

Evaluation of saturated and aromatic hydrocarbons oil–oil maturity correlation parameters (SE Pannonian Basin, Serbia)

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Abstract: Twenty three crude oils from the Serbian part of the Pannonian Basin (14 from the Vojvodina Province and 9 from the Drmno Depression) were investigated, aimed at an evaluation of oil–oil maturity correlation parameters based on the distribution and abundance of saturated biomarkers and alkylarene constituents. Factor and cluster analyses were used for this purpose. Factor analyses using varimax rotation were first run separately, *i.e.*, of maturity parameters based on the abundance of (a) *n*-alkanes and isoprenoids, (b) steranes and triterpanes, (c) alkylnaphthalenes, and (d) alkyphenanthrenes. These analyses yielded 9 important “maturity factors”. Eight of them, showing higher than 30 % of variance, were further involved in another factor analysis, as well as in cluster analysis using the Ward method. In this way, all maturity parameters based on saturated biomarkers and alkylarenes were evaluated and ranged, considering the fact that the observed factors represented their linear combinations. The results showed that in the correlation of crude oils from the Serbian part of the Pannonian Basin, the most important were maturity parameters based on isomerization reactions involving one methyl group in thermodynamically less stable α -methyl naphthalenes, ethyl naphthalenes, dimethyl naphthalenes and methyl phenanthrenes, and their change into more stable isomers with the methyl group in the β -position in the aromatic ring. Processes constituting high loadings factor 2 and factor 3 parameters were also defined. Hierarchy between the “factors” and parameters were controlled, and approved, by cluster analysis using the Ward method. Finally, the investigated crude oils were correlated by factor and cluster analyses, using all the important “maturity factors”. Differences in maturity were observed between the Vojvodina and Drmno Depression crude oils, as well as between oils originating from South Banat, North Banat and the Velebit oil field (Vojvodina locality).

Keywords: crude oils, SE Pannonian Basin, saturated biomarkers, alkylarenes, maturity, factor and cluster analyses.

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INTRODUCTION

Due to the advancement of instrumental methods, such as gas chromatography (GC), gas chromatography–mass spectrometry (GC–MS), and recently GC–MS–MS, very small (ppm) amounts of crude oil components were identified. On the other hand, biosphere → geosphere transformation processes of a large number of petroleum constituents were explained. Evidently, in addition to origin, the chemical composition of crude oils and thus their physical and physico-chemical properties depended on the depositional environment, length of migration path, thermal maturation, microbiological degradation, water washing, and lithology, temperature and pressure of the source and reservoir rocks.^{1,2}

From the point of view of exploration studies, crude oil thermal maturation may be considered as one of the most important geochemical effects. Maturation processes involve cracking, isomerization and aromatization reactions, as well as alkylation and dealkylation of aromatic rings. They commence in the source rocks; continue during migration and in the reservoir rocks. During a long geological time, they have been affected by heat, pressure and mineral catalysts,^{3–5} which resulted in the formation of thermodynamically more stable structural and stereochemical isomers or smaller molecules, as well as in transformation of saturated into aromatic hydrocarbons. The degree of maturity is most often estimated on the basis of parameters calculated from the distribution and abundance of saturated^{6–8} and aromatic hydrocarbons,^{9–16} *i.e.*, compounds which generally constitute 95–98 % of crude oils.

Isomerization processes at chiral centers or in rings were used in maturity estimation more often compared to cracking reactions, aromatization or alkylation–dealkylation processes.² Parameters based on these processes also served for corresponding correlations with vitrinite reflectance and depth of source rocks, as well as with the maximal expulsion temperature of hydrocarbons. Moreover, they also help in obtaining a better evaluation of reservoir potentials and contribute to reducing the number of dry boreholes.^{17–20}

A great number of different maturity parameters were hitherto proposed. However, practically all of them were shown to perhaps depend on several of the above-mentioned factors. Moreover, equilibria of a number of isomerization reactions, *e.g.*, moretanes → hopanes; 22*R* → 22*S* hopanes; 14 α (H)17 α (H) → 14 β (H)17 β (H) steranes; 20*R* → 20*S* steranes, are attained before the end of catagenetic changes of organic matter of the source rock. Therefore, reliable evaluation of maturity parameters and their applicability in oil–oil and oil–source rock correlations required the simultaneous critical consideration of all known maturity parameters.^{2,16}

In this paper, the applicability of almost all the hitherto known maturity parameters, based on the distribution and abundance of saturated and aromatic hydrocarbons, was investigated using as an example 23 crude oil samples origin-

nating from the Serbian part of the Pannonian Basin (14 from Vojvodina localities and 9 from the Drmno Depression). For this purpose, different advanced multivariate statistical methods^{18,21-27} were available. A new statistical approach was chosen, based on factor and cluster analyses. The investigated oils were finally correlated according to maturity, using simultaneously all statistically selected crude oil maturity parameters.

EXPERIMENTAL

The most important oil and gas deposits in Serbia were discovered in the Banat Depression (south-eastern part of the Pannonian Basin). The major part of the Banat Depression is located on the territory of Vojvodina (north of the Sava and Danube rivers), while its smaller, southern part, is situated in the vicinity of the city of Požarevac (south of the Sava and Danube), forming the separate, smaller, Drmno Depression (Fig. 1).

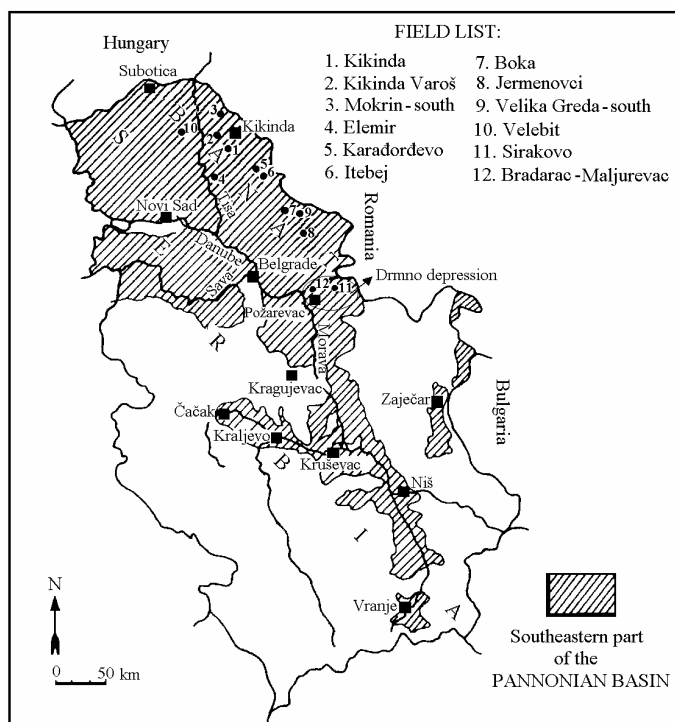


Fig. 1. Serbian Part of the Pannonian Basin with the localities of oil fields indicated.

