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The influence of pyrolysis type on shale oil generation and its composition (Upper layer of Aleksinac oil shale, Serbia)

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Abstract: The influence of pyrolysis type on the shale oil generation and its composition was studied. Different methods such as Rock-Eval pyrolysis, thermogravimetric analysis (TGA) and pyrolysis in the open and closed systems were applied. Samples from the Upper layer of Aleksinac oil shale (Serbia) were used as a substrate and first time characterized in detail. The impact of kerogen content and type on the shale oil generation in different pyrolysis systems was also estimated. Majority of the analysed samples have total organic carbon content > 5 wt. % and contain oil prone kerogen types I and/or II. Therefore, they can be of particular interest for the pyrolytic processing. The thermal behaviour of analysed samples obtained by TGA is in agreement with Rock-Eval parameters. The pyrolysis of oil shale in the open system gives higher yield of shale oil than the pyrolysis in the closed system. The yield of hydrocarbons (HCs) in shale oil produced by the open pyrolysis system corresponds to an excellent source rock potential, while HCs yield from the closed system indicates a very good source rock potential. The kerogen content has a greater impact on the shale oil generation than kerogen type in the open pyrolysis system, while kerogen type plays a more important role on the generation of shale oil than the kerogen content in the closed system. The composition of the obtained shale oil showed certain undesirable features, due to the relatively high contents of olefinic HCs (open system) and polar compounds (closed system), which may require further treatment to be used.

Keywords Aleksinac oil shale; Rock-Eval; thermogravimetry; open/closed pyrolysis system; shale oil.

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INTRODUCTION

Oil shale is an organic-rich fine-grained sedimentary rock, which is considered as an alternative energy source. It is a low grade solid fossil fuel with organic matter (OM) mainly in the form of the high molecular weight insoluble substance called kerogen, and with high mineral content. Oil shale has become an alternative energy resource due to a huge source of solid fossil hydrocarbon compounds (10×10^{15} t) in the form of kerogen on the Earth.[1,2] Hydrocarbons (HCs) can be obtained from kerogen by retorting (pyrolysis) and gasification processes.

Pyrolysis is a common method used to break down the complex kerogen structure by heating in the absence of oxygen. In this way, the low energy level substrate (kerogen) can be converted into the liquid HCs with higher energy value (shale oil). The shale oil is the main product of oil shale pyrolysis, besides it the gas and the solid residue are also formed. Yields of products depend on the OM type, type of applied pyrolysis and the operating conditions (temperature, heating rate, pressure, residence time, type of inert gas and its flow rate, particle size etc.). Shale oil is a kind of unconventional oil close to crude petroleum according to its composition. It can be used as a fuel or feedstock for the production of oil derivatives, solvents and chemicals.[3,4] However, the shale oil usually contains high content of olefinic and/or polar heteroatomic compounds which makes it less attractive than the crude petroleum. Depending on an application, further treatment to reduce the content of undesirable compounds in shale oil may be required.[3,5]

The first step in the studying of the oil shale is determination of hydrocarbon generative potential, which depends on the type, quantity and maturity of OM.[6] There are different types of pyrolysis which are used in laboratory conditions. Rock-Eval pyrolysis is widely applied for fast and preliminary screening of the sedimentary rock in order to determine the type, quantity, thermal maturity and hydrocarbon potential of OM.[7–9] Thermogravimetric analysis (TGA) is used to measure the loss weight of a sample due to the thermal decomposition and the devolatilisation of OM with the temperature rise is aimed to determine kinetic parameters and to predict thermal behaviour of oil shale.[2,4,10–14] Pyrolysis in an open and a closed system can be used for the simulation of OM maturity changes and the evaluation of hydrocarbon potential in more detail. In difference to Rock-Eval and TGA, these pyrolysis types enable determination of the composition of pyrolysis products.[15–18]

The fundamental studies of pyrolysis processes in laboratory conditions are necessary to estimate hydrocarbon potential, predict thermal behaviour of oil shale and to determine the yield and composition of pyrolysis products in order to design an efficient pyrolytic reactor for industrial applications.

Oil shale exists in many known deposits, from Cambrian to Tertiary age, in the world.[19] In Serbia there are twenty discoveries and two deposits of oil shales of Tertiary age with total estimated oil shale resources of about 5 billion tons.[20,21] The discoveries are mostly poorly investigated and need more exploration to determine their resources and quality. The Aleksinac oil shale deposit is the most important oil shale deposit in Serbia, comprising ~2.1 billion t of oil shale.[21,22]

The influence of pyrolysis type on shale oil generation and its composition was studied. For that purpose, Rock-Eval, TGA and pyrolysis in the open and the closed systems were used. The investigations were performed on the new samples from the Upper layer, of Aleksinac oil shale, which were characterized in detail. The impact of kerogen content and type on the shale oil generation in different pyrolysis systems was also estimated.

This investigation refers to content, type and thermal behaviour of OM. The conclusion is that the yield of pyrolysis products, namely the bulk composition of shale oil, represents the basis for assessing the energy efficiency of the processing oil shale, and for the increasing of its conversion into shale oil, through environmentally friendly retorting technology.

