Correlative geochemical study of crude oils from southeastern and southern parts of the Pannonian Basin

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Abstract—Several crude oils from the southeastern Yugoslav part of the Pannonian Basin are correlated for the first time on the basis of many bulk and specific parameters. The investigations involved 15 oils from oil-gas fields A and B and oil field C from the Banat depression and oil field D from South Bačka depression, and four oils from recently discovered oil shows E (the Kostolac depression). On the basis of structural group analysis and other bulk parameters such as API gravity, contents of asphaltenes and sulfur, as well as content of n-alkanes and pristane to phytane ratio, the examined oils are classified into four groups. However, the distributions and relative abundances of n-alkanes, isoprenoids (C_{n+0}, C_{n+2}), steranes, tricyclic terpanes and pentacyclic triterpanes, obtained by capillary GC and computerized GC-MS analysis, suggest classification of the examined oils into only two genetic types: A-D and E₁-E₄. The oils are of relatively high maturity. They are not biodegraded, except for both oils from field D and the oil A₉.

Key words: oil-oil correlations, Pannonian Basin crude oils, bulk correlation parameters, specific correlation parameters, classification of Pannonian Basin crude oils, molecular source parameters, maturation parameters

INTRODUCTION

During the last 30 years several oil and oil-gas fields have been discovered in Yugoslavia, i.e. the southeastern part of the Pannonian Basin. This part of the Basin had not yet been completely explored. Since oil–oil correlations can be one of the valuable tools for assisting exploration geologists, the present study was undertaken to assess the relationship between several major oil accumulations on the basis of a few bulk and molecular parameters.

The Pannonian Basin (Fig. 1) represents one part of a broad basin which was formed by rising of the Alps, Carpathian and Dinaric Alps and by lowering of the terrain between their ranges. During evolution, the depressed parts of this area were filled by Tertiary sediments whose depth reached several thousand meters in places (Aksin, 1967).

The very complex structure of the Pannonian Basin resulted from complicated geologic and tectonic relationships in this district. The role of the differential movements, mainly lowering and, to a smaller extent, lifting the basin together with the Tertiary sediments, was very important in the formation of the present tectonic configuration. A large number of marginal depressions was thus formed. In the southeastern part of the Pannonian Basin several separate tectonic units formed: the Banat (B), South Bačka (SB), Srem (S), Danubian (D) and Kostolac depressions (K). Most of the oil and gas fields in this part of the Basin were found in the largest, the Banat depression. Commercial hydrocarbon reservoirs were also found in the South Bačka and Danubian depressions. In contrast, so far, exploration in the area of the Srem depression is not economic. Finally, recent exploratory drillings in the Kostolac depression are positive, so that this area also becomes very significant.

This paper involves examination of oils from two oil-gas fields (A and B) and one oil field (C) of the Banat depression and one oil field (D) of the South Bačka depression. Furthermore, samples from four newly discovered oil shows in the Kostolac depression (E₁-E₄) were also investigated. The oil-gas fields A and B are located in the region of North Banat, the oil fields C and D in the area of North Bačka, and the oil shows E₁-E₄ in northeastern Serbia, i.e. in the southern part of the Pannonian Basin (Fig. 1).

On the basis of earlier geological investigations, carried out by the company Nafta-Gas from Novi Sad, as well as geochemical analyses of trace elements and physical and chemical properties, the crude oils from oil fields A, B, C and D are classified into three genetic types: type I oil-gas field A, type II oil-gas field B and oil field C, and type III oil field D. For the first two types of oils the presumed source rocks are of Neogene and for type III of Mesozoic age (Šarković, 1972). A recent preliminary correlation study, based on trace elements, confirmed the different genetic types of oils from oil fields A and D (Šaban et al., 1984).

Since oil–oil correlations based on qualitative and quantitative biomarker analyses have been shown to
Fig. 1. Provenance of the investigated crude oils and the structural map.
be very efficient (e.g. Welte et al., 1975; Seifert and Moldowan, 1978, 1979, 1981; Seifert et al., 1983; McKirdy et al., 1986; Palacas et al., 1986; Riva et al., 1986), this study also attempted correlation and classification of the oils on the basis of specific parameters such as the distribution of n-alkanes, isoprenoid and polycyclic alkanes. Parallel with the specific parameters, several bulk parameters were also determined: API gravity, sulfur content and structural group composition.