The Banat Depression, with a surface of approximately 13,500 km², is located in the south-eastern part of the Pannonian Basin. Twenty-three samples of crude oils from twelve Banat Depression oil fields were investigated in this study, 14 samples originating from localities in Vojvodina, and 9 samples from Drmno Depression localities. The crude oil samples originated from reservoir rocks located at depths of 752–2572 m. All Drmno depression crude oils were found in reservoir rocks of Miocene age, and the crude oils from the Vojvodina localities in reservoir rocks of Paleozoic, Mesozoic, Miocene and Pliocene ages. The stratigraphy of the Drmno Depression has previously been studied in detail and the source rocks of the corresponding crude oils were identified.²⁸⁻³⁴ Crude oils from boreholes Bradarac-Maljurevac 2 and 4 originated from Red Formations. By seis-

mic investigation, a large fault was discovered between these two boreholes (2 and 4). The boreholes Sirakovo 1, 2 and 18 are located in one zone, *i.e.*, in a deeper, faulty zone, whereas the boreholes Sirakovo 19 and 20 are situated in another, shallower zone of the Ottnangian–Carpathian sediments. Badenian oil deposits were found at depths of 1804–1808 and 1985–1989 m.^{29,30,35} Detailed stratigraphic relationships between the Vojvodina Banat Depression crude oils have hitherto not been determined. The locations of their source rocks are still unknown.

The list of the investigated samples, including data on depths, temperature, lithology and age of the corresponding reservoir rocks, is given in Table I. The locations of the corresponding oil fields are shown in Fig. 1.

TABLE I. The investigated crude oil samples with the corresponding basic geological characteristics

Sample	Oil field	Borehole	Depth, m	Reservoir temp., °C	Lithology	Age	
VOJVODINA	V1	Kikinda	23	1196–1200	105.0	Sandstone	Pliocene
	V2	Kikinda	49	1730–1781	–	Sand	Pliocene
	V3	Kikinda-Varoš	3	1897–1942	108.0	Shale	Paleozoic
	V4	Velebit	87	753–759	61.4	Sand	Pliocene
	V5	Velebit	98	752–758	–	Sand	Pliocene
	V6	Velebit	120	756–758	–	Sand	Miocene
	V7	Mokrin-south	8	2040–2047	116.0	Conglomerate	Miocene
	V8	Mokrin-south	11	2040–2045	117.0	Sandstone	Miocene
	V9	Jermenovci	1	896–899	61.7	Marly sandstone	Miocene
	V10	Boka	37/2	1196–1206	76.9	Sandstone, limestone	Miocene
	V11	Karadorđevo	10	2557–2572	139.2	Sandstone	Mesozoic
	V12	Itebej	8	2190–2198	126.6	Aleurolite	Mesozoic
	V13	Elemir	19	1657–1668	99.0	Sandstone	Miocene
	V14	Velika Greda-south	20	1006–1010	60.4	Large-grain sandstone, conglomerate	Miocene
DRMNO – POŽAREVAC	PO1	Sirakovo	1	1778–1782	101.9	Sandstone, aleurolite, breccia, conglomerate	Miocene (Ottangian–Carpathian)
	PO2	Sirakovo	2	1701–1704	98.0	Sandstone, aleurolite, breccia, conglomerate	Miocene (Ottangian–Carpathian)
	PO3	Sirakovo	18	1544–1548	92.2	Sandstone, marlstone, aleurolite, limestone	Miocene (Ottangian–Carpathian)
	PO4	Sirakovo	19	1429–1436	85.8	Sandstone, marlstone, aleurolite, limestone	Miocene (Ottangian–Carpathian)
	PO5	Sirakovo	20	1440–1444	87.8	Sandstone, marlstone, aleurolite, limestone	Miocene (Ottangian–Carpathian)

TABLE I. Continued

Sample	Oil field	Borehole	Depth, m	Reservoir temp., °C	Lithology	Age	
DRMNO – POŽAREVAC	PO6	Bradarac–Ma-ljurevac	2	2302–2307	121.9	Crystalline rock	Miocene (Red Formations)
	PO7	Bradarac–Ma-ljurevac	4	2156–2170	116.0	Marlstone, sandstone, breccia, conglomerate	Miocene (Red Formations)
	PO8	Bradarac–Ma-ljurevac	5	1985–1989	107.0	Sandstone, aleurite, breccia, conglomerate	Miocene (Baden)
	PO9	Bradarac–Ma-ljurevac	10	1804–1808	99.0	Sandstone, aleurite, breccia, conglomerate	Miocene (Baden)

The separation and purification of the saturated and aromatic fractions of the crude oils, as well as the GC and GC–MS techniques, which were used for analyses of *n*-alkanes, isoprenoids, steranes, terpanes, and individual alkylarenes, were explained in detail in previous papers.^{34,36,37}

Based on the distribution and abundance of saturated biomarkers and alkylarenes, numerous maturity parameters were calculated. The values of these parameters observed for the examined Banat Depression crude oils are shown in Tables II and III.

RESULTS AND DISCUSSION

Factor analyses using varimax rotation (program SPSS 11.5 for Windows)^{21,23,25} of the maturity parameters based on the abundance of (a) *n*-alkanes and isoprenoids, (b) steranes and triterpanes, (c) alkyl-naphthalenes, and finally (d) alkyl-phenanthrenes were first run separately.

Factor analysis of n-alkane and isoprenoid maturity parameters

The factor analysis of maturity parameters calculated on the basis of the distribution and abundance of *n*-alkanes and isoprenoids (Table II) resulted in two statistically important “maturity factors”:

$$F_{1\text{alkanes+isoprenoids}} = 0.95\text{CPI} + 0.90\text{CPI } 1 + 0.76\text{Phyt}/n\text{-C}_{18} + 0.37\text{Pr}/n\text{-C}_{17} - 0.09\text{Pr}/\text{Phyt} - 0.02\sum\text{odd}(n\text{-C}_{21} - n\text{-C}_{33})/\sum\text{even}(n\text{-C}_{12} - n\text{-C}_{20})$$

and

$$F_{2\text{alkanes+isoprenoids}} = 0.92\sum\text{odd}(n\text{-C}_{21} - n\text{-C}_{33})/\sum\text{even}(n\text{-C}_{12} - n\text{-C}_{20}) + 0.89\text{Pr}/n\text{-C}_{17} + 0.57\text{Phyt}/n\text{-C}_{18} - 0.55\text{Pr}/\text{Phyt} + 0.19\text{CPI } 1 - 0.03\text{CPI}$$

characterized by variances of 40.50 % and 38.56 %, respectively. As the cited formulae show, the first factor was defined by high loadings (> 0.70) of the parameters CPI and CPI 1, which represented the ratios of the odd *vs.* the even *n*-alkane homologues (in the C₁₄–C₃₅ and C₁₅–C₁₇ ranges, respectively), and the phytane/*n*-C₁₈ ratio. “Maturity factor” 2 was determined by high loadings (> 0.80) of the ratio of higher odd members (*n*-C₂₁–*n*-C₃₃) *vs.* lower even members (*n*-C₁₂–*n*-C₂₀) of *n*-alkane homologous series, and the pristane/*n*-C₁₇ ratio.

