Vertical variability in crude oil composition: Es-Soc Well, Socororo Field, Eastern Venezuelan Basin

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Introduction
The determination of producing intervals and oil quality in a reservoir requires the study of different geochemical parameters. In particular, oil quality reflects the compositional characteristics of hydrocarbons that impact the economic viability of an exploration, development, or production opportunity. In general, oil quality may affect the direct economic value of the crude oil. Typical oil-quality properties include API gravity, viscosity, sulfur, asphaltene, and metals (e.g., vanadium, nickel) contents, and acidity. Biodegradation can significantly impact essentially all oil-quality properties of crude oils in producing zones. More specifically, oil biodegradation typically (a) decreases API gravity, (b) reduces the content of saturated and aromatic hydrocarbons relative to polar compounds (c) increases oil viscosity, (d) increases oil acidity and (e) increases the sulfur content and the concentration of certain metals (e.g., V and Ni). As a consequence, the residual oil resulting from biodegradation becomes enriched in NSO compounds (resin and asphaltene fractions), sulfur and metals (Connan, 1984; Wenger et al., 2002; Larter et al., 2006). Knowledge of the lateral and vertical variations in the oil-quality properties as a consequence of biodegradation is an important key to the development and implementation of enhanced oil recovery methods.

Venezuela has one of the world’s largest reserves of heavy and extra heavy biodegraded crude oils in the Eastern Venezuelan Basin, which includes the widely studied Orinoco Oil Belt and the Socororo Major Area in the Maturin sub-basin. The Socororo field, and in particular the ES-SOC oil well, in the Socororo Major Area is the subject of this study. Here, we describe the vertical variability in the extractable organic matter (EOM) of sidewall core samples and oil composition. The latter was correlated to the characteristics of the source rock (e.g., lithology, organic-matter input, redox depositional conditions, and thermal maturity) in order to establish oil quality as a consequence of biodegradation.

Experimental
The samples suites consisted of a freshly recovered crude oil sample and sixteen sidewall core samples from the ES-SOC well obtained from a relative depth interval of 878 m to 1373 m. Organic carbon concentration (LECO, C-144), and sulfur content (LECO SC-432) were determined. Extractable organic matter (EOM, %m/m) was obtained using Soxhlet extraction technique with dichloromethane. The oil samples were de-asphalted to obtain a maltene fraction, which was subsequently separated into its saturated, aromatic and resin fractions by means of adsorption chromatography, using packed columns with alumina as the stationary phase. The saturated hydrocarbons were eluted with n-hexane, the aromatic hydrocarbons with toluene, and the polar compounds (resins) with a mixture of toluene and methanol. Analyses of the saturated biomarkers were performed by gas chromatography-mass spectrometry (GC-MS) on a network gas chromatograph (Model 6890N, Agilent Technologies) coupled to a mass spectrometer (Model 5975, Agilent Technologies). The GC system was equipped with DB-1 fused silica capillary column (60 m x 0.25 mm x 0.25 μm). The monitored ions were m/z = 113 for n-alkanes, pristane and phytane; m/z = 191, 177 for terpanes; and m/z = 217, 218 for steranes and diasteranes.

Results and Discussion

Crude oil type
Analysis of the C24/C23 and C26/C25 tricyclic terpanes ratios and C27-C29 regular steranes abundance indicates that the crude oil originated from marine organic matter. The ratio C35/C34 ≥ 1 suggests anoxic-suboxic conditions during source rock deposition (Figure 1). Additionally, the calculated values for the C24/C23, C22/C21 and C26/C25 tricyclic terpanes ratios and C31R/C30Hop hopanes ratios suggest that the analyzed oil originated from either a marine-carbonate or a marine-marl source rock. The calculated values for the C29 sterane isomerization ratios C2920S = 54.5% and C29ββ = 52.5% indicate that the endpoint has not been reached (C2920S = 52-55% and C29ββ = 67-71% at endpoint; Peters and Moldowan, 1993). These results suggest that the crude oils were generated prior or at the beginning of the oil window.

Figure 1. Mass chromatograms of the terpanes (m/z = 191 and 177, top) and steranes (m/z = 217, bottom) in the saturated hydrocarbon fractions isolated from ES-SOC oil samples.
Alteration by biodegradation

The EOM concentrations in the core samples exhibited values lower than 0.1% (0.02-0.89 %), except for a sample taken at the depth interval of 1360 m where EOM reached a value of 2.4% (Figure 2).

The analyzed crude oil with 14° API and a sulfur content of 2.5%, presented a SARA composition of 24% saturated hydrocarbons, 36% aromatic hydrocarbons and 40% polar compounds (resins + asphaltenes). Figure 2 shows the n-alkanes and pristane phytane distributions for the crude oil. The distributions are characterized by a wide unresolved complex mixture (UCM) contribution under a resolved peak envelope showing the presence of acyclic isoprenoids (phytane and pristane) and variations in the relative intensity of n-alkanes, indicative of alteration by biodegradation.

The abundance of C23 tricyclic terpanes, the slight alteration of steranes, and the absence of 25-norhopanes (Figure 1) indicate that the crude oil is biodegraded to at least a PM level 5 (Peters and Moldowan, 1993). In contrast, crude oils from other wells in the Socororo field showed the presence of isoprenoids pristane and phytane, absence of n-alkanes and traces of 25-norhopanes, indicating different loadings of oils to the reservoir, which were subsequently biodegraded.

Conclusions

The crude oil extracted from the ES-SOC well, Socororo field, was originated from either a marine-carbonate or a marine-marl source rock with marine organic matter input deposited in anoxic-suboxic conditions and at an early oil window level of maturity. After generation, the oil was biodegraded at a PM level 5.

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