**SAMPLING AND ANALYTICAL TECHNIQUES**

Both the oil-gas fields A and B have a larger number of oil and/or gas reservoirs located in different lithologic and chronostratigraphic horizons, while the oil fields C and D involve only one accumulation each. From oil-gas field A nine samples were analyzed (A1–A9) from different reservoirs representing separate hydrodynamic systems. Three samples were analyzed from the oil-gas field B (B1–B3), one sample from oil field C (C1), and two samples from oil field D (D1 and D2). One sample was analyzed from each of the four oil shows of the Kostolac depression (E1–E4). The sampling locations are indicated in Fig. 1.

Geological data on the reservoir rocks of the analyzed samples are shown in Table 1.

The oils were sampled in front of the spout on the collector into glass bottles prepared according to the ASTM standard procedure. The water and the dispersed solid material were separated by centrifugation. From the oils thus purified the asphaltenes were precipitated by treatment with n-heptane for 16 h at room temperature and then 15 min at the solvent boiling temperature. The solvent and the low boiling components were eliminated from the filtrate at 50°C in a rotating vacuum evaporator. The structural group composition of the obtained C19 fraction was determined by column chromatography (Seifert and Moldowan, 1978).

Gas chromatographic (GC) analyses of saturated hydrocarbons and urea adducts were carried out with a Varian 3300 gas chromatograph using a 25 m × 0.25 mm i.d. fused silica DB-1 capillary column directly connected to an FID detector. Gas chromatographic-mass spectrometric (GC-MS) analyses of urea nonadducts were performed with a system consisting of a Perkin-Elmer Sigma 1 GC fitted with a 30 m × 0.25 mm i.d. fused silica DB-1 capillary column coupled to a Hewlett-Packard 5970 mass selective detector and a Hewlett-Packard 9816 com-

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**Table 1: Generalized section of the SE part of the Pannonian Basin showing the stratigraphic relationship of the oils studied.**

<table>
<thead>
<tr>
<th>AGE</th>
<th>LITHOLOGICAL SYMBOLS</th>
<th>LITHOLOGY</th>
<th>TEMPERATURE OF RESERVOIR ROCKS (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QUATERNARY</td>
<td>CLAY WIGRAVEL, CLAY, SAND</td>
<td>A1, A2, A3, A4</td>
<td>97.7 N.D. 106.1</td>
</tr>
<tr>
<td>PLEISTOCENE</td>
<td>SAND, CLAYS, CLAY AND SANDY CLAY</td>
<td>A5</td>
<td>105.1</td>
</tr>
<tr>
<td>UPON PONTIAN</td>
<td>SANDY CLAY</td>
<td>A6</td>
<td>102.0</td>
</tr>
<tr>
<td>LOWER PONTIAN</td>
<td>MARLS, SANDY MARLSTONES, SAND</td>
<td>A7</td>
<td>107.5 N.D.</td>
</tr>
<tr>
<td>PANNONIAN</td>
<td>MARLS, SANDSTONES, MARLSTONES</td>
<td>A8</td>
<td>109.7 N.D.</td>
</tr>
<tr>
<td>SARMATIAN</td>
<td>LIMESTONES, SANDSTONES, MARLSTONES AND CLAYS</td>
<td>B1</td>
<td>104.2</td>
</tr>
<tr>
<td>TORTONIAN</td>
<td>ORGANOG ENC LIMESTONES, SANDSTONES, MARLY SANDSTONES AND CLAYS, VOLCANOG ENC SEDIMENTS AND PYROCLASTS</td>
<td>B2</td>
<td>107.5 N.D.</td>
</tr>
<tr>
<td>OLIGOCENE</td>
<td>BRECCIAS, SANDSTONES, CLAYS AND CLAYSTONES</td>
<td>B3</td>
<td>108.7 N.D.</td>
</tr>
<tr>
<td>PLEISTOCENE</td>
<td>SANDSTONES AND CLAYSTONES</td>
<td>B4</td>
<td>106.1</td>
</tr>
<tr>
<td>CRETA LIRO</td>
<td>CLAYSTONES AND SANDSTONES</td>
<td>B5</td>
<td>107.5 N.D.</td>
</tr>
<tr>
<td>JURASSIC</td>
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<td>106.1</td>
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<td>TRIASSIC</td>
<td>CLAYSTONES, BRECCIAS, DIATOMITES</td>
<td>B7</td>
<td>105.5</td>
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<tr>
<td>PALEOZOIC</td>
<td>CRYSTALLINE SCHISTS</td>
<td>B8</td>
<td>105.5</td>
</tr>
</tbody>
</table>

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**Fig. 2.** Generalized section of the SE part of the Pannonian Basin showing the stratigraphic relationship of the oils studied.
RESULTS AND DISCUSSION

The bulk and specific parameters determined for each of the 19 analyzed oil samples suggest possible correlation with regard to source material, maturity, biodegradation and migration.

