MOLECULAR AND ISOTOPE COMPOSITION OF BIOMARKERS IN IMMATURE OIL SHALE AND ITS LIQUID PYROLYSIS PRODUCTS (OPEN AND CLOSED SYSTEM)

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The molecular and isotopic composition of biomarkers in initial bitumen isolated from raw immature oil shale samples and liquid products (LPs) obtained by pyrolysis in open (OS) and closed systems (CS) are studied. The influence of pyrolysis type and variations of kerogen type on biomarkers composition and their isotopic signatures in LPs is determined. Pyrolysis experiments were performed on the two immature outcrop oil shale samples, assigned as D13 and D16 (huminite reflectance of 0.41 % Rr) from the Lower Miocene Aleksinac Basin, which is the largest and richest oil shale deposit in Serbia. The selected samples showed high content of total organic carbon (TOC > 13 wt. %), high hydrocarbon generation potential (Hydrogen Index, HI > 615 mg hydrocarbons/g TOC), but also certain variations in sources and depositional environment of organic matter (sample D13 - type I kerogen, deposited in freshwater environment; sample D16 - mixed type I/II kerogen, deposited in brackish environment; Gajica et al., 2017). Pyrolytic experiments were performed in open (OS, Pyrolyser, Model MTF 10/15/130 Carbolite, UK) and closed (CS, autoclave) systems at a temperature of 400 °C for 4 h. The biomarker signatures were evaluated using gas chromatography-mass spectrometry and carbon specific isotope analysis ($\delta^{13}C$) of individual *n*-alkanes in initial bitumen extracted from two immature oil shale samples (D13 and D16) and corresponding LPs obtained by the OS and the CS pyrolysis.

The distribution of *n*-alkanes (C_{14}–C_{35}) in LPs differs from those in bitumen of raw samples, which is reflected through the increase of lower homologues. In addition to the fact that the distribution of *n*-alkanes depends on maturity changes that particularly occur in the CS pyrolysis, it also depends on the kerogen precursor material. The prevalence of lower homologues in LPs is consistent with the predominantly algal origin of organic matter (OM) (Gajica et al., 2017). The *n*-alkane distributions in all LPs are characterized by uniform abundances of odd and even homologues, resulting in a reduction of the CPI values (~ 1) in relation to the bitumen (1.37–1.87). In initial bitumen of both raw samples, the pristane/phytane (Pr/Ph) ratio is similar (< 0.4). In LPs from the OS the values of Pr/Ph are 1.23 and 1.74. That might be explained by a preferred release of pristane than phytane from isoprenoid moieties during slight thermal treatment of kerogen (Larter et al., 1979). In LPs from the CS, the Pr/Ph ratio is ~1, that might be caused by the increase of maturity (Peters et al., 2005 and references therein). In initial bitumen, the *n*-alkan-2-ones are identified in the range of C_{12}–C_{33}. In LPs from the OS, they are present in the range C_{10}–C_{33}, whereas in LPs from the CS, C_{10}–C_{15} homologues, in very low abundance, are detected only. In initial bitumen, the fatty acid methyl esters are identified in the range of C_{13}–C_{33}. The fatty acid methyl esters are present in the range C_{11}–C_{31} in LPs from the OS, while exclusively odd C_{17}–C_{23} homologues are detected in LPs from the CS, showing notably decreasing trend with increase of number of C-atoms. In initial bitumen of raw samples, the distributions of steranes show domination of regular C_{27}–C_{29} steranes with ααα(R) configuration. Steranes with βαα(R)-configuration, typical for immature diagenetic OM, are identified in the C_{27}–C_{29} range, while ααα(S) steranes are represented by C_{29} homologue only. In the hopane distribution C_{27} 17β(H)- and 17α(H)-trisnorhopane, C_{29}–C_{32} βα moretanes, C_{29}–C_{32} αβ hopanes and C_{29}–C_{33} ββ hopanes are present. The distributions of steranes and hopanes in

LPs from the OS are almost the same with those in bitumen extracts of raw samples. On the other hand, LPs from the CS displayed notably more mature sterane and hopane distributions, which are characterized by presence of thermodynamically more stable ααα(S), αββ(S) and αββ(R) steranes, βα- and αβ-diasteranes, neohopanes (C_{27}Ts, C_{29}Ts), the prevalence of αβ- over βα- hopane isomers, and dominance of 22S- relative to 22R epimers in the C_{31}–C_{35} homohopane series. Sterane and hopane compositions and corresponding maturity parameters: C_{29} ααα 20S/(20S+20R), C_{29} αββ/(αββ+ααα), C_{31} αβ 22S/(22S+22R) and C_{30} βα/C_{30}αβ indicate a similar maturity of LPs obtained from the OS and initial bitumen, while the difference is remarkable for LPs from the CS. Generally, they suggest late diagenetic phase for LPs from the OS and catagentic stage for LPs from the CS (the calculated vitrinite reflectance is 0.76 and 0.92 for samples D13 and D16, respectively).

The isotope $\delta^{13}C$ values of individual *n*-alkanes range between –30.2 and –33.8 ‰ with average value of –31.9 ‰ in the sample D13 and from –28.7 to –32.5 ‰ (average value –30.9 ‰) in the sample D16. The $\delta^{13}C$ values of individual *n*-alkanes in LPs from the OS of samples D13 and D16 are in range from –32.6 to –35.8 ‰ (average value –34.1 ‰), and from –30.0 to –33.7 ‰ (average value –32.8 ‰), respectively. The $\delta^{13}C$ values of individual *n*-alkanes in LP from the CS of the sample D13 are between –26.6 and –30.3 ‰, average value –28.7 ‰, and from –27.8 to –31.1 ‰, average value –29.6 ‰ of the sample D16.

The molecular composition of the LPs from the OS pyrolysis is very similar to those in initial bitumen, independently on kerogen type. Due to the fast release from the reaction medium, biomarker distributions remained mostly unaltered, although slight thermal influence on *n*-alkane parameters and the Pr/Ph ratio is observed. Therefore, OS pyrolysis can be useful for assessment of source and depositional environment of OM. Pyrolysis in the CS caused more intense thermal stress; therefore the source fingerprints notably disappear. The obtained results indicate that *n*-alkan-2-ones and fatty acids methyl esters are applicable in interpretation up to late diagenetic stage, whereas at higher maturities their distributions are very scarce and represented by several short-chain homologues, only. The LPs from the CS pyrolysis have the distributions of biomarkers similar to those in crude oils generated in an early to main stage of "oil window". The biomarker data suggests that mixed type I/II kerogen attained slightly higher maturity level by the CS pyrolysis than type I kerogen. The isotopic signatures of *n*-alkanes in LPs obtained by the OS pyrolysis are isotopically lighter than in initial bitumen (~ 2 ‰), independently on kerogen type, whereas in liquid products from the CS they become heavier (~ 3 ‰ in the sample D13 and ~ 1 ‰ in the sample D16), showing more pronounced difference for type I kerogen, enriched in ^{13}C from algal biomass. The results indicate that $\delta^{13}C$ data should be used with caution in interpretation of samples having different maturity and particularly of liquid products obtained by different system pyrolysis.

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