of Green River Utah oil shale at 500 °C increased with the increase in the heating rate from 0.5 to 1 °C /min from 9.38 to 11.28% whereas the temperature for the maximum weight loss rate, $T_{\max}$, was shifted from 401 to 457 °C. The yield of total pyrogenetic water from mineral part was 0.89%. The values of activation energy (E) estimated for the overall first order multiple formation of 56 compounds varied with extent of conversion in the range 95-245 kJ/mol, and that of naphtha fraction (C_5-C_{12}) in the range 41-206 kJ/mol. Actually, the major constituents of the oil (alkanes, alkenes, aromatics) are formed by more complicated parallel and subsequent pathways being described by different rate equations and rate constants. So, the models based on TGA data and approximated to a single reaction cannot give the same kinetic constants at different transformation stages of oil shale. For example, the non-isothermal method applied by Campell et al. [8] gave for formation of 91.7 ml/kg of oil from Colorado oil shale the activation energy (E) 219.1 kJ/mol and the frequency factor (A) $2.81\text{x}10^{13}$ 1/s. The analogous kinetic constants published by Shih and Shon [9] were 197 kJ/mol and 5.63×10^{11} 1/s, and by Rajeshwar [10] in the range 116-209 kJ/mol and 9.80×10^{10}. 1/s.

A later modification of the open to air retorting has been thermal treatment of oil shales *in situ* via boreholes at appropriate heating and controlled pressure in semi-open conditions. The thermal decomposition of oil shale in place, particularly when the shale is too deep, has a number of operational, economic and environmental advantages. Proposed temperatures have been in the range 300-350 °C and processing durations from days to months. Doan et al. [11] have simulated *in situ* pyrolysis of the rich oil shale zones of the Piceance Basin Green River Formation with OM content 16.1% and total organic carbon (TOC 13.02% in a laboratory tubing reactor (H 127 mm, D 38 mm). The oil yield in Fischer Assay at 500 °C was 10.8%. The yield of hydrocarbons in Rock-Eval analysis (up to 650 °C) was high – 88.7% of TOC. The semi-open pyrolysis experiments were conducted under various operating conditions appropriate to commercially viable *in situ* pyrolysis: 1-5 MPa, heating rates 2-120 °C/h, durations 5-12.5 h, and nominal temperatures 300-425 °C. The yields of generated gas, water, oil, thermobitumen (TB) extracted with 9:1 mix of dichloromethane and methanol, and spent shale were estimated. Characteristics of the products were estimated using CHNSO, Rock-Eval, GC, NMR TLC-FID, FTIR, XANES analysis. As expected, oil yields were lower than those obtained in Fischer and Rock-Eval assays but the produced oil had high H/C ratio (1.78-1.88) and lower density (0.81-0.85 g/cm^3) than in surface retorts.

Hillier and Fletcher [12] have studied pyrolysis kinetics of Green River oil shale (24% OM) and its decarbonated and demineralized kerogen extracts using a pressurized TGA under heating rates 1 to 10 K/min, pressures 0.1 and 0.40 MPa, and temperatures up to 1000 °C. The mass loss in the stage of OM pyrolysis was 14.3% of the initial oil shale. Using the buoyancy correction technique and normalized mass losses, the activation energies determined ranged from 173 to 226 kJ/mol, and the pre-exponential factors from 2.74×10^{10} to 1.86×10^{14} 1/s. It was found that there was no significant difference among the *E* and *A* combinations determined for the oil shale and its demineralized samples nor between pressures of 0.1 and 0.4 MPa.

It is known, for example in [3, 8], that highly aliphatic solid fuels pass in pyrolysis a stage of an intermediate product, thermobitumen (TB), whereas more aromatic oil shales incline to quick condensation of aromatic rings resulting in-soluble in benzene coke. Trewella et.al. [13] has shown using ^{13}C CP/MAS NMR studies that a sample of Green River oil shale OM consists only 18-20% of aromatic carbon, and 80-82% of hydrocarbons (36-38% of alicyclic carbon, 26% of long chain normal aliphatic structures, and 8-12% of carbon linked to oxygen like esters, ethers, carboxylic acids). According to Lille et al. [14], the aromaticity $[C_{ar}/(C_{al}+C_{ar})]$ of Estonian oil shale Kukersite OM is quite analogous – 21.7% of branched or protonated aromatics or oxy-aromatics, and 71.3% of hydrocarbons [methyl, methylene (29.3%), methine (38.2%) and quaternary hydrocarbons (3.8%)]. The similar aromaticity ratios and analogous carbonaceous mineral parts of Green River and Estonian Kukersite oil shales explain that the yield of retort oil of Green River oil shale, 70%-75% [4, 7] is quite close to that of Kukersite oil shale, 66% of OM [5] in Fischer Assay.

A new technology where an intermediate product, a mixture of thermobitumen and oil was extracted before coke formation, enabled to increase the oil yield from Estonian Kukersite by 20% in comparison with Fischer Assay [3]. So, it seemed prospective that the same technology can be prospective for Green River oil shale.

Miknis et al. [15] have published an amazing result – when retorting of oil shale from Colorado Piceance Creek Basin, Mahogany Zone (Fischer Assay 19.3%, TOC 22.6%) was quenched after 20 min at 425 °C, 95% of the organic carbon (TOC) was recovered in the form of the sum of oil condensed in an ice trap (37% of TOC) and TB extracted from the residual shale with benzene in Soxhlet extractor for 24 h (58% of TOC). Contrary, the New Albany shale, with a high carbon aromaticity (42%) produced oil about 40% and less than 10% of TB. It was shown that the molecular weight and H/C ratio of the distilled oil were fairly independent of time and temperature whereas the composition and properties of TB extracted changed during the course of the reaction.