Geological setting of Aleksinac oil shale deposit

The Aleksinac oil shale deposit is located about 200 km southeast from Belgrade (Fig. S-1 of the Supplementary Material to this paper), covering an area of over 13 km^2. The resources of in-place shale oil are about 150 million t.[22] The Aleksinac oil shale deposit is divided by fault zones into three major blocks: Dubrava, Morava and Logorište.[23]

The Aleksinac oil shale is deposited in lacustrine environment during the Lower Miocene. The Lower Miocene lacustrine sequence is up to 800 m thick. These sediments comprise two layers of oil shales, Lower oil shale layer with average net thickness of about 20 m and Upper oil shale layer, having an average net thickness of about 56 m. The Aleksinac Main coal seam is between them (2–6 m, locally up to 15 m thick; Fig. S-2 of the Supplementary material). That complex is covered by Upper Miocene complex up to 700 m thick and consisting of marl, clay, sand and conglomerate.[24] Outcrops of both coal and oil shale are exposed at the surface in the area of an abandoned open-pit mine.

Within this study sixteen samples from the outcropping oil shale Upper layer of the Dubrava block (250 m thick sequence above the Main coal seam) were investigated. The samples were taken as discontinuous channel samples, from the top of bituminous marl sequence to the bottom of the Upper oil shale layer. The description of analysed samples is given in Table I.

EXPERIMENTAL

The samples were crushed and then pulverized to < 63 μm. Rock-Eval pyrolysis, TGA and pyrolysis in open and close systems were used for pyrolytic experiments.

Rock-Eval pyrolysis was carried out by Rock-Eval 6 Standard analyser. For that purpose, about 25 mg of pulverized sample was used. IPF 160000 calibration sample was used as the standard.

TABLE I. The values of Rock-Eval parameters

Sample No.	Lithology	*TOC*[c] wt. %	*S1*[d] mg HC[e] (g rock)$^{-1}$	*S2*[f] mg HC (g rock)$^{-1}$	*S3*[g] mg CO$_2$ (g rock)$^{-1}$	*HI*[h] mg HC (g TOC)$^{-1}$	*OI*[i] mg CO$_2$ (g TOC)$^{-1}$	S2/S3	*PI*[j]	$T_{\max}$[k] °C	*PY*[l] kg HC (t rock)$^{-1}$	*GP*/*OC*[m] mg HC (g TOC)$^{-1}$	*PC*[n] wt. %	*PC*/*TOC* %	*RC*[o] wt. %
D1	BM[a]	2.85	0.19	18.59	2.12	652	74	8.77	0.01	439	18.78	659	1.58	55	1.27
D2	OSh[b]	7.06	0.50	52.03	3.85	737	55	13.51	0.01	438	52.53	744	4.56	65	2.50
D3	BM	3.87	0.26	24.63	2.38	636	61	10.35	0.01	437	24.89	643	2.19	57	1.68
D4	BM	1.79	0.11	8.13	1.83	454	102	4.44	0.01	437	8.24	460	0.77	43	1.02
D5	OSh	5.44	0.28	38.36	3.09	705	57	12.41	0.01	439	38.64	710	3.37	62	2.07
D6	BM	1.31	0.07	5.24	1.36	400	104	3.85	0.02	444	5.31	405.	0.51	39	0.80
D7	BM	1.88	0.14	8.62	1.65	459	88	5.22	0.01	440	8.76	466	0.81	43	1.07
D8	OSh	5.20	0.31	37.85	2.85	728	55	13.28	0.01	439	38.16	734	3.31	64	1.89
D9	OSh	5.10	0.32	35.46	2.81	695	55	12.62	0.01	439	35.78	702	3.11	61	1.99
D10	OSh	8.22	0.38	64.17	4.14	781	50	15.50	0.01	439	64.55	785	5.57	68	2.65
D11	BM	3.83	0.21	23.75	2.42	620	63	9.81	0.01	437	23.96	626	2.13	56	1.70
D12	OSh	7.20	0.43	53.81	3.88	747	54	13.87	0.01	440	54.24	753	4.70	65	2.50
D13	OSh	13.10	1.90	112.34	4.29	858	33	26.19	0.02	443	114.24	872	9.72	74	3.38
D14	OSh	4.01	0.32	25.17	2.09	628	52	12.04	0.01	438	25.49	636	2.23	56	1.78
D15	OSh	8.61	0.76	63.88	3.93	742	46	16.25	0.01	439	64.64	751	5.59	65	3.02
D16	OSh	29.10	2.85	180.10	9.03	619	31	19.94	0.02	436	182.92	629	18.50	64	10.60

[a]BM – Bituminous marlstone; [b]OSh – Oil shale; [c]TOC – Total organic carbon; [d]S1 – Free hydrocarbons; [e]HC – Hydrocarbons; [f]S2 – Pyrolysate hydrocarbons; [g]S3 – Amount of CO$_2$ generated from oxygenated functional groups; [h]*HI* – Hydrogen index = (100S2)/TOC; [i]*OI* – Oxygen index = (100S3)/TOC; [j]*PI* – Production index = S1/(S1+S2); [k]$T_{\max}$ – Temperature corresponding to S$_2$ peak maximum; [l]*PY* – Potential yield = S1+S2; [m]*GP*/*OC* – genetic potential = 100(S1+S2)/TOC; [n]*PC* – Pyrolysable carbon; *PC*/*TOC* = 100PC/TOC; [o]RC – Residual carbon