Correlations based on bulk parameters

The composition according to different classes of compounds of the C_{11+} fraction of the oils (Fig. 3) shows the content of saturated hydrocarbons to be 65–77% in most of the samples, of aromatics 7–17% and of NSO-compounds 13–27%. Somewhat higher content of saturated hydrocarbons, 82–87%, and lower content of NSO-compounds, 7–10%, were found in samples E2–E3. Another exception was the sample B2 with only 57% of saturated hydrocarbons and 33% of NSO-compounds.

However, other bulk parameters such as API gravity, percentage sulfur and asphaltene content, as well as specific parameters obtained from saturated hydrocarbons such as content of n-alkanes relative to total saturated hydrocarbons and pristane to phytane ratio (Pr/Ph), shown in Fig. 4, indicated that a more precise differentiation of the examined oils was possible. The oils from the oil-gas field A are rather uniform, their parameters being in a narrow range. Sample A9 is the only one to differ from the others. It has a somewhat smaller API gravity (23.8 vs 35.1–42.3), higher contents of sulfur (0.52 vs 0.19–0.37%) and asphaltene content (0.69 vs 0.11–0.52%) and a lower content of n-alkanes (15.39 vs 40.67–57.94%). Compared to other oils from this field, the A9 is a heavy oil. This may be explained by possible biodegradation of this crude oil. However, a somewhat lower Pr/Ph ratio (0.46 vs 0.70–1.08) may also indicate a distinct genetic source type for this oil.

Sample A8, just as A9, also has somewhat lower API gravity (23.5) and a higher content of sulfur (0.87%) but other parameters are in the range observed for oils A1–A3, A5 and A8. Hence, according to these bulk parameters and the Pr/Ph ratio, sample A8 could not be classified as a distinct type.

The oil B2 from oil-gas field B differs from oils B1 and B3 which, on the other hand, do not differ from oils A1–A4. Sample B2 has a somewhat lower API gravity (39.4 vs 39.8–44.5), but considerably higher sulfur content (0.77 vs 0.21–0.33%), higher percentage of asphaltene content (2.26 vs 0.07–0.36%), lower content of n-alkanes (42.30 vs 54.67–50.61%) and a lower Pr/Ph

Fig. 3. The composition of analyzed oils.
Fig. 4. Summary of the bulk and some of the specific parameters for individual fields A–D and oils shows E₁–E₄.

ratio (0.66 vs 0.90–0.94). Nevertheless, the values of these parameters are not close to those found for oil A₄. Therefore, in spite of the fact that oil B₂ probably does not belong to the same type as the other two oils from field B, it could not be classified into the same genetic type with the oil A₄.

Sample C₁ from the oil field C, according to all determined bulk parameters (Fig. 4), is similar to oils B₁, B₃ and A₁–A₄, suggesting that it belongs to the same oil type.

Samples D₁ and D₂, from oil field D, have similar values, but differ substantially from all the other oils, except oil A₄, suggesting a possible classification into the same group with the latter. Almost complete absence of n-alkanes in oils D₁ and D₂ could be explained by a moderate biodegradation, as in the case of A₄.

Three samples from the oil shows E₁, E₂ and E₃ have close parameter values, but differ considerably from other oils from fields A–D, as well as from oil E₄. Samples E₁–E₃ have a high percentage of n-alkanes (66.97–71.11%) and a high Pr/Ph ratio (1.29–1.65).

The oil E₄ differs from samples E₁–E₃ in most of the parameters, particularly by the Pr/Ph ratio (0.93), but is similar to oils from the Banat depression A₁–A₄, B₁, B₃ and C₁.

On the basis of the examined bulk parameters as well as percentage of n-alkanes and Pr/Ph ratio, the 19 oils could be classified into four groups, i.e.: types: (1) A₁–A₄, B₁, B₃, C₁ and E₄; (2) A₂, D₁ and D₂; (3) E₁–E₃; (4) B₂.

