

## Effects of multiple processes on methylbenzenes in petroleum

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Methylbenzenes are present in most crude oils and are of special interest due to their specific properties, such as a relatively high volatility and solubility in water, and their relatively low resistance to biodegradation. These characteristics make methylbenzenes suitable for interpreting processes that affect the composition of crude oils such as water washing, evaporative fractionation and (early) biodegradation. Source effects can be quite conspicuous within the tri- and tetramethylbenzenes, with several low maturity oils relatively high in 1,2,3,4-TeMB and 1,2,3-TMB, derived from carotenoid precursors. Maturity affects the relative abundances of the isomers in characteristic ways, leading to enrichment of the more stable isomers. In short, methylbenzene distributions contain important information about the history and accumulation of crude oils, which can in principle be revealed by sorting out the effects that different processes have on methylbenzenes. This is especially useful for light oils and condensates, where much other geochemical information is not available. We have developed simple, quick and accurate methods for analysing all methylbenzenes quantitatively without loss of volatiles. This has allowed for the collection of data from a large variety of oils. This paper will present results from the large dataset and provide evidence for the effects that source, maturity, biodegradation and evaporation have on the composition of the methylbenzenes. Case studies will be presented underlining the practical aspects of interpreting methylbenzene data.

## Reservoir Modelling of in-Reservoir Biodegradation Explains Composition of Mixed Oil

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A suite of petroleum reservoir extracts from a North Sea reservoir were analysed to investigate the effects of biodegradation on petroleum composition. The extracts show a mixed 19° API oil composed of a lightly biodegraded oil with a suite of n-alkanes superimposed on a heavily biodegraded oil with a large unresolved complex mixture hump and suite of 25-norhopanes. Small compositional differences were observed in both the bulk fractions and biomarker parameters with depth.

The Paleocene reservoir comprises unconsolidated uniform turbiditic sands that are distal deposits of submarine fan structures. The 60 m thick reservoir unit, with a 53 m oil column, lies at a depth of 1733 m below the seabed. The reservoir sand quality is very good with average porosity and permeability of 34.5% +2.5% and 6000mD+3200mD respectively. The reservoir has not been affected by diagenetic processes and the reservoir temperature is 67°C, and thus below the temperature range (80°C) for the inhibition of hydrocarbon-degrading bacteria [1].

Modelling of the geochemical processes that have occurred in the reservoir using geological data combined with removal of oil components by biodegradation at the oil/water contact, has shown how the interactions between the geological burial history, filling, mixing and biodegradation have resulted in the oil composition found in the reservoir today. The results show that there is ongoing biodegradation and charging to the reservoir to produce the observed gradients in composition. They also show that the 'mixed' signature can be the result of a continuum of filling rather than discreet filling events.

[1] Wilhelms A., Larter S. R., Head I. M., Farrimond P., di-Primo R., and Zwach C. (2001) Biodegradation of oil in uplifted basins prevented by deep-burial sterilization. *Nature* 411, 1034-1036.

## Quantitative Whole Oil Gas Chromatography as a Tool for Understanding Biodegradation Processes in Oil Reservoirs

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Quantitative whole oil gas chromatography of oils has been used to examine the effect of moderate biodegradation on 18 oils from the Barrow Island oilfield, Australia. The Barrow Island oils came from different production wells, reservoir horizons and compartments, but have a common source (the Upper Jurassic Dingo Claystone Formation), with some organo-facies differences. Biodegradation resulted in strong depletion of n-alkanes (>95%) from most of the oils, and water washing partially or completely removed benzene and toluene. Other C<sub>5</sub>-C<sub>9</sub> hydrocarbons were variably affected by biodegradation. Quantitation (mg hydrocarbons / g oil) has enabled comparison with less or non-biodegraded oils, and thus estimation of relative % losses of each C<sub>5</sub>-C<sub>9</sub> hydrocarbon.

Adjacent methyl groups reduce the susceptibility of an isomer to biodegradation. 2-Methylalkanes are the most susceptible branched alkanes to biodegradation, 3-methylalkanes are the most resistant and 4-methylalkanes have intermediate resistance. For example, 2-methylpentane is depleted ~15% quicker than 3-methylpentane, and 2-methylhexane is depleted ~10% quicker than 3-methylhexane. Similarly, *trans*-1,2-dimethylcyclopentane is depleted ~35% quicker than 1,1-dimethylcyclopentane, and *cis*-1,3-dimethylcyclohexane is depleted ~35% quicker than 1,1-dimethylcyclohexane, because cyclic alkanes with *gem*-dimethyl substituents inhibit bacterial attack. In addition to the position of alkylation, the carbon skeleton and the degree of alkylation also control susceptibility to moderate biodegradation of cyclic, branched and aromatic C<sub>5</sub>-C<sub>9</sub> hydrocarbons.

Quantitative data help to better understand bacterial processes operating in petroleum reservoirs. This study shows that the distribution of low molecular weight hydrocarbons in oils is very useful for understanding the dynamic oil migration, mixing and alteration processes that affect many petroleum reservoirs.