1.2 Thermal Dissolution of Green River Oil Shale in autoclaves

A comprehensive overview on the sub- and supercritical extraction of western and eastern USA oil shales with various solvents was given by Das [4] referring also the earliest patent in the field declared in 1920 by Ryan [16]. The invention described a method of heating finely ground Green River oil shale in the medium of a heavy shale oil fraction at temperature high enough (315-370 °C) to convert OM to soluble material. The extraction procedure was modified in the later patent [17] where hydrocarbon containing solids passed the reactor (343-482 °C) downwardly and concurrently with a steam of a liquid organic solvent (toluene, tetralin, decalin, and petroleum or oil shale derived oil fractions), and a hot non-oxidizing gas. The maximum organic carbon conversion was 119-125% of Fischer Assay at pressure of both H_2 or N_2 3.4 MPa, residence time 1-1.5 h, and solvent flow rate 112-128 g/h.

Thermal dissolution kinetics of oil shales from Green River Utah basin Hell's Hole Canyon (OM 25.7%, C_{ar} 27%, oil yield in Fischer Assay 16.4%) was examined at the University of Utah, USA [18-20]. In these works, yield of s. c. “oil” (*X*) was estimated on the basis of OM transformed into the sum of extracted oil, water and gas being calculated using the fractions of OM (*f*) estimated by weight loss in incineration at 475 °C of the initial oil shale (o) and solid residue (s) as follows:

$$X = (f_o - f_s)/[f_o(1 - f_s)] \qquad (1)$$

So, including gas and water, and expressing the “oil yield” (actually, the total volatiles) on the basis of the reactive part of OM only, considerably higher yields than those typical in retorting and expressed on the basis of total OM or initial oil shale were obtained with each of the solvents used (cyclohexane, tetralin, and creosote oil). For example, the values of X as high as 96% were reported in 24 h runs. The dissolution highest temperature in the series was 379 °C which was at least 120 °C lower than typical retorting temperatures. The kinetics of OM decomposition was evaluated following a linear heating technique and integral, differential and difference-differential data processing. It was concluded that two parallel pathways for bitumen formation existed where the apparent kinetic constants A and E below 350 °C were 2.2×10^4 1/min and 87 kJ/mol, and above 350 °C accordingly 1.7×10^{13} 1/min and 191 kJ/mol. The quite similar to the second pair of kinetic constants, 1×10^{13} 1/min and 192 kJ/mol, were proposed by Hubbard and Robinson [21] already in 1950 for the thermal decomposition of Green River oil shale without solvents in open retorts.

1.3 Kinetics of Consecutive Decomposition of Kerogen and TB

In the works referred above, like in TGA studies of any decomposition route, kinetics of the complicated retorting process of oil shale has modelled basing on the overall weight loss rate and approximated to a single, mostly the first order reaction.

In the studies [15, 21-26], the oil shale thermal decomposition in retorting has been considered to consist of two consecutive reactions: formation of an intermediate nonvolatile but soluble in organic solvents product, thermobitumen (TB), and decomposition of TB into oil, gas and coke. As characteristic to any intermediate product, the yield of TB should pass a maximum at a certain duration decreasing with increasing temperature, and depending both on the rate factor of OM decomposition (k_1) and on the rate factor of the following decomposition of TB (k_2). The values of k_1 and k_2 estimated for pyrolysis of Colorado oil shale in open retorts are polemic. For example, Miknis et al. [15] found experimentally that at 425 °C the maximum yield, 60% of TB, was obtained after 20 min. In the same paper, the according values of k_1 and k_2, 1/s, at 425 °C estimated by different researchers were represented as follows: 1.283 and 8.033 [9], 0.0022 and 0.0005 [22], 0.0067 and 0.010 [23], and 31.03 and 12.5 [24]. According to our calculations, the time-dependence of the experi-mental yields of TB found in [15] agreed with the calculated values when the rate factors given in [22] were applied only. The faster decompo-sition of TB than of OM in [23] resulted in t_{max} 2 min., and the maximum yield of TB amounting 30%. The prevailing k_2 published in [9] predicted that no TB can be detected.

The earlier experimental studies have proved that the yield of the sum of inseparable in the extracts TB and oil (TBO) obtained in thermal decomposition without solvents in autoclaves or in thermal dissolution in water, benzene or in other solvents of Estonian Kukersite oil shale [3, 25-27], Turkish Göynük oil shale [28], and Jordanian Attarat oil shale [29] passes a maximum at a definite duration.

The high maximum yield of TBO obtained in case of Estonian Kukersite, amounting 80%, is explained by its significantly higher rate factor of OM decomposition (k_1) than that (k_2) of following decomposition of TBO. The maximum yield of TBO of Jordanian oil shale attains 60% and is depressed due to faster decomposition of TBO explained by close values of the two rate factors. For example, the ratio of k_1/k_2 of Estonian Kukersite oil shale is 59.2 at 360 °C and decreases to 9.97 at 425 °C, and that of Jordanian Attarat OM, correspondingly, 1.93 and 1.47 only [29].

Kinetic data describing the secondary decomposition of TBO of Green River oil shale in autoclaves are absent. As far as the TB extracted from the pyrolysis residue after retorting does not consist of volatile oil, the contradictory values of k_2 published in [9, 15, 22, 23, 24] cannot match with k_2 for TBO obtained in autoclaves.