The essence of the more precise classification of the examined oils on the basis of parameters presented in Fig. 4, relative to the differentiation based only on group composition (Fig. 3), consisted in separating samples A₄, D₁ and D₂ into a distinct group. Distinctive API gravity, % sulfur, % asphaltenes and % n-alkanes of these three samples compared to other oils is most probably due to moderate biodegradation. Further confirmation for the observed biodegradation of these three crude oils is obtained from the reservoir temperatures shown in Fig. 2. Reservoir temperatures of these three oils are ≤ 66°C. This is below the limit which was shown by Philippi (1977) to be the cut-off temperature of microbial transformation of petroleum in reservoirs. Since so far the paleotemperatures of these reservoirs have not been determined, the period when biodegradation occurred cannot be surely defined.

Correlations based on source parameters

According to the distributions and interrelationships of the biological marker compounds, i.e. n-alkanes, C₂₇–C₃₂ steranes, tricyclic terpanes and pentacyclic triterpanes, the oils from fields A, B, C and D (of the Banat and South Bačka depressions) can be satisfactorily correlated with each other. On the other hand, according to most of the source parameters, these oils differ considerably from oils E₁–E₄ of the Kostolac depression (Figs 5 and 6). Thus, all the oils from the Banat depression fields, except the sample A₄ which possibly was moderately biodegraded, have a smooth distribution of n-alkanes in the range C₁₅–C₃₉, with maxima at C₁₈–C₂₁, while oils E₁–E₄ have a slight domination of odd carbon numbered n-alkanes in the range C₂₃–C₂₇. Gas chromatograms of saturated hydrocarbons of two oils with similar maturity (cf. Table 2) are given as examples in Fig. 5 [A₁ in Fig. 5(a) and E₁ in Fig. 5(b)]. The observed differences in the distribution of n-alkanes may indicate a higher contribution of terrestrial organic
The distribution of 5α(20R) C_{27}-C_{29} steranes, based on m/z 217 fragmentograms, introduced in a triangular diagram (Fig. 6), corroborates that different sedimentation environments were responsible for oils A, B, C and D (i.e. open sea) and oils E_{1}-E_{4} (bays and estuaries). The composition and distribution of tricyclic terpanes [examples are given in Figs 5(a) and 5(b)], based on m/z 191 fragmentograms in the oils from fields A–D, differ from those in oils E_{1}-E_{4}. The fragmentograms show that all oils contain a homologous C_{19}-C_{20} series. However, the samples A–D contain less C_{19}-C_{21} relative to higher, C_{23}-C_{26} members, in contrast to oils E_{1}-E_{4}. Furthermore, the distribution of unidentified peaks X, Y and Z (Fig. 5), located between the C_{24} and C_{25} members, is also different. Without exception, peak Y is more pronounced than the C_{25} peak in oils A–D, in contrast to oils E_{1}-E_{4} where the intensities of peaks X, Y and Z did not differ much.

According to some authors (Aquino Neto et al., 1983; Moldovan et al., 1983), C_{19}-C_{20} tricyclic terpanes are indicators of marine origin. However, the

<table>
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<tr>
<th>n-ALKANES</th>
<th>TRICYCLIC TERPANES</th>
<th>PENTACYCLIC TERPANES</th>
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<tr>
<td>A</td>
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<td>E</td>
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Fig. 5. Distributions of n-alkanes, tri- and pentacyclic terpanes of two particular oils, illustrating the differences in the source material between the Kostolac and Banat depressions. X, Y, Z = unidentified peaks. Ts = 18α(20R)-22,29,30-trisnorhopane; Tm = 17α(20R)-22,29,30-trisnorhopane; M = moretane; G = gammacerane; O = oleanane.

Fig. 6. Distribution of 5α(20R) C_{27}-C_{29} steranes, a parameter indicating origin (e.g. Waples, 1985).
C19 and C20 tricyclic terpanes are also presumed to originate from vascular terrestrial plants (Reed, 1977; Simoneit, 1977). Abundance of tricyclic terpanes in oils E1–E4 (i.e. abundant C19 and C20) is in agreement with the distribution of n-alkanes and C27–C29 ωx (20R) steranes, providing additional evidence that sediments with a larger relative amount of terrestrial organic material were responsible for generating oils E1–E4, distinguishing them from oils A–D. The maturity of oils E1–E4, as will be shown later by maturation parameters, did not differ much from those of oils A–D. Therefore, the difference in the distribution of C19–C21 tricyclic terpanes could not be attributed to thermal stress (Aquino Neto et al., 1983; Ekweozor and Strausz, 1983).

On the basis of the distribution in the C29–C35 hopane series, typical for moderately mature to mature oils [examples of m/z 191 fragmentograms are given in Figs 5(a) and 5(b)], samples A–D do not differ from oils E1–E4. However, the oils E1–E4 contained considerable amounts of gammacerane, often observed in oils of terrestrial origin (Seifert et al., 1983), contrary to oils A–D which contained just traces of gammacerane.

