APPLICATION OF ANALYTICAL TECHNIQUES IN GEOCHEMICAL STUDIES FOR CHARACTERIZING MIXTURE OF BIODEGRADED AND NON-BIODEGRADED OILS

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Resumo – Segundo dados geoquímicos, as acumulações de petróleo da Bacia de Campos são formadas por misturas de óleos biodegradado e não-biodegradado, e a proporção relativa entre eles é fator controlador da qualidade final do petróleo no reservatório. O objetivo deste trabalho é estudar o comportamento geoquímico das misturas de óleo e desenvolver uma metodologia que permita estimar a porcentagem de contribuição do óleo não-biodegradado em misturas de óleos, utilizando análises geoquímicas de rotina. As misturas de óleos preparadas em laboratório foram analisadas por diversas técnicas analíticas para avaliar tendências quanto à variação da proporcionalidade entre os óleos biodegradado e não-biodegradado. Os valores do grau API, teor de hidrocarbonetos saturados, razões de biomarcadores e razão de *UCM* (mistura complexa de compostos não resolvidos) contribuíram para estimar a proporção das misturas a partir do método de regressão linear múltipla seqüencial. Os valores da proporção experimental e da proporção estimada das misturas apresentaram comportamentos similares, sugerindo que tal metodologia pode ser uma ferramenta útil para estimar a qualidade do petróleo no reservatório, além de ser simples e rápida, uma vez que os dados necessários são gerados a partir de análises de rotina nos laboratórios de geoquímica.

Palavras-Chave: mistura de óleos; biodegradação; 25-norhopano, biomarcador, UCM.

Abstract – The 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 oils in reservoirs. It is simple, cheap, fast and can be performed routinely in geochemical studies.

Keywords: oil mixing, biodegradation, 25-norhopane, biomarker, *UCM*.

1. Introdução

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 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 the (composite) 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 between biodegraded and non-biodegraded oils, using routine geochemical techniques. This methodology can be used as a tool to evaluate the final quality of oils in reservoirs.

2. Methodology

Two oils from the Campos Basin (biodegraded and non-biodegraded oils) 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 as well as by 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.

3. 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.

According to Cerqueira *et. al*. (2002), studies demonstrated that the API gravity and the percentage of saturated hydrocarbons can be used to estimate the contribution biodegraded and non-biodegraded oils in the mixtures (Figure. 1).

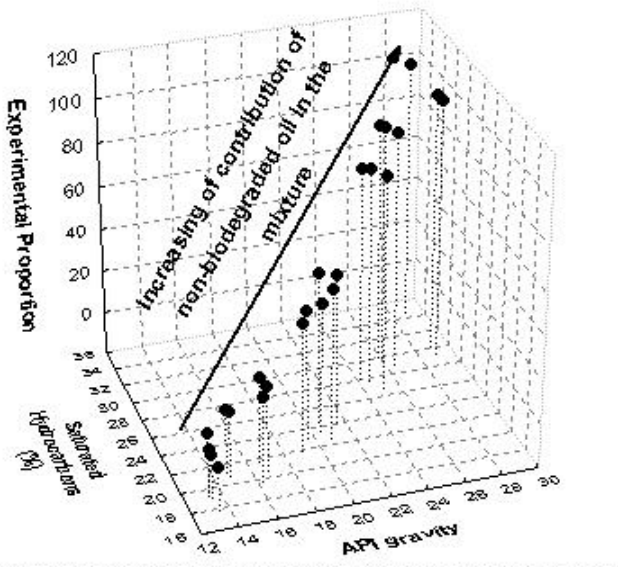

Figure 1. Experimental proportion variation of the mixtures with their API gravity and the percentage of saturated hydrocarbons.

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*+Σ*n*-alkanes) ratio, obtained from areas in the GC trace of the artificial mixtures of biodegraded oil (B oil) and non-biodegraded oil (A oil),

showed considerable trends of variation with the increase of the proportion of non-biodegraded oil (A oil) in the mixture (Figure 2).