The aim of this study was experimental study in laboratory autoclaves of the effects of nominal temperature and process duration on the yield of decomposition products in the low-temperature thermal decomposition of Utah oil shale, estimation of the optimal conditions, evaluation kinetics of the low-temperature thermal decomposition of OM and TBO, and comparison of the results with those of Estonian and Jordanian oil shales.

2. EXPERIMENTAL

2.1 Characterization of the Initial Sample

The oil shale sample studied was taken from USA Green River formation Utah basin and delivered by Indrek Aarna, Head of R&D Eesti Energia AS.

The conditional OM estimated as weight loss in incineration at 550 °C of the dried sample was quite low for the basin, 13.59% and moisture content 0.35%.

The dried oil shale sample consisted of 13.5% C, 1.22% H, 0.34% N, and 0.61% S.

The oil yield in Fischer Assay of the dry oil shale at 525 °C was 7.69 and on the basis of OM 56.6%.

2.2 Liquefaction Procedure

Pyrolysis of the Utah oil shale was carried out like of Jordanian oil shale [29] in glass test tubes placed in 58 cm^3 stainless steel autoclaves. In every experiment autoclaves with 10 g of the air dried powdered to 0.04-0.1 mm samples were placed into a cold muffle oven. The constant nominal temperature varied in the range 360-420 °C was attained during 60 minutes. The isothermal pyrolysis stage, varied in the range 0.5-7 h, was measured from the time when the muffle oven reached the nominal temperature prescribed.

Influence of the pyrolysis conditions was evaluated by yields of the pyrolysis products: gas, extracts obtained in a Soxhlet apparatus with subsequently applied solvents (hexane, benzene, tetrahydrofurane), and solid residue. The total benzene extract (TBO) consisting of the inseparable high-molecular intermediate product TB and oil included hexane soluble extract called maltenes, and hexane insoluble precipitate called asphaltenes. The insoluble in benzene but soluble in tetrahydrofurane extract, called asphaltol, represented higher molecular hetero-compounds than TB.

2.3 Analysis

The mass of gas formed was determined by the weight loss after discharging of volatiles from the open autoclave at room temperature. The pyrolysis liquid products, TBO, pyrolytic water and asphaltol were extracted subsequently in a Soxhlet's extractor with boiling benzene, and next with tetrahydrofurane (THF). The mass of the insoluble in the solvents solid residue (SR) was estimated after drying of the remains in the extraction cartridge at 105-110 °C during 1 hour (deleting the corresponding weight of the dried cartridge after passing the same operations). The sum of hygroscopic and pyrolytic water in benzene extract was separated by azeotropic distillation and weighted [31]. The solvents applied were removed from the TBO and asphaltol solutions in a vacuum rotation evaporator at 60-70 °C. The distillation residues of the benzene and THF extracts obtained in the rotation evaporator were left in the open flask and weighted after 24 hours for evolution of the solvent traces remained. Like in the earlier works, removing traces of benzene from TBO has been a problematic procedure. The quantity of TBO can be underestimated due to evaporation of low-boiling decomposition products or overestimated when a part of the solvent, having higher boiling temperature or being incorporated with destruction products, is not removed. So, the mass of benzene soluble extract was preferred to determine by subtracting the mass of gas, water and solid residue from the initial mass of the dried shale.

The TBO extracted was divided into two fractions: soluble in hexane maltenes (oil) and insoluble asphaltenes, being more prone to coke-formation. For this aim, hexane in the ratio 10:1 was added to an aliquot of the not entirely dried benzene extract resulting precipitation of asphaltenes. After 24 hours the precipitate was filtrated, washed, dried and weighted.

The compound groups in TBO were estimated by preparative thin-layer chromatography separating about 500 mg of the sample on the 24 x 24 cm plates coated with a 2 mm silica gel layer (60 mm, Fluka), and using *n*-hexane as the eluent. Five groups of compounds were separated and extracted from silica gel with ethyl ether: aliphatic hydrocarbons (AlHC), monocyclic aromatic hydrocarbons (MAHC), polycyclic aromatic hydrocarbons (PAHC), neutral hetero-atomic (NHet) and highpolar hetero-atomic (HPHet) compounds.

3. RESULTS AND DISCUSSION

3.1 Thermal Decomposition

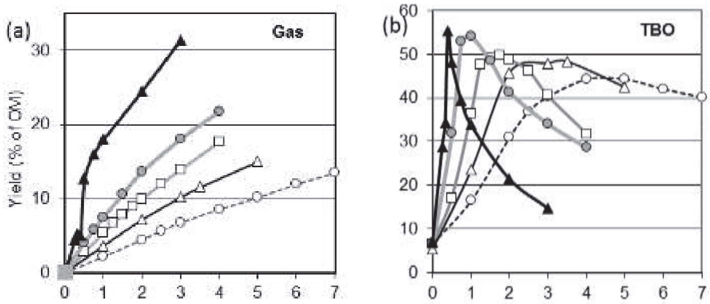
The maximum yield of TBO obtained in thermal decomposition of Utah oil shale in autoclaves was only 6-7.5%, and the maximum transformation degree of the oil shale – about 9% of the dry shale. The results are close to the oil yield obtained in retorting of the sample in Fischer Assay in this work (7.69%), and to the total weight loss in TGA (9.4-11.3%) [6], but about twice less than those reported by others [6, 7, 11, 12, 18-20] in retorting of Green River samples with OM content overcoming 20%.