TABLE II. Maturation parameters calculated from the distributions and abundances of saturated biomarkers

Sample	CPI	$\frac{\sum_{\text{odd}}(n-C_{21}-n-C_{33})}{\sum_{\text{even}}(n-C_{12}-n-C_{20})}$	$\frac{\text{Pr}}{\text{Phyt}}$	$\frac{\text{Pr}}{n-C_{17}}$	$\frac{\text{Phyt}}{n-C_{18}}$	$\frac{C_{29}\alpha\alpha(S)}{(\alpha\alpha(S)+\alpha\alpha(R))}$	$\frac{C_{29}\beta\beta(R)}{(\beta\beta(R)+\alpha\alpha(R))}$	$\frac{C_{27}\text{dia}}{\text{dia+ster}}$	$\frac{C_{31}(S)}{(S)+(R)}$	$\frac{C_{30}M}{C_{29}H}$	$\frac{C_{30}M}{C_{29}H}$	$\frac{\text{Ts}}{(\text{Ts}+\text{Tm})}$	$\frac{C_{29}\text{Ts}}{C_{29}H}$
V1	1.05	0.83	1.25	0.50	0.46	0.45	0.55	0.26	0.59	0.11	0.09	0.46	0.27
V2	1.05	0.85	1.19	0.51	0.50	0.44	0.54	0.21	0.58	0.13	0.10	0.46	0.25
V3	1.08	0.92	1.53	0.46	0.35	0.50	0.57	0.31	0.58	0.10	0.09	0.53	0.33
V4	1.16	1.11	1.72	0.64	0.48	0.49	0.57	0.27	0.59	0.14	0.09	0.53	0.29
V5	1.31	1.04	1.61	0.70	0.59	0.49	0.57	0.29	0.59	0.10	0.10	0.56	0.31
V6	1.20	0.97	1.49	0.95	0.46	0.48	0.57	0.26	0.59	0.11	0.10	0.55	0.32
V7	1.08	0.86	1.58	0.33	0.25	0.49	0.57	0.33	0.59	0.10	0.08	0.57	0.38
V8	1.11	0.95	1.73	0.39	0.27	0.51	0.57	0.35	0.60	0.10	0.08	0.59	0.37
V9	0.98	0.86	1.73	0.39	0.27	0.51	0.57	0.35	0.60	0.10	0.08	0.59	0.37
V10	0.97	0.77	1.26	0.56	0.60	0.33	0.34	0.03	0.57	0.15	0.14	0.34	0.21
V11	1.02	0.80	1.05	0.87	0.90	0.47	0.49	0.13	0.60	0.11	0.11	0.32	0.17
V12	1.08	0.92	1.24	0.84	0.73	0.48	0.56	0.17	0.60	0.10	0.15	0.33	0.18
V13	1.03	0.84	1.15	0.81	0.70	0.50	0.59	0.23	0.58	0.10	0.15	0.37	0.17
V14	1.04	0.92	1.72	0.63	0.39	0.39	0.46	0.13	0.60	0.11	0.10	0.44	0.25
PO1	1.06	0.79	2.41	0.16	0.08	0.57	0.56	0.52	0.60	0.13	0.08	0.46	0.76
PO2	1.01	0.70	1.45	0.12	0.08	0.53	0.54	0.51	0.61	0.14	0.10	0.48	0.70
PO3	0.93	0.73	1.35	0.14	0.14	0.46	0.56	0.18	0.61	0.13	0.09	0.39	0.43
PO4	1.00	0.81	1.09	0.14	0.13	0.50	0.59	0.19	0.60	0.14	0.12	0.41	0.46
PO5	0.99	0.80	0.87	0.12	0.15	0.47	0.58	0.17	0.61	0.12	0.09	0.41	0.44
PO6	1.00	0.76	2.09	0.22	0.13	0.55	0.60	0.57	0.62	0.12	0.09	0.54	0.81
PO7	0.98	0.72	1.12	0.76	0.30	0.40	0.39	0.04	0.61	0.14	0.08	0.24	0.20
PO8	1.01	0.74	1.19	0.16	0.16	0.48	0.59	0.19	0.61	0.12	0.11	0.43	0.45
PO9	0.81	0.79	0.87	1.02	0.59	0.45	0.56	0.12	0.60	0.12	0.08	0.11	0.07

CPI = $1/2 \left[\frac{\sum_{\text{odd}}(n-C_{15}-n-C_{33})}{\sum_{\text{even}}(n-C_{14}-n-C_{32})} + \frac{\sum_{\text{odd}}(n-C_{15}-n-C_{33})}{\sum_{\text{even}}(n-C_{16}-n-C_{34})} \right]$; CPI 1 = $1/2 \left[\frac{(n-C_{15}+n-C_{17})}{n-C_{16}} \right]$; Pr – Pristane; Phyt – Phytane; $C_{29}\alpha\alpha(R) - C_{29}14\alpha(H)17\alpha(H)20(R)$ -sterane; $C_{29}\alpha\alpha(S) - C_{29}14\alpha(H)17\alpha(H)20(S)$ -sterane; $C_{29}\beta\beta(R) - C_{29}14\beta(H)17\beta(H)20(R)$ -sterane; ster – $C_{27}14\alpha(H)17\alpha(H)20(R)$ -sterane; $C_{27}\text{dia} - C_{27}13\beta(H)17\alpha(H)20(S)$ -diasterane; $C_{31}(S) - C_{31}17\alpha(H)21\beta(H)22(S)$ -hopane; $C_{31}(R) - C_{31}17\alpha(H)21\beta(H)22(R)$ -hopane; $C_{30}M - C_{30}17\alpha(H)21\beta(H)$ -hopane; $C_{30}H - C_{29}17\alpha(H)21\alpha(H)$ -moretane; $C_{29}H - C_{29}17\alpha(H)21\beta(H)$ -hopane; $C_{29}M - C_{29}17\beta(H)21\alpha(H)$ -moretane; Ts – $C_{29}18\alpha(H)$ -22,29,30-trisnormeohopane; Tm – $C_{27}17\alpha(H)$ -22,29,30-trisnormeohopane; $C_{29}\text{Ts} - C_{29}18\alpha(H)$ -30-normeohopane