The distribution of n-alkanes, the Pr/Ph ratio, the distribution of steranes and smaller tricyclic terpanes, and the content of gammacerane, suggest that oils from fields A–D are predominantly of marine origin, and oils E1–E4 of terrestrial origin. Nevertheless, surprisingly, the oils E1–E4 contained very small quantities of oleanane (oleanane/C30 hopane = 0.03–0.07), an indicator of terrestrial origin (Riva et al., 1986), while the triterpane was found in the oils A–D in much higher relative concentrations (oleanane/C30 hopane = 0.14–0.20) with the exception of samples B3 and A4 (0.07 and 0.09, respectively). This observation suggests that oils A–D are not exclusively of marine origin and the oils E1–E4 not only of terrestrial origin.

In contrast to the conclusions based on bulk parameters, molecular source parameters indicate that the examined oils could be classified into only two genetic types, i.e. oils A–D generated in source rocks of predominantly marine origin and oils E1–E4 originating from source rocks with an additional extensive terrestrial input. However, the results obtained suggest that in some cases the oils from individual depressions originate from different source rocks. This is indicated by the values of parameters which may be indicative of the distance of oil migration and which sometimes differ even for oils from reservoirs that are close together (Fig. 1). The following parameters were considered: the ratio % saturated hydrocarbons/% aromatic hydrocarbons which is higher with longer migration, % of NSO-compounds which is lower with longer migration (e.g. Waples, 1985), and molecular sterane parameter, the ratio 13β(H), 17α(H)(20S)-diasterane/14α(H), 17α(H)(20R)-sterane (C29–C30), which, assuming that geochromatography occurs during migration, increases with longer migration distance (Seifert and Moldowan, 1981; Philp, 1985) (Table 1).

**Correlations based on maturation parameters**

According to the maturation parameters ωx(20S)/ωx(20R) C29 steranes and (22S)/(22R) C31 hopanes (Table 2), the maturity of the 19 oils is uniform and at equilibrium (values around 1.0 and 1.5, respectively; e.g., Waples, 1985).

The ratios of isoprenoid hydrocarbons pristane and phytane with the n-alkanes C17 and C18, respectively, also indicate uniformity and high maturity of the oils (Fig. 7). However, the oils A4, D1 and D3 differ from the others on the basis of their moderate biodegradation indicated earlier in the group parameters discussion of these three oils.

Also, on the basis of further sterane and terpane maturation parameters such as: ββ(20R)/ωx(20R) C29 steranes; C27ωx(20R) sterane/βα(20R) diasterane; Tm/Ts; C19ω/C23 tricyclic terpanes; C30 hopane/C29 + C30 moretane (e.g. Seifert and Moldowan, 1978; Palacas et al., 1986), the oils within the individual oil fields could be differentiated to a certain degree (Table 2).

The ratios Tm/Ts and C19ω/C23 tricyclic terpanes are considered to be among the useful maturation parameters for the oils derived from source rocks containing similar types of organic matter (Palacas et al. 1986; Philp, 1985). On the basis of these two parameters the oils from each examined field were ranged according to increasing maturity (Table 2). Other parameters from Table 2 corroborated these maturity ranges pretty good.

**CONCLUSIONS**

On the basis of bulk correlation parameters as well as content of n-alkanes and pristane to phytane...
Different values of parameters which may be indicative of the distance of oil migration observed for oils from closely located reservoirs may indicate diverse locations of source rocks even of oils within the same genetic type.

All examined oils were found to be of high and relatively uniform maturity based on the two most reliable biomarker maturation parameters, \( \frac{22S}{22R} \) C32 hopane and \( \frac{\alpha_20S}{\alpha_20R} \) C29 sterane. On the basis of other maturation parameters, calculated from the distributions of tri- and pentacyclic terpanes and steranes, the oils from the same oil fields are slightly differentiated.

The oils are not biodegraded with the exception of samples A9, D1, and D2, which are moderately biodegraded.

Acknowledgements—The authors are grateful to Nafta-Gas, Novi Sad, for the interest in this work and for the financial help. The assistance of Mr Forche with the GC-MS runs, from the Institute for Petroleum Research, Clausthal-Zellerfeld, F.R.G., is greatly appreciated. This work was supported in part by the Research Fund of the S.R. Serbia (Yugoslavia).

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