Yields of the thermal decomposition products on the basis of OM are presented in Fig. 1. The data in Fig. 1a show that the gas yield increases with time and temperature and has not attained any steady state in the experiments. The yield of TBO in Fig. 1b has a maximum reaching 45-55% of OM at durations 4-5, 2.5-3.5, 1.5-2.5, 0.75-1, and 0.5 decreasing with increasing nominal temperatures 360, 370, 380, 400 and 425 °C. Noteworthy is that differing from Estonian [26] and Jordanian [29] oil shales, the maximum yield TBO of the Utah oil shale OM in autoclaves is even lower than the oil yield of the sample obtained sample in Fischer Assay (57% of OM).

The yield of soluble in THF asphaltol (Fig. 1c) is small, 1-3%, in comparison with that in Jordanian oil shale, attaining 14% [29].

The yield of SR on the OM basis passes a minimum, 35-37% (Fig. 1d) at durations matching with the corresponding durations for the TBO maximum. In the first stage the yield of SR decreases in time due to the thermal decomposition of OM into TBO and gas. In the second stage the coke formation in the secondary decomposition of TB and asphaltol prevails resulting increase in the yield of SR.

The irregular changes in the yield of pyrolytic water (Fig. 1e) suggest that water can incorporate or separate from the pyrolysis products formed, like that was noticed in Jordanian oil shale thermobitumenization [29].



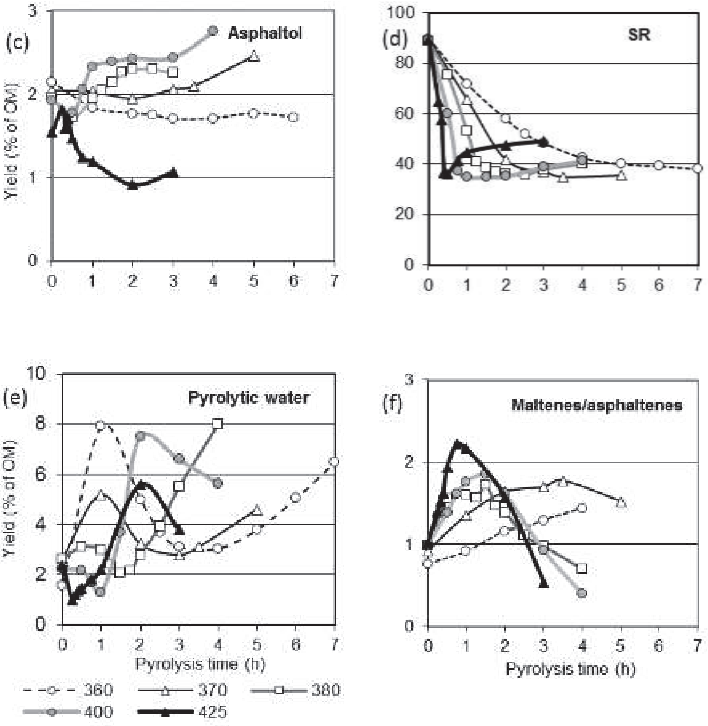


Figure 1: Effect of Temperature and Isothermal Duration on the Yields of Gas (a), TBO (b), Asphaltols (c), Solid Residue (d) and Pyrolytic Water (e), and on the Ratio of Maltenes and Asphaltenes in TBO (f)

The both constituents of TBO, maltenes and asphaltenes, show a maximum yield and following sharper decomposition of maltenes than asphaltenes. So the ratio maltenes/asphaltenes has a maximum (Fig. 1f), and prolongation of the pyrolysis after TBO maximum does not benefit the composition of TBO formed from the Utah oil shale. So, the fast and flash pyrolysis can be suggested for liquefaction of Green River oil shale because up to attaining the TBO maximum yield, the higher the nominal temperature, the more the share of maltenes in TBO,.

The results obtained evident that the technology being excellent for extraction of liquid products from Estonian oil shale cannot be suggested for the Green River Utah oil shale because under the optimum conditions more than one third of its OM is transformed into spent shale, and one tenth into gas in autoclaves.

3.2 Group Composition of TBO

The group composition of TBO extracted from the pyrolysate produced without any solvent in this work from Utah oil shale with yield 47.39 % of OM, and for comparison, of those from Jordanian Attarat oil shale with yield 58% [29], and from Estonian Kukersite oil shale with yield 86% [26] at nominal temperature 380 °C are presented in Table 1.

Table 1: Group Composition of TBO (%)

Symbol	USA	Jordan	Estonia
AlHC	24.4	8.2	3.4
MAHC	5.5	8.4	1.2
PAHC	11.6	32.9	6.4
NHet	10.0	13.2	9.5
HPHet	48.5	37.3	79.5

AlHC – aliphatic hydrocarbons, MAHC – monoaromatic hydrocarbons, PAHC – polyaromatic hydorcarbons, NHet – neutral hetero-atomic compounds. HPHet – highpolar hetero-atomic compounds.

According to Table 1, the main compound group in TBO obtained in low-temperature pyrolysis of Utah oil shale is the group of high-polar hetero-atomic compounds (HPHet) like in case of TBO obtained from Jordanian oil shale, nevertheless being about two times less than that in TBO from Estonian Kukersite. As a specific feature of Green River Formation, the second place in TBO has content of aliphatic hydrocarbons amounting 24.4% while those of Jordanian oil shale show 8.2% and in Estonian Kukersite TBO 3.4% only.

