Characterization of shale oil fractions by ultrahigh resolution mass spectrometry

Justin Birdwell[1], A. Rum Sim[2], Yunju Cho[2], Sunghwan Kim[2]

[1]U.S. Geological Survey, USA, [2]Kyungpook National University, Republic of Korea

The complexity of petroleum-like products generated by oil shale retorting makes comprehensive characterization of whole oil samples a very difficult proposition. Even though ultrahigh resolution mass spectrometric techniques such as Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) can be used to resolve and assign molecular formulae to thousands of unique compounds in a whole oil sample, a great deal of additional information can be obtained by first fractionating the oil into saturates, aromatics, resins, and asphaltenes (SARA) and characterizing each fraction separately. For example, FT-ICR MS applied to a whole shale oil can reveal as many as 11,000 compounds; analysis of shale oil fractions may more than double the number of detected compounds. Results from whole oil FT-ICR MS analysis of retort oils generated from Eocene Green River Formation oil shales from different lithofacies and using various pyrolysis methods were presented at the 31st Oil Shale Symposium. In this study, those retort oils have been characterized in more detail by applying FT-ICR MS to SARA fractions and topped oils (containing only C_{15+} compounds). The aromatic and polar (resins + asphaltenes) fractions were rich in nitrogen-containing compounds, as was found for the whole oils. However, the saturate fractions contained primarily phenyl- and sulfur-substituted cyclic alkanes. Retort oil fractions generated from different oil shale lithofacies were similar in their class distributions, but did show differences in the aromaticity and carbon number distributions within particular classes, with Mahogany zone oil shales from the Piceance and Uinta Basins producing lighter, less conjugated aromatic compounds than illitic shale from the Garden Gulch Member of the Piceance Basin. These results show that the combination of chemical fractionation with molecular characterization by ultrahigh resolution mass spectrometry can be used to examine the great diversity of compounds present in petroleum products generated from oil shale. Knowledge of the composition of the chemical fractions in shale oils may be useful for understanding production and processing issues that may arise as oil shale development moves forward.