TABLE III. Maturation parameters calculated from the distributions and abundances of di- and tricyclic aromatic hydrocarbons (an explanation of the abbreviations is given in the Appendix)

Sample	MNR	ENR	DNR 1	α/β DN 1	DNx	TNR 1	TNR 2	TNR 3	TNy	MPI 1	MPI 3	MPR 1	DMPI 1	DMPI 2	PAI 1	MDR	MTR
V1	1.51	1.87	2.82	0.41	4.25	0.27	0.56	3.11	2.54	0.85	1.17	1.38	1.19	0.36	2.05	1.02	2.94
V2	1.54	1.92	2.97	0.53	4.33	0.37	0.67	2.17	2.63	0.87	1.20	1.41	1.12	0.45	2.04	0.91	3.43
V3	1.57	1.95	2.44	0.47	4.37	0.36	0.61	3.33	2.65	0.86	1.25	1.43	0.99	0.43	1.90	0.94	2.85
V4	1.23	0.85	2.13	0.62	3.23	0.59	0.82	2.83	2.13	0.72	0.83	1.00	1.25	0.57	2.49	0.79	2.29
V5	1.28	0.86	2.62	0.55	3.77	0.23	0.76	2.89	2.28	0.75	0.87	1.02	1.09	0.44	2.50	0.85	2.51
V6	1.25	0.87	1.84	0.66	3.23	0.56	0.84	3.16	2.09	0.71	0.90	1.07	1.07	0.44	2.13	0.78	2.14
V7	1.82	3.80	6.62	0.21	7.19	0.25	0.67	3.22	3.07	0.90	1.41	1.69	0.63	0.39	1.79	1.76	5.68
V8	1.75	3.22	3.84	0.30	7.10	0.77	0.99	2.48	3.04	0.87	1.37	1.64	0.61	0.38	1.73	1.75	3.70
V9	0.80	0.78	1.61	0.94	2.36	0.44	0.76	0.92	1.66	0.65	0.77	0.83	1.20	0.47	2.30	0.74	1.34
V10	0.93	0.82	1.17	0.84	2.48	0.42	0.47	2.63	1.97	0.80	0.80	0.92	0.87	0.25	3.54	0.74	1.62
V11	1.37	1.99	1.53	0.89	4.07	0.74	0.79	1.21	2.51	0.79	1.07	1.31	1.04	0.53	1.99	1.22	3.01
V12	1.63	1.96	1.28	1.09	4.79	0.65	0.76	1.46	2.67	0.88	1.26	1.45	1.35	0.38	1.97	1.14	2.86
V13	1.53	1.91	1.73	0.99	4.31	0.59	0.77	2.70	2.60	0.88	1.19	1.40	1.43	0.64	2.14	1.23	2.79
V14	1.14	0.97	1.62	1.11	2.90	0.21	0.58	2.51	2.03	0.69	0.81	0.97	1.00	0.31	2.39	0.86	2.56
PO1	1.61	1.67	4.34	0.33	4.38	1.18	0.87	1.80	2.61	0.86	1.27	1.48	0.92	0.23	1.87	1.95	7.26
PO2	1.65	2.19	7.11	0.24	6.53	1.23	0.90	1.82	2.73	0.76	1.27	1.23	0.69	0.51	1.52	3.42	5.40
PO3	2.20	4.18	9.50	0.20	7.29	1.47	0.94	5.80	3.07	0.87	1.33	1.61	1.19	0.44	1.80	2.43	5.24
PO4	1.98	2.95	5.82	0.19	7.81	1.50	0.99	3.74	3.08	1.23	1.49	1.88	1.37	0.55	3.02	1.03	3.44
PO5	2.22	3.11	6.32	0.20	10.21	1.55	0.92	4.35	3.07	1.12	1.66	1.91	1.02	0.45	2.17	1.44	6.06
PO6	1.43	2.23	3.74	0.45	2.88	1.18	0.85	1.87	2.33	0.85	0.99	1.11	1.13	0.49	2.67	0.73	1.52
PO7	1.19	2.35	2.31	0.42	3.98	1.15	0.82	1.33	2.20	0.67	0.81	0.99	0.79	0.26	2.21	0.84	1.75
PO8	1.44	1.84	3.17	0.31	5.39	1.48	0.98	3.09	2.90	0.90	1.14	1.28	1.02	0.43	2.39	0.85	2.35
PO9	1.73	5.82	2.33	0.33	7.37	1.06	0.67	5.38	2.96	1.17	1.44	1.70	1.32	0.42	2.91	0.76	1.36

Parameter Pr/Phyt was found to have no importance as a maturity indicator, a fact which could have been expected, since it has often been shown that this ratio, in addition to maturation, significantly depends on depositional environment and origin.^{2,38} Moreover, it was shown earlier, with Drmno Depression crude oils only, that this ratio may be used as a maturity parameter only for oils generated during the early stage of catagenesis.^{39–43} Due to categorization into Factor 1, parameters CPI, CPI 1 and Phyt/*n*-C₁₈ may be supposed to be more reliable as maturity indicators for the Banat Depression crude oils, compared to parameters $\Sigma_{\text{odd}}(n\text{-C}_{21} - n\text{-C}_{33})/\Sigma_{\text{even}}(n\text{-C}_{12} - n\text{-C}_{20})$ and Pr/*n*-C₁₇, which, based on high loadings, defined Factor 2. Such a presumption is corroborated by the fact that in “maturity Factor” 2, the loadings value of the Pr/Phyt ratio was significantly higher than in Factor 1 (0.57 vs. 0.09), indicating that Factor 2 involved alkane parameters which, in addition to maturation, significantly depend on the depositional environment and origin. A better applicability of Phyt/*n*-C₁₈ parameters compared to the analogous Pr/*n*-C₁₇ in maturity estimation of crude oils and sediments from the Serbian part of the Pannonian Basin was already observed in earlier investigations.^{43,44} This observation may be explained by the fact that most of these samples have a relatively high content of pristane, due to genetic factors and depositional environment effects, a fact which certainly limits the application of the Pr/*n*-C₁₇ ratio as a maturity indicator.