3.3 Kinetics of OM Thermal Decomposition

Oil shale thermobitumenization involves parallel reactions of primary decomposition of OM into gas, TBO, oil and coke, and consecutive secondary decomposition of TBO into oil, gas, and coke. For an approximate characterization and comparison kinetics of the complicated pyrolysis process of oil shales from various formations, the rate factors for the isothermal total decomposition of OM (k_1) in the first stage and TBO (k_2) under any nominal temperature tested were estimated presuming a simple first order reaction as follows:

$$\ln(C_0/C) = -k_i(t - t_0) \qquad (1)$$

where C_0 was the percentage of OM remained in the solid product or yield of TBO at time t_0 on the basis of initial OM, and C their decreased yield after duration t. The values of k_i were found from the slopes of the linear function described by Eq. 1 with zero intercept and presented in Fig. 2. For this aim, only the linear part of the function was considered where the coke formation was insignificant and OM in solid residue consisted of kerogen only.

The apparent kinetic constants, frequency factor A and activation energy E, were found from the slope (b) and reciprocal (a) of the linear trendlines of the logarithmic form of Arrhenius relationship

$$\ln k = \ln A - E/(\mathrm{R}T) \qquad (2)$$

The trendlines obtained introducing into Eq. 2 the values of k_i estimated as slopes in Fig. 2 a and b are depicted in Fig. 3a.

The regression coefficients, a and b, of the linear trendlines in Fig. 3a, and the according apparent kinetic constants ($A = \exp(a)$, $E = -b\mathrm{R}$, $\mathrm{R} = 0.008314$ kJ/mol K) of the Utah oil shale estimated firstly in this work and those published earlier for Jordanian Attarat oil shale [29] and Estonian Kukersite oil shale [26] are given in Table 2.

As a rule, an increase in E occurs with an increase in A and follows a linear relationship called Compensation Effect.

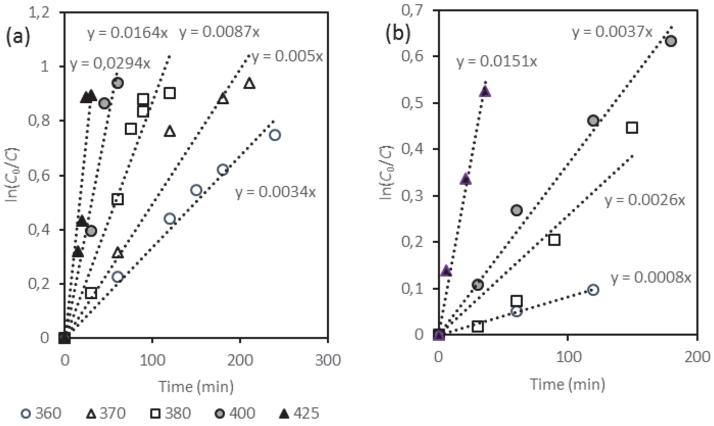


Figure 2: Trendlines to Estimate Rate factors for the Total Decomposition of OM (a) and TBO (b) of Utah Oil Shale

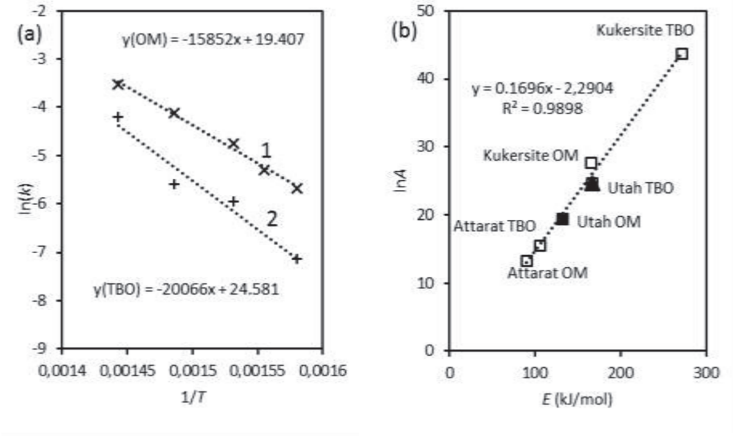


Figure 3: Arrhenius Plot of Rate Factors for Decomposition of Utah Oil Shale OM (trendline 1) and TBO (trendline 2) (a), and Compensation Effect between the Kinetic Constants of Various Oil Shales (b)

Table 2: Apparent Kinetic Constants for Decomposition of OM and TBO in Autoclaves

Oil shale	*a*	–*b*	*A* (1/min)	*E*, (kJ/mol)
Utah:				
OM	19.41	15852	2.69×10^{8}	132
TBO	24.58	20066	4.73×10^{10}	167
Attarat [29]:				
OM	13.3	10850	5.91×10^{5}	90
TBO	15.6	12684	5.61×10^{6}	106
Estonian Kukersite [26]:				
OM	27.6	19801	9.69×10^{11}	165
TBO	43.7	32603	9.15×10^{18}	271

The plot of kinetic constants given in Table 2 and depicted in Fig. 3b reveals that a linear regression

$$\ln A = 0.170(\pm0.009)E - 2.29(\pm1.43) \qquad (3)$$

is kept ($R^2 = 0.990$) between the apparent kinetic constants for subsequent decomposition of OM and TBO of different oil shales located in Utah, Attarat and Estonia.

The co-effect of the kinetic constants having an opposite influence on the rate factor is explained by Arrhenius exponential equation

$$k = A\exp(-E/RT) \qquad (4)$$

The values of k at various temperatures calculated introducing the kinetic constants from Table 2 into Eq. (4) are depicted in Fig. 4a.

