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INFLUENCE OF BIODEGRADATION ON THE CHARACTERISTICS OF RESIN AND ASPHALTENE IN LIAOHE OILFIELD

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Previous studies indicated that during biodegradation there are a systematic decrease in paraffin content (also possible in aromatic content) with increasing degradation while an increase in polar fraction, asphaltene remain rather stable during such process. Geochemical analysis in our study indicated that biodegradation can affect the characteristics of both resin and asphaltene in biodegraded oils in Liaohe basin.

There is an increase in O/C atomic ratio of asphaltene when the oil has undergone light biodegradation range from non-biodegraded oil to level 3 on the scale (abbreviated as 'PM level') [Peters, K. E., Moldowan, J. M., 1993. The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, Englewood Cliffs, NJ, p.363]. Obviously oxygen is introduced into asphaltene in this range. It is an interesting phenomenon that O/C atomic ratio in resin decreases significantly in the same range. Condensation reactions in this range should have reduced the oxygen-rich functional groups in heavy fractions.

Published carbon isotopic data of crude oils from Liaohe (Yongge et al., 2005) with various biodegradation suggested that biodegradation doesn't affect the isotopic values of whole oil (<0.2‰), a sequential loss of n-alkanes leads to ^{13}C depletion (maximum 1.5‰) of the bulk residual saturate fraction while the $\delta^{13}C$ of aromatics, resins and asphaltenes become richer in ^{13}C (maximum 0.8‰ in aromatics, 1.7‰ in resin and 1.3‰ in asphaltene) during biodegradation.

There is an increase in N/C atomic ratio in both resin and asphaltene within light to moderate biodegradation range. N/C atomic ratio in asphaltene is higher than N/C atomic ratio in resin, so we can deduce that condensation reaction in reservoir make macromolecules richer in N content. Published data of nitrogen isotopic data of Liaohe crude oils (Chuanping et al., 2001) also showed that $\delta^{15}N$ value of heavy fractions become heavier with increasing biodegradation. Nitrogen element should be introduced into heavy fractions of crude oils from

reservoir water by bacteria during biodegradation. The increase in nitrogen content should be attributed to nitrogen being introduced into asphaltene through the condensation reactions between bacterial metabolites (also remains) and macromolecules of asphaltene and resin during biodegradation.

There is a gradual decrease in S/C atomic ratio in asphaltene with increasing biodegradation. The decrease in S content can be attributed to the "dilution effect" of condensation reactions. Kinetic parameters of asphaltene and the sulfur content indicated that there is good positive relationship between S content and percent of potential with Ea ≤ 50kcal/mole in a kinetic model with fixed frequency factor $A = 10^{-14}$. C-S bonds (272KJ/mole) is easier to be broken than C-C bonds (346KJ/mole) during pyrolysis because of the lower bond energy. The S/C atomic ratios of resin are also decreased with increasing biodegradation but at a lower extent compared with asphaltene.

There should be condensation reactions during biodegradation which is similar to condensation reactions of organic molecules during diagenesis. Metabolites, and also by-products of the decomposer organisms and their remains may be selectively bonded to macromolecule backbone of heavy fractions. For example, fatty acids may be easily bonded to macromolecule backbone of heavy fractions during biodegradation by ester bond. Thus structure, isotopic composition and elemental composition of asphaltenes in biodegraded oils are influenced to some extent. Since all compounds involved in biodegradation have the same carbon source, and those bacterial metabolites are also sourced from degradable light compounds in petroleum, which are clipped from asphaltene or kerogen in oil-generation stage, those metabolites may again be bonded to macromolecule backbone of heavy fractions by condensation during biodegradation. That's why pyrolysis products of asphaltenes in biodegraded oils are similar to the original oils in both chemical composition and isotopic composition.

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