Thermogravimetric analysis (TGA) was conducted using a Q5000 thermometric analyser (TA Instruments, UK). Approximately 3–3.5 g of sample was heated at heating rates of 10 and 50 °C min^{-1} from 30 to 600 °C. Nitrogen was used as the purge gas with the flow rate of 25 $\text{cm}^3\ \text{min}^{-1}$. During non-isothermal analysis, the loss of mass was recorded as a function of temperature.

The pyrolysis experiments in open and closed systems were performed on selected samples, which have shown the highest hydrocarbon potential according to data from Rock-Eval pyrolysis and TGA. For these experiments the bitumen-free samples which contain kerogen with native minerals were used.

The open system (Pyrolyser, Model MTF 10/15/130 Carbolite, UK) and the closed system (autoclave) pyrolyses were carried out under a nitrogen atmosphere during 4 h at a temperature of 400 °C, with heating rate of 5°C min^{-1}. The initial masses of the bitumen-free samples used in open system and close pyrolysis system were ~1.5 and 5 g, respectively. Liquid pyrolysis products were extracted using hot chloroform.

The liquid pyrolysates were separated into aliphatic-, aromatic- and NSO- (polar fraction, which contains nitrogen, sulphur, and oxygen compounds) fractions, using column chromatography over SiO_2 and Al_2O_3. The aliphatic hydrocarbon fractions were eluted with *n*-hexane, the aromatic HCs with benzene, and the NSO-fractions with a mixture of methanol and chloroform (1:1 volume ratio). Aliphatic fractions were further analysed by gas chromatography–mass spectrometry (GC–MS). Detailed description of this analysis is given in the previous publications.[25,26]

The solid residues obtained from both pyrolyses were dried and weighed. The yield of gas was calculated as: 100 % – (yield of shale oil + yield of solid residue).

RESULTS AND DISCUSSION

Rock-Eval pyrolysis and TGA were used to determine the type, quantity, maturity and hydrocarbon potential, as well as the thermal behaviour of OM of oil shale samples. The samples which showed the highest hydrocarbon potential according to above mentioned pyrolytic techniques are subjected to pyrolysis in the open and the closed systems. These pyrolyses are used to determine the optimal conditions for the obtaining of high yields of shale oil, rich in HCs.

Rock-Eval pyrolysis

Rock-Eval pyrolysis was used as a preliminary method for the determination of the hydrocarbon generative potential of oil shale OM. The values of parameters obtained by Rock-Eval pyrolysis are given in Table I. The literature reference values as criteria for the determination of hydrocarbon potential and kerogen type for immature source rock, as well as for OM maturity, are listed in Table II.[27]

Quantity of organic matter

The total organic carbon (TOC), as a measure of the quantity of OM, including the amounts of soluble (bitumen) and insoluble (kerogen) OM in sedimentary rock, in the range from 1.31 to 29.10 wt. % (average 6.79 wt. %; Table I). TOC values of all samples, with the exception of D4, D6 and D7, are higher than 4 wt. %, and correspond to the immature source rocks with excellent generative potential (Tables I and II).[27] Pyrolysis of oil shale can be cost effective, only in case if OM can be a source of energy for its own pyrolysis process that produce a certain amount of shale oil for further usage. Majority of the analysed samples have TOC values > 5 wt. %, which is considered a threshold of interest for the cost effective retorting processing of oil shale.[6] However it was shown that the oil shale containing TOC ~ 2.5 wt. % at least can produce energy that is spent for its own pyrolytic process.[6,28] Therefore, the samples having TOC in range 2.5–5 wt. % can be also of certain interest for retorting processing. Only three samples of bituminous marlstone (D4, D6 and D7) have TOC values < 2 wt. % (Table I). This means that they cannot be considered as source of energy.

TABLE II. The reference values for hydrocarbon potential, kerogen type (related to immature source rocks) and maturity[27]; for abbreviations of the parameters, see legend of Table I; K – kerogen

HC potential	*TOC* wt. %	S1 mg HC^{e} (g rock)$^{-1}$	S2, mg HC (g rock)$^{-1}$	K	HI mg HC (g TOC)$^{-1}$	*OI* mg CO$_2$ (g TOC)$^{-1}$	S2/S3	Maturity	*PI*	$T_{\max}{}^{j}$ °C
Poor	< 0.5	< 0.5	< 2.5	I	> 600	< 40	> 15	Immature	< 0.10	< 435
Fair	0.5–1	0.5–1	2.5–5	II	300–600	15–70	10–15	Early mature	0.10–0.15	435–445
Good	1–2	1–2	5–10	II/III	200–300	–	5–10	Peak	0.25–0.40	445–450
Very good	2–4	2–4	10–20	III	50–200	50–150	1–5	Late mature	> 0.40	450–470
Excellent	> 4	> 4	> 20	IV	< 50	–	< 1	Postmature	–	> 470