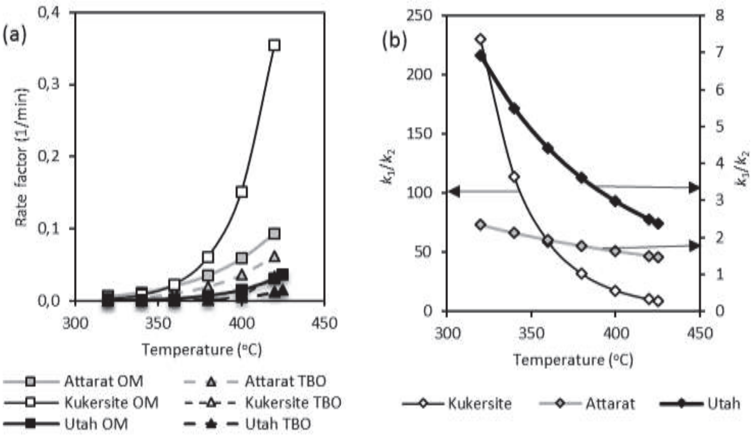


Figure 4: Effect of Temperature on the Rate Factors for Decomposition of Oil Shale OM (k_1) and TBO (k_2) (a), and on the Ratio of the Rate Factors (b)

The curves in Fig. 4a explain that the opposite effect of kinetic constants results the lowest rate factors for the thermal decomposition of Utah OM and TBO in spite of *A* and *E* of Utah oil shale were between those of Estonian Kukersite and Jordanian Attarat oil shales (Fig. 3b). The effect of temperature on the rate factors is vital above 360 °C having a really great influence on the rate of Kukersite OM decomposition being a controlling stage before the maximum yield of TBO has been attained. When temperature increases from 320 to 425 °C, the ratio of the factors (Fig. 4b) of Utah oil shale decreases from 6.9 to 2.4, overcoming that of Attarat oil shale decreasing from 2.4 to 1.5 only, and essentially succumbing to the ratio of Kukersite decreasing from 230 to 10. So, the decomposition rate of TBO of Utah oil shale, like that of Attarat oil shale, is comparable with its formation rate from the initial kerogen. As a result, the maximum yield of TBO from both Utah and Attarat oil shales remains essentially lower than that from Kukersite.

OM of the three oil shales consist of highly aliphatic type I kerogens. The main characteristics of the kerogens are gathered in Table 3.

According to Table 3, the OM content in the oil shales increases in the row of the samples from the deposits as follows: USA Green River – Jordan – Estonia.

Table 3: Characterization of OM of the Oil Shales

Characteristic	USA, Green River, Utah	Jordan, Nebi Musa	Estonia, Kukersite
OM, % [5]	19.4 (13.59)*	22	35.5
Maximum yield of TBO (%, of OM)	45-55	55-60 [29]	80-90 [26, 27]
$C_{ar}/(C_{al}+C_{ar})$	0.21 [7]	0.21 [3]	0.217 [29]
Elemental composition of OM (%) [5]			
C	78.3	75.4	77.3
H	9.9	10.0	9.8
S	1.6	7.0	1.7
N	2.1	(O + N)	0.4
O	8.1	7.6	10.8
H/C	1.51	1.59	1.52
k_1/k_2			
340 °C	5.5	2.1	114
380 °C	3.6	1.8	31.9
420 °C	2.5	1.5	10.4

*In the sample applied in this work.

Hillier et al. [7] have shown that the content of OM has a little influence on the yield of volatiles on the basis of OM in retorting of Green River oil shale. For example, the oil yield is 75.1% for the oil shale with OM 24% and 79% for the demineralized kerogen. Contrary, in the paper [32] the yield of TBO from Estonian Kukersite decreases with increasing content of OM when OM content in the shale is less than 50%.

According to Hillier thesis [30] the kinetic constants determined for retorting of Green River oil shale and the demineralized samples were statistically the same, opposing the data in Table 4, and the TGA results of Aboulkas [33] where the activation energy for evolution of volatiles (E) from isolated Moroccan OM is lower than that from the initial shale.

The aromaticy and the H/C atomic ratio of the oil shales are quite close. The main difference between the shales is content of heteroatoms in OM. The content of oxygen is the highest in Estonian Kukersite OM. The specific feature of Jordanian oil shale is the highest sulfur content, and that of Green river oil shale OM – the highest nitrogen content. It can be supposed that both the catalytic and absorbing influence of mineral matter, and number and nature of cross linkage bonds in kerogen and TBO fragments as well are responsible for the difference in the thermal decomposition of the shales.

4. CONCLUSIONS

Experimental series on the low-temperature pyrolysis in autoclaves of Utah oil shale from Uintah basin of Green River formation in USA with content of organic matter (OM) 13.6% revealed the following results.

- The gas yield increases with increasing time (0–7 h) and temperature (360–425 °C). The yield of benzene extract, representing a mixture of an intermediate product thermobitumen with oil (TBO) passes a maximum, 45-55% of OM, and the yield of solid residue a minimum, 35-40% of OM. The increase in the nominal temperature from 360 to 425 °C decreases the according optimum duration from 4-5 to 0.4 h.
- The maximum yield of TBO from Utah oil shale is close to the oil yield of retort oil in Fischer Assay, opposing the Estonian and Jordanian oil shales where the yield of TBO overcomes roughly by 20% the yield of the retort oil.
- The main compound groups of TBO extracted from Utah oil shale are polar hetero-atomic compounds making 48.5 and aliphatic hydrocarbons making and 24.4%, differently to the group composition of TBO from Estonian Kukersite and Jordanian oil shale where the according values are 80 and 3.4%, and 37.3 and 8.2%.
- The kinetic study explains that formation of TBO from OM of Utah oil shale is suppressed by the intensive secondary decomposition of TBO into gas, asphaltol and coke. The activation energy for the overall primary decomposition of OM into gas, TBO, asphaltol and coke is 132, and for the overall subsequent transformation of TBO into gas, asphaltol and coke, 167 kJ/mol. The corresponding frequency factors are 2.69×10^{8} and 4.73×10^{10} 1/min. The co-effect of the values of E and A on the rate factors reveals that an increase in the

temperature from 320 to 425 °C decreases the ratio of the rate factors of the primary and secondary decomposition (k_1/k_2) of Utah oil shale from 6.93 to 2.38, and that of Estonian Kukersite OM from 230 to 9.67.