Factor analysis of sterane and terpane maturity parameters

Factor analysis of maturity parameters calculated based on the distribution and abundance of sterane and terpane biomarkers (Table II) resulted in two statistically important “maturity factors”:

$$F_{1\text{steranes+terpanes}} = 0.92C_{29}\text{Ts}/C_{29}\text{H} + 0.77C_{31}(S)/((S)+(R)) + 0.73C_{27}\text{dia}/(\text{dia}+\text{ster}) + 0.69C_{29}\alpha\alpha(S)/(\alpha\alpha(S)+\alpha\alpha(R)) - 0.51C_{29}\text{M}/C_{29}\text{H} + 0.39C_{29}\beta\beta(R)/(\beta\beta(R)+\alpha\alpha(R)) + 0.38\text{Ts}/\text{Ts}+\text{Tm} + 0.30C_{30}\text{M}/C_{30}\text{H}$$

and

$$F_{2\text{steranes+terpanes}} = -0.86C_{30}\text{M}/C_{30}\text{H} + 0.78C_{29}\beta\beta(R)/(\beta\beta(R)+\alpha\alpha(R)) + 0.72\text{Ts}/(\text{Ts}+\text{Tm}) + 0.61C_{29}\alpha\alpha(S)/(\alpha\alpha(S)+\alpha\alpha(R)) + 0.53C_{27}\text{dia}/(\text{dia}+\text{ster}) - 0.20C_{29}\text{M}/C_{29}\text{H} + 0.14C_{29}\text{Ts}/C_{29}\text{H} - 0.08C_{31}(S)/((S)+(R))$$

characterized by variances of 38.54 % and 32.38 %, respectively.

High loadings (> 0.65) in the first “maturity factor” were observed for parameters based on isomerization reactions on chiral carbon atoms in the side chains of C₂₉ sterane and C₃₁ hopane (20R → 20S; 22R → 22S), as well as for ratios of typical geoisomers, C₂₇ diasterane and C₂₉Ts, and the corresponding precursors of C₂₇ regular sterane or C₂₉ hopane. The second factor was determined, with high loadings values (> |0.70|), by parameters based on higher energy demanding

isomerizations in rings ($\alpha\alpha \rightarrow \beta\beta$ C₂₉-steranes and C₃₀ $\beta\alpha$ -moretanes \rightarrow C₃₀ $\alpha\beta$ -hopanes) and the Ts/(Ts+Tm) ratio. Separation of the related parameters C₂₉Ts/C₂₉H and Ts/(Ts + Tm) into different factors confirmed that the difference in stability of Ts and Tm (3.8 kJ mol⁻¹) is higher than in the case of C₂₉Ts and C₂₉-hopane.⁴⁵ Consequently, the transformation Tm \rightarrow Ts requires more energy, a fact which explains the finding of the Ts/(Ts+Tm) ratio in Factor 2. The ratio of C₂₉ $\alpha\alpha$ -sterane *S*- vs. *R*-isomers, in addition to significant loadings in Factor 1, showed a certain degree of significance in Factor 2 as well (loadings of 0.61), confirming a well-known geochemical fact that isomerization reactions in sterane biomarkers side chains, as higher energy demanding, occur during advanced catagenesis, compared to analogous terpane maturation transformations.^{15,16,46} Formulae F_{1steranes+terpanes} and F_{2steranes+terpanes} show that the C₂₉-moretane vs. C₂₉-hopane ratio has no critical value for a significant loading of 0.60 or 0.70 in either of the two factors. This is not surprising, due to the fact that earlier it was shown that the C₂₉-terpane content in crude oils significantly depends on origin as well, and that it is considerably higher in crude oils originating from calcareous deposits.⁴⁷

Factor analysis of alkylnaphthalene maturity parameters

The factor analysis of diarene maturity parameters (Table III) resulted in two statistically important "maturity factors":

$$F_{1\text{alkylnaphthalenes}} = 0.86\text{ENR} + 0.84\text{MNR} + 0.83\text{TNR } 3 + 0.83\text{TNY} + 0.83\text{DNx} - 0.64\alpha/\beta\text{DN } 1 + 0.63\text{DNR } 1 + 0.29\text{TNR } 1 + 0.07\text{TNR } 2$$

and

$$F_{2\text{alkylnaphthalenes}} = 0.94\text{TNR } 2 + 0.84\text{TNR } 1 + 0.56\text{DNR } 1 - 0.52\alpha/\beta\text{DN } 1 + 0.44\text{DNx} + 0.42\text{MNR} + 0.38\text{TNY} + 0.16\text{ENR} - 0.04\text{TNR } 3$$

characterized by variances of 49.12 % and 30.28 %, respectively. Factor 1 was determined by high loadings of maturity parameters based on isomerization of thermodynamically less stable methyl- (MN), dimethyl- (DMN), trimethyl- (TMN) and ethylnaphthalenes (EN) with alkyl groups in the α -position into the corresponding thermodynamically more stable β -isomers. Specifically, parameters MNR, DNx, TNR 3, TNY and ENR, characterized by the highest loadings in the more significant "maturity factor", comprise isomerization of just one aromatic ring alkyl substituent (α -MN \rightarrow β -MN; $\alpha\alpha$ -DMN \rightarrow $\alpha\beta$ -DMN; $\alpha\beta\alpha$ -TMN \rightarrow $\alpha\beta\beta$ -TMN; α -EN \rightarrow β -EN). Parameters α/β DN 1 and DNR 1, also conforming with the loadings limit of 0.60 in Factor 1, though with less significance compared to the above mentioned parameters, comprise isomerization of two methyl groups on the naphthalene ring ($\alpha\alpha$ -DMN \rightarrow $\beta\beta$ -DMN), a change requiring more energy. Consequently, it is not surprising that the loadings values of α/β DN 1 and DNR 1 parameters are close to the significance limit value in Factor 2 as well. Factor 2 is determined by the parameters TNR 1 and TNR 2, also based on isomerization of

two methyl groups ($\alpha\beta\alpha$ -TMN \rightarrow $\beta\beta\beta$ -TMN). However, in this case the thermodynamically most stable $\beta\beta\beta$ -isomer, *i.e.*, 2,3,6-TMN, the formation of which requires the most energy, is also involved.

Factor analysis of alkylphenanthrene maturity parameters

The factor analysis of the phenanthrene maturity parameters (Table III) resulted in three statistically important “maturity factors”:

$$F_{1\text{alkylphenanthrenes}} = 0.96\text{MPI } 1 + 0.95\text{MPR } 1 + 0.92\text{MPI } 3 + 0.47\text{MTR} + \\ + 0.20\text{MDR} + 0.15\text{DMPI } 1 + 0.06\text{DMPI } 2 + 0.05\text{PAI } 1$$

$$F_{2\text{alkylphenanthrenes}} = -0.90\text{PAI } 1 + 0.88\text{MDR} + 0.75\text{MTR} - 0.48\text{DMPI } 1 + \\ + 0.35\text{MPI } 3 + 0.24\text{MPR } 1 - 0.20\text{MPI } 1 + 0.11\text{DMPI } 2$$