The content of free hydrocarbons (S1), indicates the amount of HCs present in the rock in a free or absorbed state, varying from 0.07 to 2.85 mg HC (g rock)$^{-1}$ (average 0.56 mg HC (g rock)$^{-1}$; Table I). Most of the analysed samples have low S1 values < 0.5 mg HC (g rock)$^{-1}$, which may suggest poor potential or low thermal maturity of the OM (Tables I and II).[27,29] However, S2 > 20 mg HC (g rock)$^{-1}$ in most of the samples, which is indicative for the excellent immature source rock, implies that the low S1 values could be attributed to low maturity, not to poor generative potential (Tables I and II).[27]

Quality of organic matter

Values of hydrogen index (*HI*), oxygen index (*OI*) and S2/S3 ratio indicate that majority of the analysed samples predominantly contain types I and/or II kerogen (Tables I and II). Predominance of type I kerogen was observed exclusively in the sample D13, whereas the samples D4, D6 and D7 are characterised by the prevalence of type II kerogen with certain input of type III kerogen.[27,30]

Maturity of organic matter

Production index (*PI*) indicates the HCs amount that has been produced naturally, relative to the total amount of HCs which the sample can produce. Values of *PI* in range from 0.01 to 0.02 indicate an immature *OM*, confirming that low *S1* values resulted from low thermal maturity (Tables I and II).[27]

$T_{\max}$ corresponds to the temperature of the maximum generation of HCs during pyrolysis (*S2* peak maximum). $T_{\max}$ value depends on the kerogen type, and for kerogen type I is higher than others.[16,30,31] $T_{\max}$ ranges from 436 to 444 °C in analysed samples, indicating immature to early mature stage (Tables I and II).

Hydrocarbon generative potential

As it was mentioned hydrocarbon generative potential depends on type, quantity and level of thermal maturity of OM.[6] Results from Table I clearly indicated that OM of all samples is immature to early mature. Therefore, in such a case hydrocarbon generative potential depends on OM type and quantity. Previous discussion (*TOC*, *HI*, *OI*, S2/S3) indicate that all samples, except bituminous marlstones D4, D6 and D7 are rich in OM, represented by oil prone kerogen type I or II or their mixture.

In Rock-Eval terms the *TOC* consists of pyrolysable (PC) and residual (RC) carbon. PC corresponds to the carbon content present in the HCs (S1 + S2). 100*PC*/*TOC* >30 % are typical for an oil prone source rock, while 100*PC*/*TOC* < 30 % indicates a gas prone source rock.[31] Most of the samples have 100*PC*/*TOC* in range from 55 to 65 % (Table I), implying the high oil potential. Based on the percentage of *PC* in *TOC*, the samples D4, D6 and D7 stand out with the lowest value (~40 %; Table I) and the sample D13 with the highest value (> 70 %; Table I). These results are consistent with the estimated kerogen type. RC represents the carbon in kerogen which has very a low potential to generate liquid HCs. The RC percentage of the *TOC* decreases in the following order III>II>I kerogen type.[31] Analysed samples have relatively low RC values (Table I), which confirms high quality of OM.

PY value represents the maximum quantity of HCs that a sufficiently matured source rock might generate.[7] *PY* values range from 5.31 to 182.92 kg HC (t rock)$^{-1}$ (average value 47.57 kg HC (t rock)$^{-1}$, Table I) and increase as *TOC* values increase. In all samples *PY* is higher than 2 kg HC (t rock)$^{-1}$ which is considered as a limiting value for a possible oil source rock.[32,33] Comparing the obtained *PY* values with reference data, as well as based on the *PY vs*. *TOC* diagram (Fig. 1), almost all samples have excellent, D4 and D7 have good, whereas only the sample D6 has a fair to good source rock generative potential.[6,32,34]

The ratio of genetic potential (*GP*/*OC*) is obtained by the normalisation of *PY* values to *TOC* content of analysed samples.[35] It ranges from 405 to 872 mg HC (g TOC)$^{-1}$, and have the same trend as *PY* values, except for the sample D16 that has significantly lower GP/OC ratio, due to the notably higher TOC content (Table I).

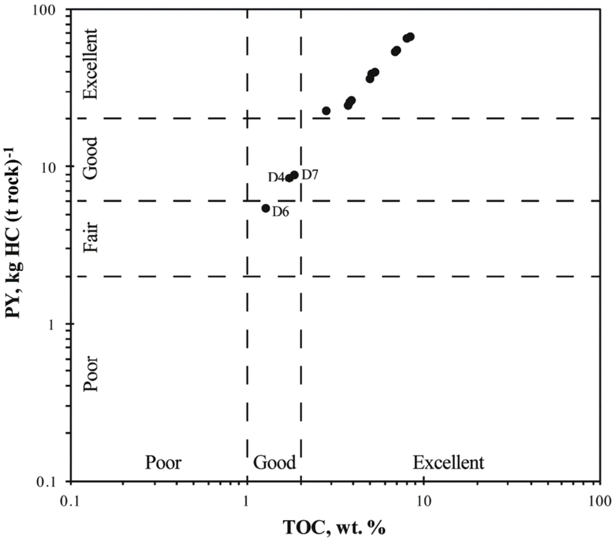

Fig. 1. Plot *PY vs. TOC*.