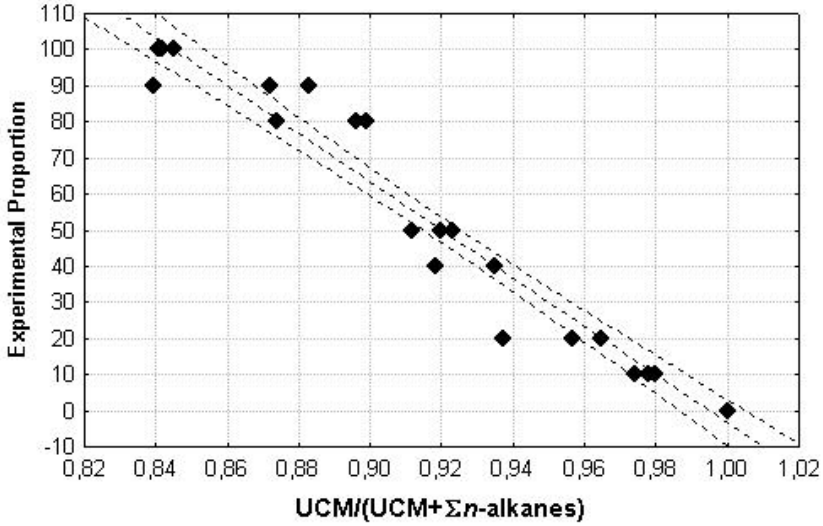

Figure 2. Variation of the UCM/(UCM + Σ *n*-alkanes) ratio obtained from areas in the GC trace of mixtures of biodegraded (Boil) and non-biodegraded (A oil) oils as a function of the proportion (A oil) in the experimental mixtures.

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 then 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 (Figure 3).

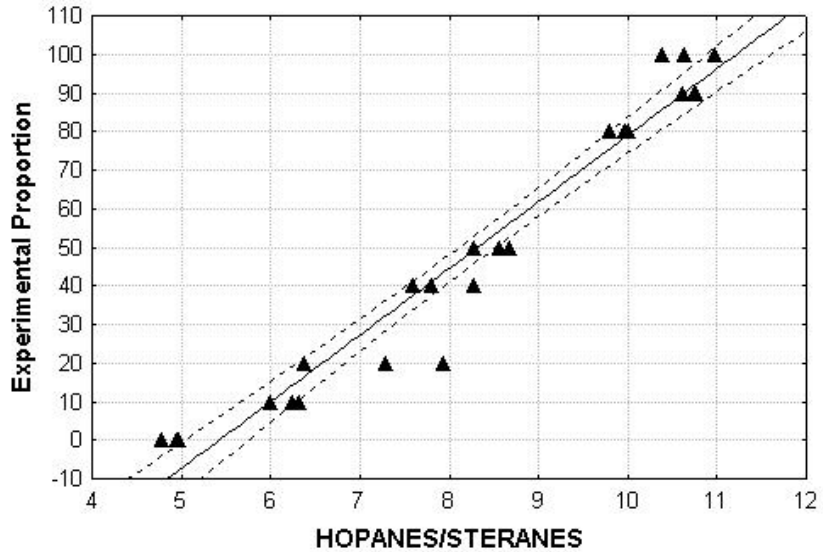

Figure 3. Experimental proportion variation of the mixtures with the biomarker ratio (Hopanes/Steranes), calculated from GC-MS peak heights.

We proposed a mathematic equation to estimate the contribution proportion of biodegraded oil in the artificial mixing that had prepared in laboratory using a multivariate linear method (Equation 1). The relationship between the experimental and the estimated amount of contribution of the biodegraded oil in the mixtures was quite similar.

$$Y_i = \alpha_0 + \alpha_1 X_1 + \alpha_2 X_2 + \alpha_3 X_3 + \alpha_4 X_4 + \varepsilon \quad (1)$$

- Y = Independent variable (contribution proportion)
- $\alpha_0 - \alpha_4$ = Coefficients

- $X_1 – X_4$ = Dependents variables (API gravity, percentage of saturated hydrocarbons, UCM/(UCM+Σ*n*-alkanes) ratio and biomarker ratio)

ε = error

3. Conclusions

When it is suspected that oil 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) in the fingerprint pattern from gas chromatography (GC) analysis of the (composite) oil together with the presence of both 25-norhopanes and *n*-alkanes.

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+Σ*n*-alkanes) ratio as dependent variables.

4. References

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