and

$$F_{3\text{alkylphenanthrenes}} = 0.93\text{DMPI } 2 + 0.73\text{DMPI } 1 - 0.23\text{MTR} + 0.14\text{MPI } 1 - \\ - 0.08\text{MDR} + 0.07\text{MPI } 3 + 0.07\text{MPR } 1 - 0.05\text{PAI } 1$$

characterized by variances of 37.22 %, 32.38 % and 18.62 %, respectively. The most important triarene “maturity factor” was defined by the MPI 1, MPR 1 and MPI 3 ratios, based on the isomerization of one methyl group in the thermodynamically less stable α -methylphenanthrenes (1-MP and 9-MP), into the corresponding more stable isomers with the methyl group in the β -position (2-MP and 3-MP). Factor 2 was determined by high loadings of the MTR and MDR parameters, based on dealkylation reactions of trimethyl- (TMP) and dimethylphenanthrene (DMP) into the corresponding methylphenanthrenes (MP), as well as the PAI 1 ratio, based on the alkylation–dealkylation transformation phenanthrene (P) \rightleftharpoons methylphenanthrenes (MP). In a number of investigations, it was shown that dealkylation processes requiring more energy occurred at more advanced thermal maturity, compared to the isomerizations α -MP \rightarrow β -MP.^{5,11,36,37,46,48} Hence, generally, factor analysis of maturity parameters calculated on the basis of the distribution of different types of petroleum hydrocarbons clearly indicates the energy changes required for individual maturation processes.

In the last, Factor 3, high loadings values were observed with dimethylphenanthrene indexes DMPI 1 and DMPI 2, also defined by isomerizations ($\alpha \rightarrow \beta$) in dimethylphenanthrene molecules. The low percent of variance (18.62 %) in this case was not surprising, considering the fact that the corresponding parameters involved a large number of isomers of different stability (see Appendix), which co-eluted during the GC and GC–MS analyses.

Re-evaluation of all extracted “maturity factors”

All “maturity factors” observed in individual factor analyses showing higher than 30 % of variance (*i.e.*, all factors extracted from separate analyses, except $F_{3\text{alkylphenanthrenes}}$), were involved in another factor analysis, and also in cluster

analysis using the Ward method (Table IV, Fig. 2). In this way, all maturity parameters based on saturated biomarkers and alkylarenes were re-evaluated, considering the fact that the observed “maturity factors” represented their linear combinations. For this purpose, a loadings value of $|0.70|$ was taken as the significance limit, aimed at a more reliable consideration of “maturity factors”.

TABLE IV. Results of the final factor analysis of “maturity factors” based on saturated biomarkers and alkylarenes maturity parameters

Variables	Varimax rotated component matrix		
	Factor (% of variance)		
	1 (29.07)	2 (26.80)	3 (22.86)
F ₁ alkanes+isoprenoids	-0.32	-0.10	0.83
F ₂ alkanes+isoprenoids	-0.65	-0.31	-0.37
F ₁ steranes+terpanes	0.10	0.90	-0.06
F ₂ steranes+terpanes	0.29	0.03	0.89
F ₁ alkylnaphthalenes	0.92	-0.02	0.03
F ₂ alkylnaphthalenes	0.03	0.88	-0.20
F ₁ alkylphenanthrenes	0.92	0.08	-0.14
F ₂ alkylphenanthrenes	0.09	0.67	0.36

The most important Factor 1 in the final factor analysis was defined by the F₁alkylnaphthalenes and F₁alkylphenanthrenes factors (loadings > 0.90), which represented linear combinations of parameters based on isomerization of one alkyl group from the α - into β -positions in the aromatic rings of MN, EN, DMN, TMN and MP (Table IV). Factor 2 was determined by high loadings of factor F₁steranes+terpanes, based on isomerization reactions in the aliphatic chains of saturated biomarkers, and transformations of steranes into diasteranes and C₂₉-hopane into C₂₉Ts, and factor F₂alkylnaphthalenes, based on the isomerization of two methyl groups $\alpha \rightarrow \beta$ in the rings of trimethylnaphthalenes, including the most stable $\beta\beta\beta$ -isomer, 2,3,6-TMN. In the last significant factor, Factor 3, high loadings were observed with F₁alkanes+isoprenoids and F₂steranes+terpanes, which includes the ratio of odd vs. even *n*-alkanes, the parameter Phyt/*n*-C₁₈, as well as parameters based on transformations in the rings of polycyclic saturated biomarkers (steranes and terpanes), and Tm \rightarrow Ts (Table IV). The presumption derived from individual factor analysis of *n*-alkane and isoprenoid maturity ratios that parameters determining the factor F₂alkanes+isoprenoids were not reliable maturity indicators was in this way corroborated, since the mentioned factor showed relatively low maximal loadings value (-0.65) compared with other “maturity factors” (Table IV). Also, the relatively low maximal loadings value observed for factor F₂alkylphenanthrenes (0.67), defined by alkylation–dealkylation methylphenanthrene processes, compared to other “maturity factors”, was not surprising,

since it was often suggested that during catagenesis alkylation reactions occur first on the phenanthrene ring and only later, in the stage of the “oil window”, the reaction changes direction into the reverse dealkylation process. Application of dealkylation phenanthrene parameters as maturity indicators is, therefore, limited only to crude oils characterized by higher degrees of thermal maturity,^{5,11,36,46} which is in agreement with their smaller significance in the factor analysis.

Hierarchy within the observed factors/parameters was additionally checked by cluster analysis using the Ward method (Fig. 2).

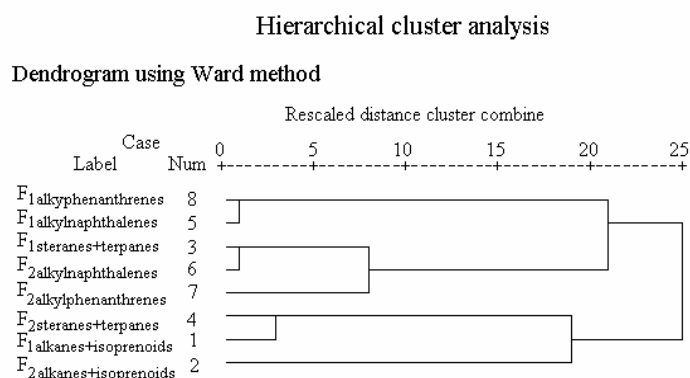


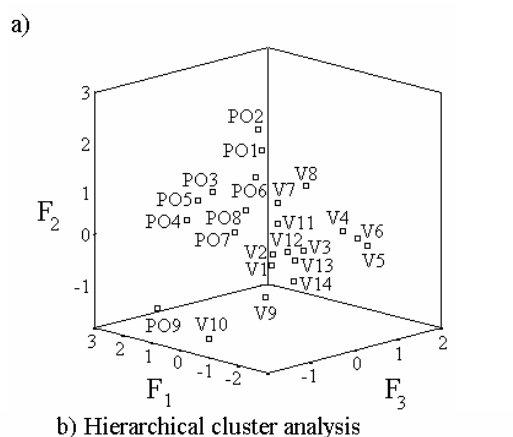
Fig. 2. Dendrogram from cluster analysis using the Ward method of “maturity factors” based on maturity parameters of saturated biomarkers and alkylarenes.