Summarizing the Rock-Eval data (Table I), the conclusion can be drawn that all samples contain immature *OM*. The most of analysed samples have high potential for oil generation, except three samples of bituminous marlstone (D4, D6 and D7) that display the lowest quantity (*TOC*, S2, *PY*; Table I) and the lowest quality of *OM* (*HI*, *OI*, S2/S3, *PC*, Table I and Fig. 1), which clearly implicates a poorer hydrocarbon generative potential.

Thermogravimetric analysis (TGA)

General information about thermal behaviour of oil shale, according to the composition of *OM* and the heating rate, can be obtained using TGA results. During a complex multistage process of decomposition of oil shale, numerous reactions occur simultaneously, and the TGA measures the overall weight loss of these reactions.[2,4,12,36] These reactions control the distribution of the products, because during the pyrolysis process of oil shale various products are formed and some of them can serve as new reactants in further reactions. At the beginning of the pyrolysis process primary reactions occur that lead to the distillation of volatile, low molecular weight compounds. With a further increase of temperature in addition to the increased rate of volatilization due to the evaporation of high molecular weight compounds, secondary reactions may occur, such as cracking of the produced vapour and the formation of some insoluble char.[37–39] The TGA results of the studied samples are presented in Figs. 2 and 3.

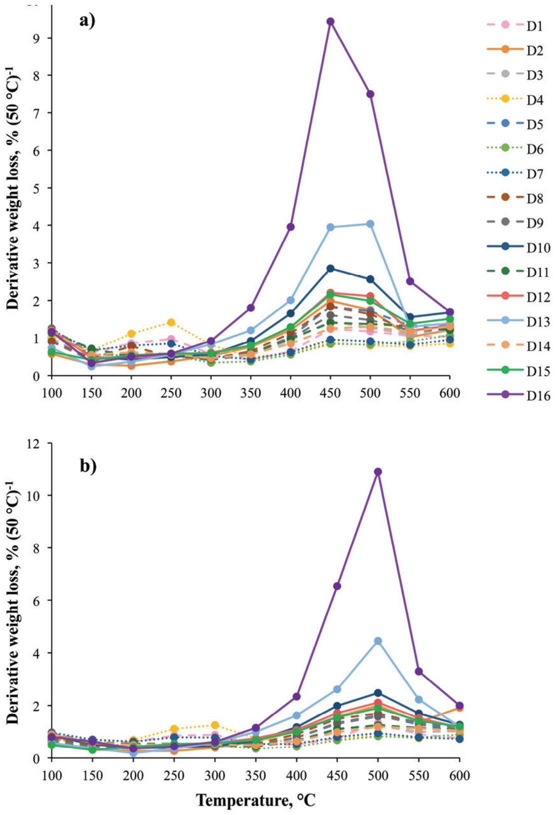

Fig. 2. DTG curves at heating rates of 10 (a) and 50 °C min^{-1} (b). [For full color versions of the figures from this paper, refer to its electronic version at web pages of the journal: http://shd.org.rs/jscs].

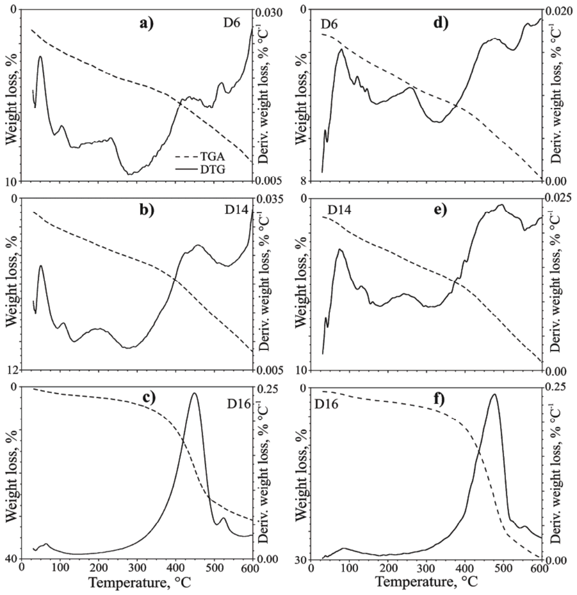

Fig. 3. The characteristic weight loss (TGA, dashed line) and derivative weight loss (DTG, full line) curves of representative samples (D6, D14 and D16) at heating rates of 10 (a–c) and 50 °C min^{-1} (d–f).