Acknowledgements

This work was financed by EU Structural funds National R&D program „Energy technology“ (AR12004), and by Estonian Research Council Grant 9331.

5. REFERENCES

1. Knaus, E. Killen, J., Biglarbigi, K., Crawford, P., “An Overview of Oil Shale Resources. In Oil Shale: A solution to the Liquid Fuel Dilemma”, Ogunsola, O., et al.; ACS Symposium Series; American Chemical Society: Washington, February 23, 2010. doi: 10.1021/bk-2010-1032.ch001.
2. Dyni, J. R., “Geology and resources of some world oil shale deposits”, Scientific Investigations Report 2005–5294 United States Department of the Interior; United States Geological Survey, 2006. Retrieved 2008-08-18.
3. Johannes, I., Tiikma, L. Zaidentsal, A., Luik, L., “Kinetics of Kukersite low-temperature pyrolysis in autoclaves”, *Journal of Analytical and Applied Pyrolysis*, 2009, **85**, 508-513.
4. Das, K., “Solvent and supercritical extraction of oil shale”, Technical Note. U.S. Department of Energy Office of Fossil Energy. Morgantown, West Virginia 26507-0880, 1989.
5. Urov, K., Sumberg, A., “Characteristics of oil shales and shale-like rocks of known deposits and outcrops”, Monograph. *Oil Shale*, 1999, **16**, Special, 3-64.
6. Tiwari, P., Deo, M., “Compositional and kinetic analysis of oil shale pyrolysis using TGA–MS”, *Fuel*, 2012, **94**, 333-341.
7. Hillier, J. L., Fletcher, T. H., Solum, M. S., Pugmire, R.J., “Characterization of macromolecular structure of pyrolysis products from a Colorado Green River oil shale”, ACS Publications, *Industrial & Engineering Research*, 2013, **52**, 15522-15532.
8. Campbell, J. H., Koskinas G. H., Stout, N. D., “Kinetics of oil generation from Colorado oil shale”, *Fuel*, 1978, **57**(6), 372-376.
9. Shih, S. M., Sohn, H. Y., „Nonisothermal determination of the intrinsic kinetics of oil generation from oil shal“,. *Ind. Eng. Chem. Proc. Des. Dev.*, 1980, **19**(3), 420–426.
10. Rajeshwar, K., “The kinetics of the thermal decomposition of green river oil shale kerogen by non-isothermal thermogravimetry”, *Thermoc.Chim. Acta*, 1981, **45**(3), 253-363.
11. Doan, T. V., Bostrom, N. W., Burnham, A. K., Kleinberg, R. L., Pomerantz, A. E., Allix, P., “Green river oil shale pyrolysis: Semi-open conditions”, *Energy and Fuels*, 2013, **27**, 6447-6459.
12. Hillier, J. L., Fletcher, T. H., “Pyrolysis kinetics of a Green River oil shale using a pressurized TGA”, *Energy Fuels*, 2011, **25**, 232-239.
13. Trewella, M. T., Poplett, I. J. F., Grint, A., “Structure of Green River oil shale kerogen”, *Fuel*, 1986, **65**, 541-546.
14. Lille, Ü., Heinmaa, I., Pehk, T., “Molecular model of Estonian kukersite kerogen evaluated by 13C MAS NMR spectra”, *Fuel*, 2003, **82**, 799–804.
15. Miknis, F. P., Turner, F. P., Berdan, L., Conn, P. J., “Formation of Soluble Products from Thermal Decomposition of Colorado and Kentucky Oil Shales”, *Energy &Fuels,* 1987, 1, 477-483.
16. Ryan, H. D., “Bituminous Materials from Shale”, U.S. Patent No 1327572. 1920, U.S. Patent No 1327572.
17. Philman, N. H., Yorba, L. C., “Oil shale extraction process”, USA Patent 4533460. 1985, 208/11 LE.
18. Kafesjian, A.S., “Studies of thermal solution of Utah oil shale kerogen”, PhD Thesis, 1983, University of Utah.
19. Leavitt, D. R., “Comparison of extracts and yields from the thermal solution of typical Green River oil shale and Sunbury oil shale”, PhD Thesis, 1987, University of Utah.
20. Leavitt, D. R., Tyler, A. L., Kafesjian, A.S., “Kerogen decomposition kinetics of selected Green River and Eastern US oil shales from thermal solution

experiments", *Energy and Fuels*, 1987, 1, 520-525.

