THE APPLICABILITY OF ASPHALTENE TREATMENT (MILD OXIDATION AND PYROLYSIS) IN THE INVESTIGATION OF CRUDE OILS

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Introduction

Asphaltenes isolated both from crude oils and extracts of source rocks have been widely studied in order to characterize initial substrates more precisely (Bowden et al., 2006; Liao and Geng, 2002; Liao et al., 2006). In these studies, the distributions of saturated biomarkers (*n*-alkanes, steranes and terpanes) were studied in detail, whereas less attention was dedicated to aromatic hydrocarbons.

In our study, asphaltenes were isolated from two non-biodegraded oils, by precipitation using *n*-heptane, and subjected to a thorough extraction of adsorbed compounds using Soxhlet method during 72 h. Thereafter, they were treated by mild oxidation, using H_2O_2/CH_3COOH (Ox 1) and $NaIO_4/NaH_2PO_4$ (Ox 2) (Liao and Geng, 2002), and close system pyrolysis during 4 hours at the temperatures of 250 °C (Pyr 250) and 400 °C (Pyr 400). The obtained products were separated into saturated, aromatic and polar fractions using column chromatography. Oil maltenes underwent the same procedure. Saturated and aromatic fractions were analyzed by gas chromatography-mass spectrometry. The aim of this study is to check which of asphaltene treatment techniques, used here, shows the best similarity in distributions of biomarkers and aromatic hydrocarbons and in the values of corresponding parameters with those obtained for maltenes. In order to investigate a wide range of compounds in the products of asphaltene treatment and in maltene fractions, as well as the influence of maturity of crude oils on the results, two non-biodegraded oils of different maturity were used: immature Zr-4 oil from the Pannonian Basin, Serbia (calculated vitrinite reflectance, Rc in range 0.6 – 0.7 %) and mature SI oil from the Middle East (Rc = 0.8 – 0.9 %). Apart from the direct comparison of results, a mathematical method of least squares was also performed to confirm a degree of accordance of values for numerous geochemical parameters in the asphaltene treatment products and maltenes.

Results

The ratio of pristane to phytane (Pr/Ph) is lower in asphaltene oxidation products and higher in Pyr 400 products than in maltenes. The best fit with Pr/Ph ratio in maltenes is observed for Pyr 250. The Pr/*n*-C_{17} and Ph/*n*-C_{18} in all of asphaltene treatment products show no agreement with the values of these parameters in maltenes.

Concerning terpane parameters, the ratio of C_{30}-moretane to C_{30}-hopane, gammacerane index and the ratio of tricyclic terpanes to hopanes show best fit with maltenes in Ox1 and Ox2 asphaltene products. None of the following parameters: C_{29}Ts/C_{29}-hopane, Ts/(Ts + Tm), C_{35}(S)/C_{34}(S) hopane, as well as sterane/hopane ratio, shows good agreement between maltenes and asphaltene treatment products. On the other hand, C_{31}(S)/C_{31}(S+R) hopane ratio in maltenes fit well with all experiments performed on asphaltenes. Oleanane index (OI) for

SI oil displays a good concordance in maltenes and in both asphaltene oxidation products, but none of the experiments resulted in fitting of this parameter in Zr-4 oil. This can be attributed to the fact that OI in SI oil is apparently lower than in Zr-4 oil.

Sterane parameters, C_{29} αββR/(C_{29} αββR + C_{29} αααR), C_{29} αααS/(C_{29} αααS + C_{29} αααR) and C_{27} diasterane βαS/(C_{27} diasterane βαS + C_{27} αααR sterane) show perfect agreement between maltenes and Pyr 400. Distribution of regular C_{27}-C_{29} αααR-steranes exhibits somewhat lower agreement than the above mentioned sterane ratios. The best fit is also observed for Pyr 400, although this treatment resulted in a slight decrease of C_{29} and a slight increase in the contents of C_{28} and C_{27} homologues.

It is well known that alkylated aromatics are prone to oxidation. This is confirmed by the complete absence of naphthalene, fluorene and their methylated counterparts in Ox 1 and Ox 2. Dimethylnaphthalene and trimethylnaphthalene maturity ratios (DMNR, DNR-X, TNR 1, TNR 2 and TNy) show an agreement in maltenes and Pyr 400. On the other hand, both pyrolysates have considerably higher values of methylfluorene maturity ratio than maltenes. Phenanthrene parameters MPI 1, MPI 3, PAI 1 and DMPI 2 display a substantial concordance between Ox 2 products and maltenes. Somewhat better fitting is observed for SI than for Zr-4 oil, which can be attributed to higher maturity of SI oil, since it is known that phenanthrene maturity ratios are more useful at higher maturities (Szczerba and Rospondek, 2010). Nevertheless, the obtained result indicates that methylphenanthrenes are not prone to $NaIO_4/NaH_2PO_4$ oxidation treatment, opposite to H_2O_2/CH_3COOH. Phenanthrene ratios in both pyrolysates are higher than in maltenes, with the exception of PAI 1 in SI oil. The ratio of benz[a]anthracene to chrysene in Ox 2 products also exhibits very good fit with the values of this parameter in maltenes. Maturity ratios based on methylpyrenes (MPy) and methylchrysenes (MC), 2-MPy/(1-MPy + 2-MPy), 2-MC/1-MC and MCHR, as well as benzo[e]pyrene to benzo[a]pyrene ratio, show good agreement between maltenes and Pyr 400.

Conclusions

The obtained results imply the lack of a unique method which can result in good fitting of all biomarker and alkylaromatic ratios in asphaltene treatment products and maltenes. However, among the performed asphaltene treatments two methods deserve attention: oxidation by $NaIO_4/NaH_2PO_4$, which showed the best fit for terpane and phenanthrene parameters, and Pyr 400 that exhibited good accordance for sterane, naphthalene, methylpyrene, methylchrysene and benzopyrene ratios. Generally better fitting is observed for maturity parameters than for those reflecting source and depositional environment. No influence of maturity of initial oil was noticed on biomarker and naphthalene parameters, as well as on benz[a]anthracene to chrysene ratio, whereas mature SI oil showed somewhat better concordance for phenanthrene, pyrene, chrysene and benzopyrene ratios.

References

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