Thermal behavior of oil shale

On the graphs of Fig. 2 there are two peaks that correspond to the temperatures of the maximal rate of weight loss. The first peak at temperatures of about 200 °C corresponds to the loss of moisture, including adsorbed and interlayer water from clay minerals.[36] The weight loss at temperatures $\leq$ 300 °C can be attributed to the evaporation of the free bitumen and the physical changes in kerogen which caused the softening of kerogen and molecular rearrangement that lead to the release of the gas, prior to its decomposition into bitumen.[10,40]

The second peak occurs in the temperature range from 300 to 550 °C, which corresponds to the major mass loss and it is attributed to loss of HCs. The obtained results (Fig. 2) are in agreement with literature data, which showed that the lowest temperature for the primary degradation of kerogen is about 350 °C and it continues up to 550 °C.[2,10,12] Generally, the temperature range between 300 to 600 °C is considered as the main stage of decomposition of OM, and the weight loss occurred mainly due to the volatalisation of bitumen and the decomposition of kerogen and bitumen, that leads to the release of low molecular weight volatiles and the formation of char.[10,11,14,41] In this temperature range the mineral decomposition contributes to a lesser degree. The main stage of mineral decomposition requires the temperatures above 600 °C.[10–12,14]

The obtained results indicate that only the bituminous marlstone samples D4, D6 and D7 have a greater loss of weight at temperatures up to 300 °C, than at temperatures of the main stage of the decomposition of kerogen (Figs. 2 and 3).

This is consistent with the significant proportion of gas prone kerogen type III in OM of these samples (Tables I and II). The rest of the samples showed greater loss of weight in the temperature range 450–550 °C (Fig. 2), consistent with oil prone kerogen type I/II. However, in this temperature range greater weight loss is observed for the samples D16, D13, D10, D12, D15 and D2, which produce higher amounts of hydrocarbons by Rock-Eval pyrolysis and have higher content of *TOC* (S2 > 50 / mg HC (g rock)$^{-1}$, *TOC* > 7 wt. %; Table I). The obtained result suggests that among Rock-Eval parameters, S2 and *TOC* fit the best with TGA behaviour for immature samples.

Influence of heating rate on weight loss

TGA and DTG curves (Figs. 2 and 3) imply that the heating rate has an influence on weight loss. It is visible from the position, the abundance and the shape of peaks. The temperature range at which maximum weight loss occurs for slower heating rate is 400–450 °C (maximal temperature ~425 °C; Figs. 2a and 3a–c), while for faster heating rate it corresponds to temperatures between 450 and 500 °C (maximal temperature ~475 °C; Figs. 2b and 3d–f). These indicate that with the increasing heating rate the complete decomposition occurs at higher temperature and thus the decomposition peak shifts to higher temperature.

Furthermore, the faster heating rate results in the decrease of the weight loss of the decomposition peaks (Figs. 2 and 3). In the samples that were recorded with the faster heating rate (50 °C min^{-1}; Figs. 2b and 3d–f) the shape of the decomposition peak was sharp, while in the samples that were recorded with the slower heating rate (10 °C min^{-1}; Figs. 2a and 3a–c) the kerogen decomposition gave a response to the graphics in the form of a wider and blunter peak. These results could be explained by variations in the rate of heat and mass transfers, exposure time to a particular temperature and the changes in the kinetics of thermal decomposition with the change in the heating rate.[2,42,43] With the slower heating rate the particles are heating more uniformly, the exposure time to a particular temperature is longer and the pyrolysis process is slower. This allows better heat and mass transfers and the components are gradually one by one released from kerogen. By the faster heating rate the components are generated faster, and they cannot diffuse out of pores, therefore they require higher temperature and then they are released from kerogen at the same time. Furthermore, the external surface of oil shale samples is exposed to higher temperature than the insight particles, which can cause the secondary reactions which reduce the HCs weight loss.

Considering that the weight loss of oil shale is associated with the potential to generate HCs, namely the ability to generate the shale oil, the greater loss of weight implies the greater potential for generation of HCs. Samples D16, D13, D10, D12, D15 and D2 showed the greatest loss of weight, while the samples D4, D6 and D7 displayed the smallest weight loss (Figs. 2 and 3). The obtained results from thermogravimetric analysis are consistent with the amount of HCs generated during the Rock-Eval pyrolysis (S2, PC; Table I) and determined quantity and quality of *OM* (Tables I and II).

The open and closed pyrolysis system

Five samples (D2, D10, D13, D15 and D16) that have shown the highest hydrocarbon potential based on Rock-Eval parameters and TGA were subjected to pyrolysis in the open and closed systems in order to evaluate the hydrocarbon potential in more detail simulating maturation changes, as well as to determine the yields of pyrolysis products and bulk composition of shale oil. The results from the open and closed pyrolysis system are given in Table III.

Distribution of pyrolysis products

In the open system, the highest yield of shale oil is observed for the sample D16, which is expected since it has the highest quantity of *OM* (*TOC*; Table I) and the highest loss of weight (Figs. 2 and 3). The sample D13 has the highest yield of shale oil in the closed system. This sample showed the highest yield of shale oil normalized to *TOC* content in both pyrolysis systems. The result could be attributed to the fact that the sample D13 was the exclusive sample which *OM* predominantly consists of type kerogen I that is the richest in hydrogen and therefore can produce the greatest amount of liquid pyrolysate (Tables I and II). This also coincides with HI, GP/OC and the content of PC in D13 sample (Table I).