21. Hubbart, A. B., Robinson, W.E., "A thermal decomposition study of Colorado oil shale", p. 24, US Bureau of Mines. RI 4744, 1950.
22. Wallmann, P. H., Tamm, P. W., Spars, B. G., "Oil shale retorting kinetics. Oil shale tar sands and related materials", *ACS Symp. Ser.*, 1981, **163**, 93-113.
23. Braun, R. L., Rothman, A. J., "Oil-shale pyrolysis: Kinetics and mechanism of oil production", *Fuel*, 1975, **54**, 129-131.
24. .Wen, C. S., Kobylinski, T. P., "Low-temperature oil shale conversion", *Fuel*, 1983, **62**, 1269-1273.
25. Kask, K. A., "About bituminizing of kerogen of oil shale Kukersite", Report I. *Transactions of Tallinn Polytechnic Institute.* Series A. 1955, No. 63, 51-64 [In Russian].
26. Johannes, I., Tiikma, L. Zaidentsal, A., "Comparison of the thermobitumenization kinetics of Baltic oil shale in open retorts and autoclaves", *Oil Shale*, 2010, **27**, 17-25.
27. Luik, H., "Supercritical Extraction of the Estonian Kukersite Oil Shale", *Advances in Energy Research*, 2011, **2**, Chapter 10, pp. 283-298.
28. Yanik, J., Secim, P., Karakaya, S., Tiikma, L., Luik, H., Krasulina, J., Raik, P., Palu, V., "Low-temperature pyrolysis and co-pyrolysis of Göynük oil shale and terebinth berries (Turkey) in an autoclave", *Oil Shale*, 2011, **28**, 469-486.
29. Tiikma, L. Johannes, I., Luik, H., Lepp, A., "Extraction of oil from Jordanian Attarat oil shale in autoclaves", *Oil Shale* (in press).
30. Hillier, J. L., "Pyrolysis kinetics and chemical structure considerations of a Green River oil shale and its derivatives", Ph.D. Dissertation, Chemical Engineering Department, Brigham Young University, Provo, UT, 2011.
31. Fetzer, W. R., "Determination of moisture by distillation", *Anal. Chem*. 1951, **23**, (8), 1062-1069.
32. Johannes, I., Luik, H., Tiikma, L., Vink, N., Luik, L., "Effect of organic matter content and type of mineral matter on the oil yield from oil shales", *Oil Shale*, 2012, **29** (3), 206-221.
33. Aboulkas, A., El Harfi, K., „Effects of acid treatment on Moroccan Tarfaya oil shale and pyrolysis of oil shale and their kerogen", *J. Fuel Chem. Technol*., 2009, **37**(6), 659–667.

APPENDIX III. CURRICULUM VITAE

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi	Galina Šarajeva
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Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2011 -...	Keemia- ja materjalitehnoloogia, doktoriõpe
Tallinna Tehnikaülikool	2007	Tehnikateaduste magistrikraad
Tallinna Tehnikaülikool	2005	Tehnikateaduste bakalaureusekraad
Narva Humanitaargümnaasium	2002	Keskharidus

4. Keelteoskus (alg-, kesk- või kõrgtase)

Keel	Tase
Eesti keel	Kõrgtase
Vene keel	Kõrgtase (emakeel)
Inglise keel	Kesktase

5. Täiendusõpe

Õppimise aeg	Täiendusõppe läbiviija nimetus
2011-2012	Doktorikool „Funktsionaalsed materjalid ja tehnoloogiad“ (Tartu Ülikool ja Tallinna Tehnikaülikool)

6. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
15.09.2011-…	Tallinna Tehnikaülikool, keemia ja materjalitehnoloogia teaduskond, polümeermaterjalide instituut, põlevkivi ja taastuvkütuste teaduslaboratoorium	insener
01.01.2005-31.12.2010	AS KPK Teedeehitus	laborant

7. Kaitstud lõputööd

Magistritöö: Praerasvade kasutusvõimaluste uurimine, Tallinna Tehnikaülikool, TTÜ Virumaa Kolledž, Kütuste tehnoloogia teadus- ja katselaboratoorium, 2007. Juhendaja: Rein Muoni

8. Uurimisprojektid

ETF9331 Diktüoneema põlevkivi orgaanilise aine vedeldamine superkriitiliste lahustite ja reagentidega. 2012-2015

SF0140028s09 Põlevkivi ja kütuste segude termokeemilise töötlemise uued tehnoloogiad. 2009-2014

AR12004 Põlevkivi maksimaalse vääristamise alused. 2012-2015

CURRICULUM VITAE

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Date and place of birth	24.10.1983 Narva

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3. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2011-...	Chemical and Materials Technology, doctoral studies
Tallinn University of Technology	2007	M. Sc. in Engineering
Tallinn University of Technology	2005	B. Sc. in Engineering
Narva Humanitarian Gymnasium	2002	Secondary education

4. Language competence/skills (fluent; average, basic skills)

Language	Level
Estonian	Fluent
Russian	Fluent (native language)
English	Average

5. Special Courses

Period	Educational or other organisation
20011-2012	Graduate school „Functional Materials and Processes“ (University of Tartu and Tallinn University of Technology)

6. Professional Employment

Period	Organisation	Position
2011-…	Tallinn University of Technology , Faculty of Chemical and Materials Technology, Department of Polymer Materials, Laboratory of Oil Shale and Renewables Research	Chemistry engineer
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7. Defended theses

M. Sc. thesis: The research of the potential of waste cooking oil, Tallinn University of Technology Virumaa College of TUT, Laboratory of Fuels Technology, 2007. Supervisor: Rein Muoni

8. Research projects

ETF9331 Liquefaction of the organic matter of dictyonema oil shale with supercritical solvents and reagents (2012-2015)

SF0140028s09 New technologies of thermochemical processing of oil shale and blended fuels 2009-2014

AR12004 Fundamentals to oil shale maximum upgrading 2012-2015

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and Destruction of Polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase Transformations in Hydrothermal Sintering Processing of Phosphate Rock. 1995.

4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi Apatites. 1995.

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