Application of Analytical Techniques in Geochemical Studies for Characterizing Mixture of Biodegraded and Non-biodegraded Oils

E.C.de Sá ¹, S.M.Barbanti ², L.Landau ¹

¹Laboratório de Métodos Computacionais em Engenharia-LAMCE/COPPE/PEC/UFRJ – Cidade Universitária – Ilha do Fundão. Centro de Tecnologia, Bloco I-2000/sala I-214. P.O.Box 68552-Rio de Janeiro-21949-900. E-mail:elizcs@lamce.ufrj.br
²Centro de Pesquisas e Desenvolvimento Leopoldo A. Miguez de Mello-COPPETEC/UFRJ - Av. Hum, Quadra 7, 21949-900, Rio de Janeiro, RJ

Abstract

According to geochemical studies, the majority of the petroleum accumulations in the Brazilian continental margin sedimentary basins are the result of the mixture of biodegraded and non-biodegraded oils from multiple episodes of charging, and the relative amount of each one controls the final oil quality. In this work, we propose to develop a methodology to predict the amount of contribution of biodegraded oil in the mixture, using results from several geochemical analyses. The results of API gravity, the percentage of saturated hydrocarbons, biomarkers ratios and the ratio derived from values of UCM (unresolved complex mixture) allow the evaluation of trends of variations between the end members (biodegraded and non-biodegraded oils) according to the increasing of contribution of biodegraded oil in the mixture. The linear multiple regression method was used to estimate the amount of contribution of biodegraded oil in the mixtures which were simulated in laboratory. The relationship between the experimental and the estimated values of the contribution of biodegraded oil in the mixtures are quite similar. Thus, the methodology proposed could be used as a tool to evaluate the final quality of oil in reservoirs. It is simple, cheap, fast and can be performed routinely in geochemical studies.

Keywords – oil mixing, biodegradation, 25-norhopane, biomarker, UCM, API gravity

Introduction

Biodegradation of crude oil in the reservoirs is an important alteration process with major economic consequences for oil production and refining operations. Most of the world’s petroleum is biodegraded and while the effects of biodegradation on the molecular composition and physical properties of crude oil are relatively well known, the actual process taking place during biodegradation of crude oil in deep reservoirs remain obscure (Larter et. al. 2003).

Geochemists have made substantial advances in identifying the geochemical sequences of subsurface oil degradation (Connan, 1984). However, in many cases, it is geological factors such as oil mixing that dominate the final oil composition and physical properties. Reservoirs can be charged by multiple phases, continuously or periodically, resulting in complex fluid quality distributions (Huang et. al., 2004).

The mixing of biodegraded and non-biodegraded oils is indicated by the presence of a pronounced unresolved complex mixture (UCM) in the fingerprint pattern from gas chromatography (GC) analysis of whole oil together with the presence of both 25-norhopanes and n-alkanes (Rooney et. al., 1998). Since reservoir charging is a dynamic process, Later et. al., (2003) proposed that fresh charge mixing concurrent with biodegradation is the key to understanding oil biodegradation.
In this work, we propose to develop a methodology to predict the amount of biodegraded oil in the mixing of biodegraded and non-biodegraded oils, using routine geochemical analyses. This methodology can be used as a tool to evaluate the final quality of oil in reservoirs.

**Methodology**

Two oil samples from the Campos Basin, biodegraded (B oil) and non-biodegraded (A oil), were selected to prepare mixtures in different proportions to simulate the process of oil mixing which usually occurs in reservoir. Each one of mixtures was prepared three times to evaluate the standard deviation and minimize the analytical error. The mixtures were analyzed by routine geochemical techniques such as liquid chromatography (LC), gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS), thin layer chromatography (TLC-FID), determination of sulfur, nickel and vanadium content and API gravity.

**Results and Discussion**

Based on the results obtained by the routine geochemical techniques, we have done a wide study to find parameters to predict the amount of contribution of biodegraded oil in the oil mixing in reservoirs.