TABLE III. The yields of pyrolysis products and the bulk composition of obtained shale oil

System	Sample No.	Yield of shale oil[a] %	Yield of solid residue[a] %	Yield of gas[b] %	Yield of shale oil[c] mg (g TOC)$^{-1}$	Yield of HC[a] ppm	Yield of HC[c] mg (g TOC)$^{-1}$	Bulk composition of shale oil		
								Aliphatic HCs %	Aromatic HCs %	NSO %
Open	D2	1.98	91.02	7.00	280	1520	21.52	8.85	20.69	70.46
	D10	2.22	88.82	8.96	270	4516	54.94	15.33	30.00	54.67
	D13	5.70	87.24	7.08	434	4347	32.82	12.53	26.38	52.63
	D15	2.12	91.05	6.83	246	4488	52.12	17.11	29.61	53.29
	D16	10.65	79.22	10.14	366	7222	24.82	29.80	41.72	28.48
Closed	D2	1.03	92.60	6.37	146	1866	26.91	7.69	28.21	64.10
	D10	1.39	88.59	10.02	169	1665	20.68	7.19	25.49	67.32
	D13	4.39	85.82	9.79	335	1790	13.66	4.53	18.40	77.07
	D15	1.33	91.69	6.98	154	1630	18.58	3.27	28.76	67.97
	D16	3.90	70.31	25.79	134	2255	7.75	5.35	24.92	69.73

[a] The yield relative to bitumen-free sample; [b] yield of gas = 100 % – (yield of shale oil+ yield of solid residue); [c] the yield relative to the TOC

The yield of HCs in pyrolysates from the open system corresponds to the values for an excellent source rock potential, with exception of the sample D2 which shows a very good potential (Table III). This is consistent with Rock-Eval parameters and TGA data, since among the five analysed samples, D2 has the lowest *TOC*, S2 and weight loss in the temperature range 450–550 °C (Table I; Fig. 2). On the other hand, the yield of HCs in pyrolysates of all samples from the closed system indicates a very good source rock potential (Table III).[27]

The lower yields of shale oil in the closed system than in the open system resulted from secondary reactions that occur in this reaction medium and contribute to the formation of gas and solid residue. In an open system, as in TG analyzer, secondary processes are occurring less because the HCs generated by the primary kerogen cracking are released from the reaction medium fast, being carried by an inert gas, and then immediately collected in a cold trap. On the other hand, in a closed system due to the retention of all products in a reaction medium and the influence of pressure, they are in close contact with each other for longer time. Therefore, after primary reactions, generated products (oil, gas and carbon residue) interact with hot particles and secondary reactions occur, such as further thermal oil cracking, coking of oil vapour on carbon residue, as well as recombination, condensation and aromatisation processes.[44,45] This resulted in higher yields of gas and solid residue in the closed system (Table III). Additionally, the yield of solid residue can be affected by the coke aggregates and its accumulation on the solid residue.[46] Coke formation has been attributed to the dehydrogenation, polymerisation and condensation reactions of asphaltenes, aromatic compounds and alkenes.[1,46–48] Therefore, solid residue represents the insoluble portion of kerogen products (coke and char) that remains in the spent shale associated with mineral matter.

Since oil shale contains a significant part of mineral matter in which OM is finely dispersed, it has an important role in kerogen decomposition. Minerals have catalytic and adsorption influence on reaction products and can induce cracking and/or coking of them.[1,48]

Bulk composition of obtained shale oil

The bulk composition of the analysed samples shows that by maturation in the closed system the lower amount of HCs is obtained thus higher percentage of NSO-compounds (Table III). This can be an undesirable feature of the obtained shale oil and may require additional treatment before utilization. Furthermore, the composition of HCs in the pyrolysates from the closed system show notably higher content of aromatic than aliphatic compounds (Table III), which resulted from the secondary reactions of cyclisation and aromatisation.[5] On the other hand, the bulk composition of pyrolysates from the open system shows a greater amount of total HCs, which is associated with the higher contribution of aliphatic relative to aromatic HCs in comparison to the close system pyrolysis (Table III). The analysis of composition of aliphatic fractions in shale oils obtained by closed and open pyrolysis systems using GC–MS indicate that main components in both cases are *n*-alkanes and terminal *n*-alkenes (Fig. 4).

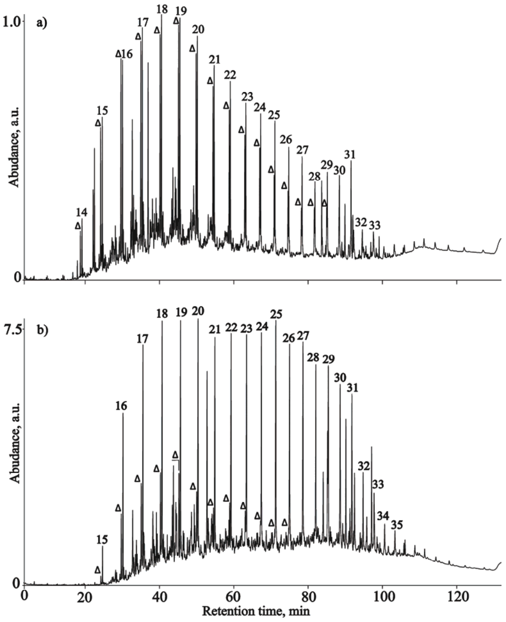

Fig. 4. The characteristic total ion current of aliphatic fraction of from the open (a) and closed (b) system. *n*-Alkanes are labelled according to their carbon number; Δ – terminal *n*-alkenes.