Two groups of “maturity factors” clearly separated in the dendrogram, which are shown in Fig. 2. The first group is composed of “maturity factors” which, showing high loadings values, defined Factors 1 and 2 in the collective factor analysis (Table IV). “maturity factors” which showed significant loadings values in Factor 3 of the collective factor analysis (Table IV), formed the second group. The “maturity factor” F₂alkanes+isoprenoids joined the latter group as a special member, confirming that the parameters Pr/*n*-C₁₇ and $\Sigma_{\text{odd}}(n\text{-C}_{21}\text{-}n\text{-C}_{33})/\Sigma_{\text{even}}(n\text{-C}_{12}\text{-}n\text{-C}_{20})$ which define it, are less important in the estimation of the maturity of Banat depression crude oils. Fig. 2 also shows that the factors in the first group are divided into two subgroups, which completely correspond with high loadings “maturity factors” in Factor 1 and 2 from the collective factor analysis (Table IV). Finally, the distance of the “maturity factor” F₂alkylphenanthrenes, based on dealkylation reactions of TMP, DMP and MP, from factors F₁steranes+terpanes and F₂alkylnaphthalenes (Fig. 2) is in concordance with the lower loadings value of this “maturity factor” in Factor 2 in the collective factor analysis (Table IV). These observations indicate the full agreement of the results of factor and cluster analyses of “maturity factors” and confirmed the maturity parameters based on the isomerization of one methyl group from α - into β -positions

in naphthalene and phenanthrene aromatic rings to be most reliable in the investigation of the thermal maturity of crude oils originating from the Serbian part of the Pannonian Basin.

Correlation of the investigated oils based on maturity parameters

The investigated crude oils were classified according to maturity, using for this purpose factor and cluster analyses, and taking into consideration, simultaneously, all eight “maturity factors” from the individual factor analyses showing variances higher than 30 %, *i.e.*, all parameters calculated on the basis of the distribution and abundance of constituting saturated and aromatic hydrocarbons (Fig. 3).



Dendrogram using Ward method

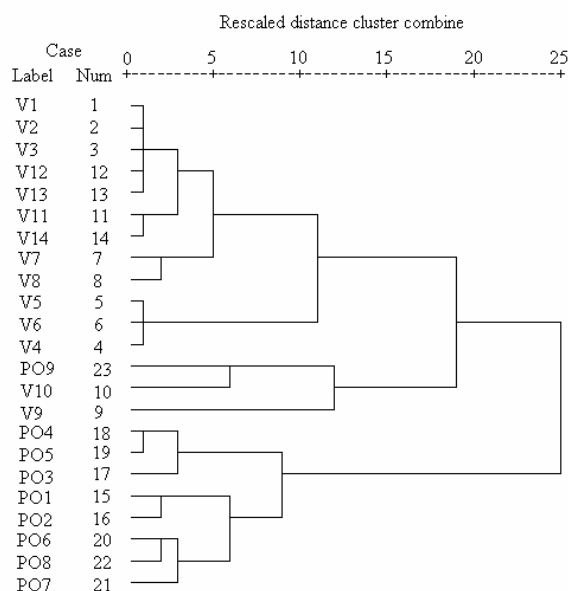


Fig. 3. Correlation of investigated oils according to maturity using factor (a) and cluster (b) analyses of all “maturity factors”.

Based on factor analysis, a 3D diagram was constructed, the axes of which represent three factors derived from collective factor analysis (Fig. 3; Table IV). In Fig. 3, three groups of oils are clearly distinguished: the first composed of samples from the Drmno Depression (PO1–PO8); the second composed of samples from the localities Jermenovci (V9), Boka (V10), and one single crude oil from the Drmno Depression (PO9); the third included all the other investigated Vojvodina crude oils. Within the last (third) group, the crude oils V4–V6, from the Velebit locality, are somewhat separated.

The observed categorization showed the Drmno Depression crude oils to differ from the Vojvodina crude oils not only according to their genetic type, but also according to their thermal maturity. Moreover, in this way, the presumption is confirmed that South Banat crude oils, in the first place the oils from Jermenovci and Boka, differ from North Banat and Bačka crude oils.^{40,49} The exceptional close relation of sample PO9 from the Drmno Depression with the South Banat crude oils (Fig. 3a) indicates a certain connection of the samples originating from these two localities, a fact also observed in geological investigations (A. Kostić, personal communication). The finding of the Velebit crude oils in a separate subgroup is also in agreement with up-to-date geological and geochemical investigations, which, on the one hand, suggested homogeneity of this oil field, and, on the other, differences from North Banat crude oils.^{25,40,50}

The investigated oils were also classified by Ward cluster analysis (Fig. 3b) using all eight “maturity factors”, *i.e.*, all constituting parameters. The results observed were in full accordance with the results obtained by factor analysis (Fig. 3a): the Drmno Depression crude oils PO1–PO8 were clearly separated, the exception being the sample PO9. Furthermore, within the “large” second dendrogram branch, a group of oils was observed composed of sample PO9 and South Banat oils Jermenovci and Boka (V9 and V10). A slight separation of Velebit oils was also observed. Hence, factor and cluster analyses were in full agreement in both the evaluation of maturity parameters, as well as in the maturity classification of the crude oils.

CONCLUSIONS

Crude oil maturity parameters based on the distribution and abundance of saturated biomarkers and alkyl arenes were evaluated using a novel approach in factor and cluster analyses. For this purpose, 23 samples of crude oils originating from the Serbian part of the Pannonian Basin were investigated. Furthermore, the investigated crude oils (from localities in Vojvodina and the Drmno Depression) were correlated by simultaneous consideration of a large number of selected “maturity” parameters.

The results of factor and cluster analyses suggested that parameters based on the isomerization of one alkyl group from α - into β -positions on the aromatic ring

of methylnaphthalenes, ethylnaphthalenes, dimethylnaphthalenes, trimethylnaphthalenes and methylphenanthrenes, were the most important parameters in maturity investigations of Banat Depression crude oils. They were followed by maturation indexes based on the isomerization on chiral centers ($R \rightarrow S$) in the side chains of polycyclic saturated sterane and terpane biomarkers, as well as ratios based on the isomerization of two methyl groups from α - into β -positions on the aromatic ring of trimethylnaphthalenes. The last statistically important factor was defined by ratios based on isomerization in the rings of polycyclic sterane and terpane alkanes and parameters CPI, CPI 1 and Phyt/ n -C₁₈, calculated from the distribution and abundance of n -alkanes and isoprenoids.

