



## 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<sub>2</sub> 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<sub>2</sub> 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<sub>5</sub>-C<sub>12</sub>) 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 ( $A$ )  $2.81 \times 10^{13}$  1/s. The analogous kinetic constants published by Shih and Shon [9] were 197 kJ/mol and  $5.63 \times 10^{11}$  1/s, and by Rajeshwar [10] in the range 116-209 kJ/mol and  $9.80 \times 10^{10}$  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<sup>3</sup>) 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  $2.74 \times 10^{10}$  to  $1.86 \times 10^{14}$  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  $^{13}\text{C}$  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  $\text{H}_2$  or  $\text{N}_2$  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:



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

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  $2.2 \times 10^4$  1/min and 87 kJ/mol, and above 350 °C accordingly  $1.7 \times 10^{13}$  1/min and 191 kJ/mol. The quite similar to the second pair of kinetic constants,  $1 \times 10^{13}$  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 experimental yields of TB found in [15] agreed with the calculated values when the rate factors given in [22] were applied only. The faster decomposition 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<sup>3</sup> 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 (AIHC), 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%.

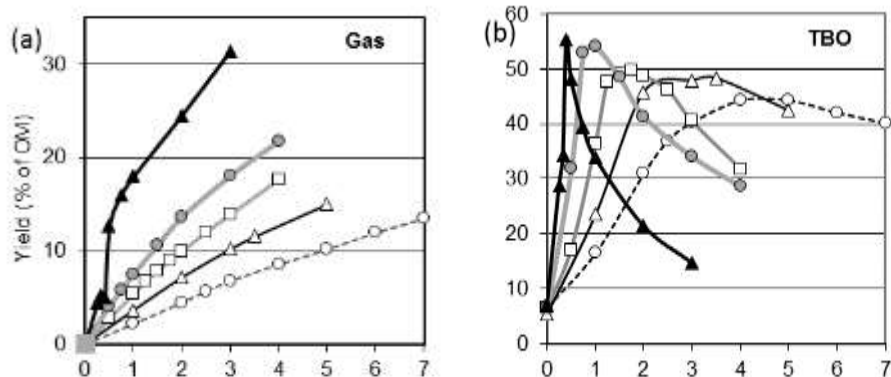
Yields of the thermal decomposition products on the basis of OM are presented in Fig. 1. The data in Fig. 1a show that the gas yield increases with time and temperature and has not attained any steady state in the experiments. The yield of TBO in Fig. 1b has a maximum reaching 45-55% of OM at durations 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].



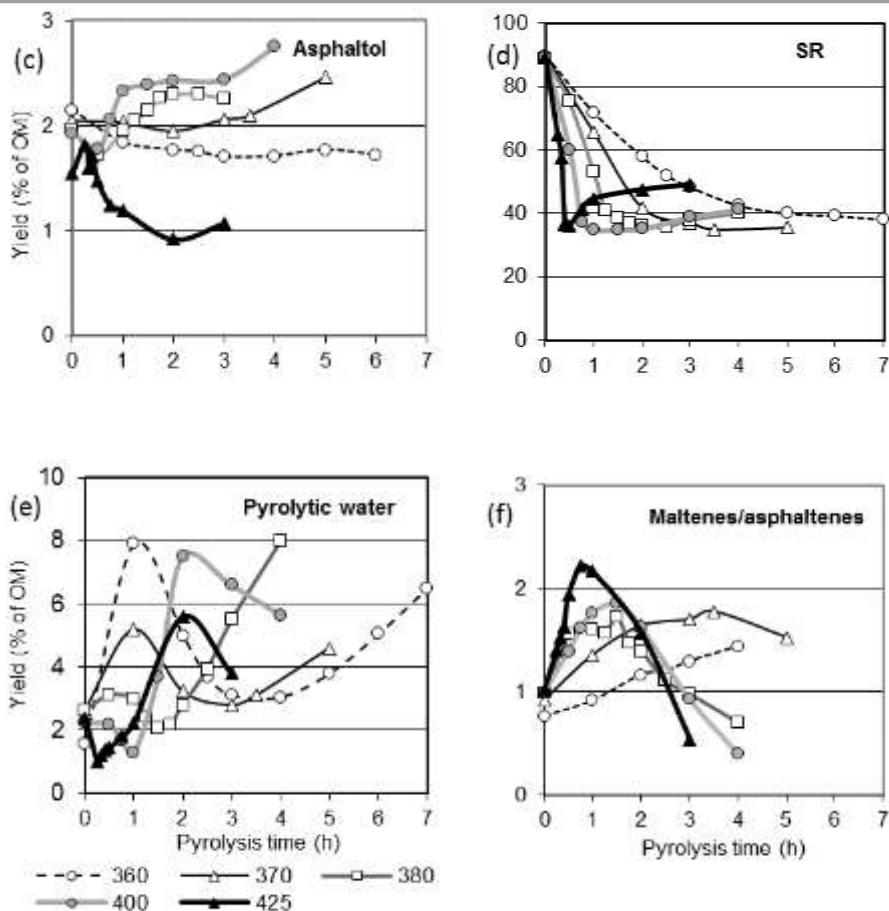


Figure 1: Effect of Temperature and Isothermal Duration on the Yields of Gas (a), TBO (b), Asphaltols (c), Solid Residue (d) and Pyrolytic Water (e), and on the Ratio of Maltenes and Asphaltenes in TBO (f)

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
AIHC	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

AIHC – aliphatic hydrocarbons, MAHC – monoaromatic hydrocarbons, PAHC – polyaromatic hydrocarbons, 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:

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

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

$$\ln k = \ln A - E/(RT) \quad (2)$$

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 ( $A = \exp(a)$ ,  $E = -bR$ ,  $R = 0.008314$  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.