The shale oil from the open system contain higher amount of olefinic HCs than those obtained in autoclave. This result is expected, since, it is well known that during pyrolysis in the open system large quantities of olefins can be formed due to the vapour-phase free radical cracking reactions. The formed radicals cannot interact with each other due to the prompt removal from the pyrolysis medium.[49] Depending on application, the presence of olefins may be an undesirable characteristic of shale oil that can requires further treatment.

The pyrolysis in the open system results in higher yield of shale oil than the pyrolysis in the closed system. The quality of obtained shale oil has undesirable features due to content of olefinic HCs (open system) and NSO-compounds (closed system) and may require further treatment to be used.

CONCLUSION

New samples from the Upper layer of Aleksinac oil shale (Dubrava block) were investigated in detail, by the different types of pyrolysis, aimed to determine the capability and the most appropriate conditions for its conversion into shale oil. Rock-Eval pyrolysis and TGA were employed to determine the type, quantity, thermal maturity and hydrocarbon potential of OM, as well as the thermal behaviour of oil shale samples. Pyrolysis in the open and the closed systems was used to determine the optimal conditions for obtaining high yields of shale oil, rich in HCs.

Majority of the analysed samples have *TOC* > 5 wt. %, which represents the content of *OM* in oil shale of particular economic interest, and contain kerogen types I and/or II with a high potential for oil generation. Only the samples D4, D6 and D7 of bituminous marlstone have *TOC* < 2 wt. % and contain kerogen type II with certain input of gas prone kerogen type III, which make them undesirable for the retorting process.

The weight loss obtained by TGA is in agreement with Rock-Eval parameters. This is particularly important for D4, D6 and D7 samples, since no significant loss of weight in the main stage of the kerogen decomposition confirmed lower hydrocarbon potential.

Pyrolysis in the open system produces higher yield of shale oil than in the closed one. The yields of HCs in pyrolysates from the open system correspond to the values for an excellent source rock potential, whereas yields of HCs in pyrolysates from the closed system indicate a very good source rock potential. The obtained results showed that the quantity of OM (*TOC*) has a greater impact on the shale oil generation than the kerogen type (HI) in the open pyrolysis system. On the other hand, HI plays a more important role on the generation of shale oil than *TOC* in the closed pyrolysis system. This indicates that only in the pyrolytic conditions which simulate significant increase of maturity, the kerogen type has remarkable impact on conversion of oil shale into shale oil.

The shale oil from the open and the closed pyrolysis has high content of the olefinic HCs and NSO-compounds, respectively, which can be undesirable components. Depending on application, further treatment to reduce these compounds in shale oil may be required.

The obtained results indicate that samples from the Upper layer of Aleksinac oil shale deposit have heterogeneous thermal behaviour. Consequently, it is necessary to perform preliminary analyses to estimate their hydrocarbon potential and processability by retorting before the investigated area can be considered for exploitation.

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ИЗВОД

УТИЦАЈ ТИПА ПИРОЛИЗЕ НА ГЕНЕРИСАЊЕ И САСТАВ СИНТЕТИЧКЕ НАФТЕ (ПОВЛАТНИ СЛОЈ АЛЕКСИНАЧКИХ УЉНИХ ШКРИЉАЦА)

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Испитиван је утицај типа пиролизе на генерисање синтетичке нафте и њен састав. Примењене су различите методе као што су Rock-Eval пиролиза, термогравиметријска анализа и пиролиза у отвореном и затвореном систему. Узорци из повлатног слоја алексиначких уљних шкриљаца коришћени су као супстрат и по први пут су детаљно окарактерисани. Утицај количине и типа керогена на генерисање синтетичке нафте у различитим пиролитичким системима је такође процењен. Већина анализираних узорака има садржај укупног органског угљеника већи од 5 % и садржи кероген типа I и/или II који има висок потенцијал за генерисање нафте. Стога они могу бити од посебног интереса за пиролитичке процесе. Термичко понашање и губитак масе анализираних узорака на основу термогравиметријске анализе у сагласности су са Rock-Eval параметрима. Пиролиза уљних шкриљаца у отвореном систему даје веће приносе синтетичке нафте него пиролиза у затвореном систему. Принос угљоводоника у синтетичкој нафти добијеној у отвореном систему одговара одличном потенцијалу за матичне стене, док принос угљоводоника у затвореном систему указује на врло добар потенцијал. Садржај керогена има већи утицај на генерисање синтетичке нафте него тип керогена у отвореном ситему, док тип керогена има значајнију улогу од његове количине за генерисање синтетичке нафте у затвореном систему. Састав добијене синтетичке нафте има одређене непожељне карактеристике, због релативно већег садржаја олефинских угљоводоника (отворен систем) и поларних једињења (затворен систем), које могу захтевати даљи третман пре употребе.

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