The factor and cluster analyses indicated a limited applicability of indexes based on P, MP, DMP and TMP alkylation-dealkylation transformations, Pr/Phyt, and Pr/ n -C₁₇ parameters, and ratios of higher odd vs. even n -alkane members, in the maturity evaluation of crude oils from the Serbian part of the Pannonian Basin.

In individual factor analyses of parameters calculated on the basis of the distribution of individual types of saturated and aromatic hydrocarbons, good agreement was observed between the distribution of the parameters among the factors, and the energy necessary for the corresponding maturation changes.

Correlation of crude oils based on the simultaneous consideration of a large number of selected “maturity” parameters showed the Vojvodina and Drmno Depression crude oils to differ not only according to genetic type, but also according to thermal maturity.

According to maturity, three groups of samples were distinguished among the Vojvodina crude oils: North Banat localities, the Velebit oil field, and South Banat locality. Furthermore, certain similarities were observed in the thermal maturity of South Banat (Jermenovci and Boka) and Drmno Depression (Bradarac–Maljurevac) crude oils. Both conclusions are in agreement with presumptions based on geological investigations.

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APPENDIX

$$\text{MNR} = 2\text{-MN}/1\text{-MN}^9$$

$$\text{ENR} = 2\text{-EN}/1\text{-EN}^{10}$$

$$\text{DNR 1} = (2,6\text{-} + 2,7\text{-DMN})/1,5\text{-DMN}^{10}$$

$$\alpha/\beta\text{DN 1} = (1,4\text{-} + 1,5\text{-} + 1,8\text{-} + 2,3\text{-DMN})/(2,6\text{-} + 2,7\text{-DMN})^{51}$$

$$\text{DNx} = (1,3\text{-} + 1,6\text{-DMN})/(1,4\text{-} + 1,5\text{-DMN})^{43,52}$$

$$\text{TNR 1} = 2,3,6\text{-TMN}/(1,3,5\text{-} + 1,4,6\text{-TMN})^{13}$$

$$\text{TNR 2} = (1,3,7\text{-} + 2,3,6\text{-TMN})/(1,3,5\text{-} + 1,3,6\text{-} + 1,4,6\text{-TMN})^{53}$$

$$\text{TNR 3} = 1,3,6\text{-TMN}/1,2,5\text{-TMN}^{12}$$

$$\text{TNy} = (1,3,6\text{-} + 1,3,7\text{-TMN})/(1,3,5\text{-} + 1,4,6\text{-TMN})^{43,52}$$

$$\text{MPI 1} = 1,5(2\text{-} + 3\text{-MP})/(P+1\text{-} + 9\text{-MP})^9$$

$$\text{MPI 3} = (2\text{-} + 3\text{-MP}) / (1\text{-} + 9\text{-MP})^{11}$$

$$\text{MPR 1} = 2\text{-MP} / 1\text{-MP}^{10}$$

$$\text{DMPI 1} = 4(2,6\text{-} + 2,7\text{-} + 3,5\text{-} + 3,6\text{-DMP} + 1\text{-} + 2\text{-} + 9\text{-EP}) / (P + 1,3\text{-} + 1,6\text{-} + 1,7\text{-} + 2,5\text{-} + 2,9\text{-} + 2,10\text{-} + 3,9\text{-} + 3,10\text{-DMP})^9$$

$$\text{DMPI 2} = (2,6\text{-} + 2,7\text{-} + 3,5\text{-DMP}) / (1,3\text{-} + 1,6\text{-} + 2,5\text{-} + 2,9\text{-} + 2,10\text{-} + 3,9\text{-} + 3,10\text{-DMP})^{10}$$

$$\text{PAI 1} = (1\text{-} + 2\text{-} + 3\text{-} + 9\text{-MP}) / P^{54}$$

$$\text{MDR} = \Sigma \text{MP} / \Sigma \text{DMP}^{43,52}$$

$$\text{MTR} = \Sigma \text{MP} / \Sigma \text{TMP}^{43,52}$$

MN – Methylnaphthalene; EN – ethylnaphthalene; DMN – dimethylnaphthalene; TMN – trimethylnaphthalene; P – phenanthrene; MP – methylphenanthrene; DMP – dimethylphenanthrene; EP – ethylphenanthrene.

ИЗВОД

ЕВАЛУАЦИЈА МАТУРАЦИОНИХ ПАРАМЕТАРА ЗАСНОВАНИХ НА ЗАСИЋЕНИМ И АРОМАТИЧНИМ УГЉОВОДОНИЦИМА У КОРЕЛАЦИЈИ НАФТА–НАФТА (ЈУГОИСТОЧНИ ДЕО ПАНОНСКОГ БАСЕНА, СРБИЈА)

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У овом раду је, применом новог приступа у факторској и кластерској анализи, евалуиран значај матурационих параметара заснованих на расподели и обилности засићених биомаркера и алкиларена у корелацији нафта–нафта на примеру 23 узорка сирове нафте из дела Панонског басена у Србији (14 са локалитета у Војводини и 9 из депресије Дрмно). Факторске анализе су, уз примену *varimax* ротације, најпре извођене посебно са матурационим параметрима израчунатим из расподеле и обилности (а) *n*-алкана и изопреноидних алифатичних алкана, (б) стерана и тритерпана, (в) алкилнафталена и (г) алкилфенантрена. Ове анализе резултирале су са 9 значајних “матурационих фактора”. Осам од њих, који су показивали проценат варијације већи од 30 %, укључени су у нову факторску и кластерску анализу, уз примену Ward методе. На тај начин су сви матурациони параметри засновани на расподели и обилности засићених биомаркера и алкиларена били процењени и ранжирани, имајући у виду чињеницу да фактори предствљају њихове линеарне комбинације. Резултати су показали да су за корелацију нафте из дела Панонског басена у Србији најзначајанији матурациони параметри засновани на изомеризацији једне алкил-групе из α - у термодинамички стабилније β -положаје на ароматичном прстену метилнафталена, етилнафталена, диметилнафталена, триметилнафталена и метилфенантрена. Такође, одређени су параметри/типови матурационих реакција који су у великој мери дефинисали факторе 2 и 3. Редослед и сагласност између фактора, односно параметара, проверена је и потврђена кластерском анализом уз примену Ward методе. Коначно, испитивани узорци сирове нафте су корелисани помоћу факторске и кластерске анализе, користећи све значајне “матурационе факторе”. Разлике у степену термичке зрелости уочене су како између узорака из Војводине и депресије Дрмно, тако и између узорака из Војводине који потичу из лежишта јужног Баната, северног Баната и нафтног поља Велебит.

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