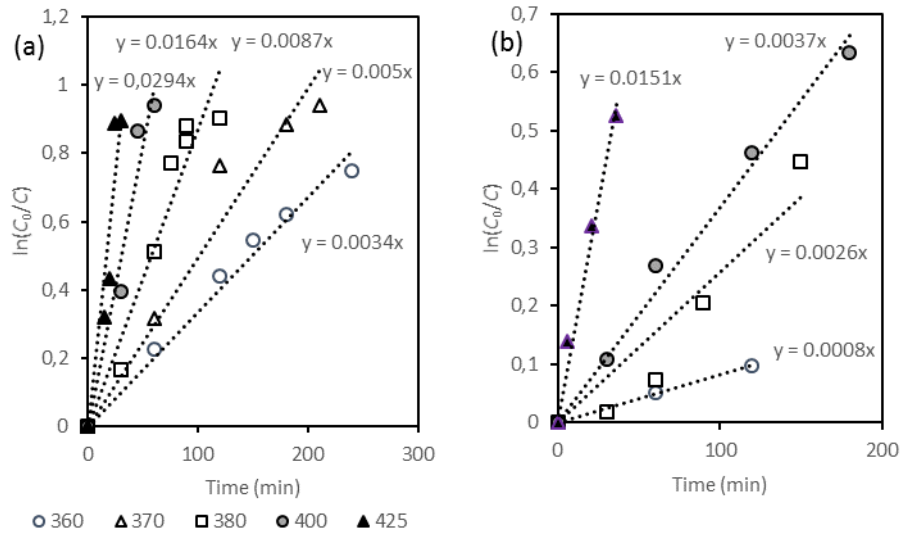


Figure 2: Trendlines to Estimate Rate factors for the Total Decomposition of OM (a) and TBO (b) of Utah Oil Shale

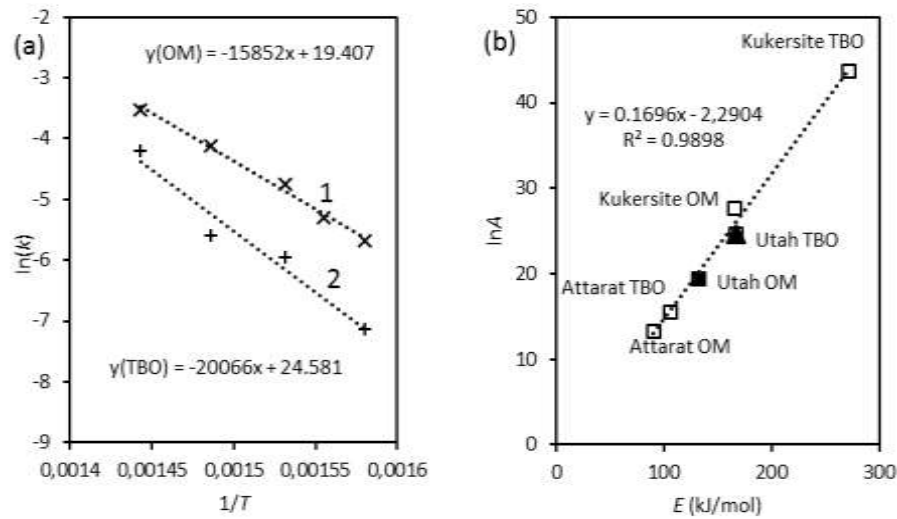


Figure 3: Arrhenius Plot of Rate Factors for Decomposition of Utah Oil Shale OM (trendline 1) and TBO (trendline 2) (a), and Compensation Effect between the Kinetic Constants of Various Oil Shales (b)



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

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

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

$$\ln A = 0.170(\pm 0.009)E - 2.29(\pm 1.43) \quad (3)$$

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

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

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

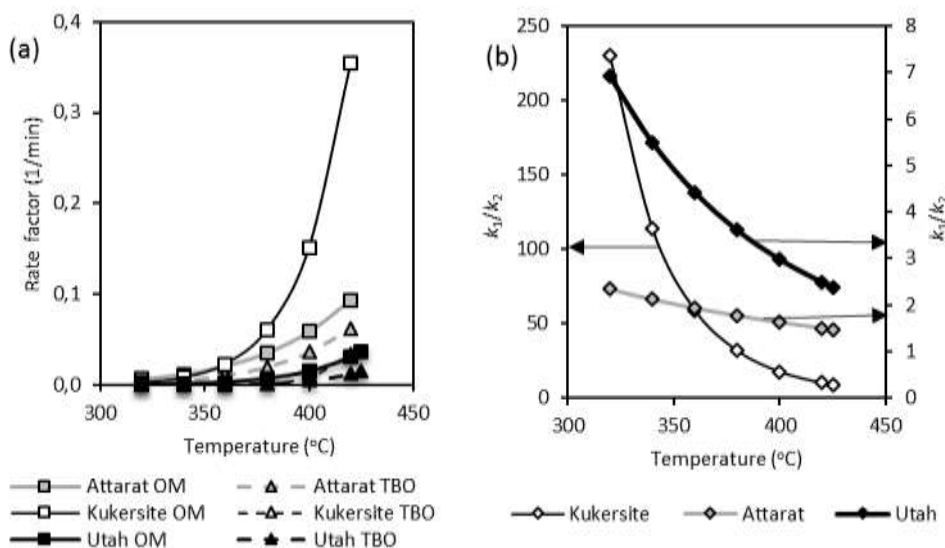


Figure 4: Effect of Temperature on the Rate Factors for Decomposition of Oil Shale OM ( $k_1$ ) and TBO ( $k_2$ ) (a), and on the Ratio of the Rate Factors (b)

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 aromaticity 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 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  $2.69 \times 10^8$  and  $4.73 \times 10^{10}$  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.

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