The results obtained from the determination of API gravity and percentage of saturated hydrocarbons showed suitable correlations to estimate the proportion between the biodegraded and non-biodegraded oil in the mixture, as it had already observed by Cerqueira et al., (2002) (Fig. 1).

The ratios from gas chromatography presented an invariable behavior with the increasing percentage of biodegraded oil in the mixture. These data suggest that the increasing percentage of saturated hydrocarbons (isoprenoids and n-alkanes) came only from the non-biodegraded oil in the mixture. However the UCM/(UCM+\(\Sigma n\)-alkanes) ratio obtained from areas in the GC trace of the mixtures of biodegraded oil (B oil) and non-biodegraded oil (A oil), showed considerable trends of variation with the increase of the proportion of biodegraded oil (B oil) in the mixtures (Fig. 2).

The ratios derived from biomarkers analyses (GC-MS) were considered another tool to evaluate the proportion between the biodegraded and non-biodegraded oils in the mixtures. Several biomarker ratios were calculated, but only some of them were really studied to be used to estimate the contribution of the biodegraded oil in the mixture such as hopanes/steranes, 25-norhopanes/C\(_{30}\)-hopanes, C\(_{29}\)-25-norhopanes/C\(_{29}\)-hopanes, diasteranes/regular steranes, tricyclics terpanes/hopanes and C23-tricyclic terpane/hopanes (Fig. 3).

According to the mathematic equation proposed by the multivariate linear method, the results obtained for the estimated amount of the contribution of the biodegraded oil in the mixtures are quite similar to the experimental results.

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Y_i = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 + \epsilon
\]

- \(Y_i\) = Independent variable (contribution proportion)
- \(\alpha_0 - \alpha_4\) = Coefficients
- \(X_1 - X_4\) = Dependents variables (API gravity, percentage of saturated hydrocarbons, UCM/(UCM+\(\Sigma n\)-alkanes) ratio and biomarker ratio)
- \(\epsilon\) = error.
Conclusions
When it is suspected that an is a composite of biodegraded and non-biodegraded oils mixed in reservoirs, it can be identified by different geochemical parameters such as presence of a pronounced unresolved complex mixture (UCM) together with the presence of 25-norhopanes and \( n \)-alkanes.

The gas chromatography ratios did not present trends of variation with the increasing of proportion of biodegraded oil in the mixtures. These data showed that the increasing concentration of saturated hydrocarbons (isoprenoids and \( n \)-alkanes) came only from the non-biodegraded oil in the mixture. Therefore the presence of saturated hydrocarbons did not reflect the proportion between biodegraded and non-biodegraded oil in the mixtures.

The biomarker ratios showed significant variations with the progressively increase of the proportion of biodegraded oil in the mixtures. Hopanes/Steranes ratio tends to increase with the increasing of proportion of biodegraded oil in the mixtures because the biodegradation seems to affect steranes earlier than hopanes in most geological cases (Peters & Moldowan, 1993).

Molecular composition and physical properties showed significant variations with the increasing proportion of biodegraded oil in the mixture such as a decrease in the hydrocarbons content and an increase in oil density, sulphur content and viscosity.

The multivariate linear method can be used as a tool to estimate the contribution proportion of each oil in the mixture, using API gravity, the percentage of saturated hydrocarbons, biomarker ratio and UCM/(UCM+\( \sum n \)-alkanes) ratio as dependent variables.

References


Fig. 1: Experimental proportion variation of the mixtures with their API gravity and the percentage of saturated hydrocarbons.

Fig. 2: Variation of the UCM/(UCM+$\Sigma n$-alkanes) ratio obtained from areas in the GC trace of mixtures of biodegraded (B oil) and non-biodegraded (A oil) oils as a function of the proportion (A oil) in the experimental mixtures.
Fig. 3: Experimental proportion variation of the mixtures with the biomarker ratio (Hopanes/Steranes), calculated from GC-MS peak heights.