Geochemical characterization of discovery new gas-condensates reservoir on Golfo de Venezuela Basin, Offshore, Venezuela

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1. Background

Offshore exploration studies are currently one of the main objectives of the Venezuela oil industry; these have been extended in several areas: East, Nor-east, Center and western (Golfo de Venezuela) part of the country, being the latter the area of interest on this work.

Since Oil Industry nationalization, adjacent area to Golfo de Venezuela (Figure 1) has been explored moderately; several surface geology studies have been conducted in the area surrounding (Guajira, Falcón and Paraguaná), recorded geophysical studies (gravity, magnetic, seismic reflection and refraction) between the 50' and 70'. These were the base for hydrocarbon potential study conducted Guevara et al. (1977), in which indicated that there are geological conditions for hydrocarbons accumulation and were delineated 20 prospectives blocks.

However, until past decade was that began drilling in the Gulf of Venezuela, the first exploration began in 2009 when was drilled the first wells in the northeast of the area and which confirms the existence of gas and light oil on Tertiary carbonate facies. Due to this discovery, has been of great interest since it is estimated that more than 10 TFC remain on the area, generating an intense exploration activity that including drilling new wells, geophysical (3D seismic), geological, sedimentological, stratigraphic, and geochemical evaluations, in order to have a better understanding of petroleum system present on the area and to assess the genesis of hydrocarbons discovered.

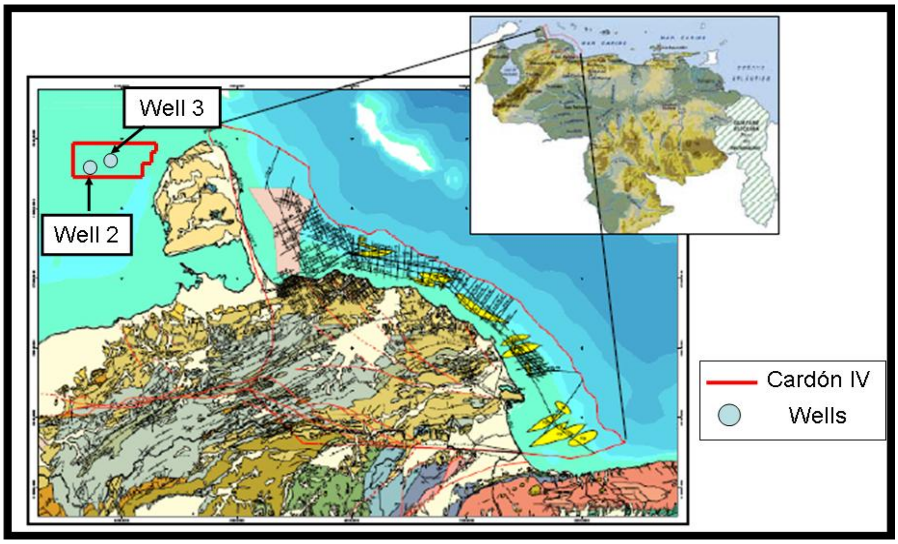


Figure1. Relative location of Golfo de Venezuela

2. Aims

The origin of light oil (gas and condensates) discovered at the Northeast of Gulf of Venezuela is the great interest to study and understanding of petroleum system in the area. In this sense, the main objective of this work was to carry out the geochemical characterization of fluids and to establish oil-oil correlations to determine if there is more than one oil family on the area.

3. Methods

Gas and condensates samples were collected from Well 2 and Well 3 to characterize fluids present in Cardon IV field. The interval evaluated corresponds to a sequence calcareous from early Miocene (Cuauderalito Member; Pinto et al., 2011) with a thickness of approximately 750 ft, located (by electric logs) between 9000 - 9700 ft to depth.

Chemical composition and molecular gas determination was based on the procedure described in analytical norm COVENIN 2569-89. The method is based on physical separation by gas chromatography of the components of a sample and its subsequent comparison with the components corresponding to a reference mixture. The composition of the sample was calculated by comparing the heights, peak areas or both, with the values δ obtained with the reference standard.

Isotopic composition was determined using isotope ratio GC (GC-C-IRMS). The system used was a continuous stream or "Online" mode and is comprised of a gas chromatograph (Trace GC Ultra, Thermo Scientific) connected to an interface (GC Combustion III, Finigan) and coupled to a mass spectrometer of isotopic ratios (Delta V Plus, Thermo Scientific). To assess the system conditions and ensure the reproducibility of results was analyzed together with samples, a reference material (RM 8561, biogenic methane gas). The chromatographic conditions of analysis were: CP-PoraBond chromatographic column Q (25MX, 0.32 mm), injector temperature 100°C, and column temperature 24°C (isothermal), using helium carrier gas with constant flow of 1.5 mL/min.

On the other hand, for liquid hydrocarbons, their samples characterizations were performed the following tests:

- API gravity and metals (V, Ni and S) determination. API was determined both densimetry techniques and hydrometer methods while S was determined via X-ray fluorescence.
- GC of C_{15}^- fraction was performed on a gas chromatograph HP-6890 equipped with a capillary column of 1.05 μm NAP type, programming with temperature, helium carrier gas and FID detector (flame ionization detector).
- SARA composition, which fractions were obtained with a high performance liquid chromatography (HPLC). On the saturated fraction was made CG-C_{15}^+ fraction and the identification of biomarkers by GC-MS besides of molecular sieve. The inclusion of molecular sieve is an analytical procedure applied for the separation of normal paraffins to iso and cycloparaffins using molecular sieves. Scientific basis lies in the ability of adsorption of straight chain $-CH_2-CH_2-$ by pores of 5 Å molecular sieves, improving the quality of analytical results obtained from GC and GC-MS.

- $\delta^{13}C$ determination of total oil and saturated and aromatic fractions relative to VPDB (δ13C VPDB: -30.66 ± 0.05 ‰). These fractions were analyzed by continuous flow and the total oil, for "dual inlet", using acetanilide as internal standard. Each sample was analyzed to determine its value $\delta^{13}C$ isotopic VPDB, at least 5 times.

Additionally, the study of specific compounds (Diamondoids) was conducted by application of certified standards for each of the compounds analyzed which were: adamantane, 1-methyladamantane, 1, 3-dymethyladamantane, 1, 3, 5-trimethyladamantane, 2-methyladamantane, cis-dimethyladamantane, trans-1,4-dimethyadamantane, 1,2-dimethyladamantane, 1-ethyladamantane, 1-ethyl-3-methyadamantane, 2-ethyladamantane, diamantine and 1-methyldiamantane. These were analyzed in Agilent 6890N GC coupled with Agilent 5973N MS.

4. Results

4.1. Geochemical gas characterization

The results of gas chromatography reflect values below 95 mol% in CH_4 showing characteristics of wet gas (Schoell, 1983) coupled with a value greater than 4% for C_2H_6 (ethane) and more than 7% of compounds C_2^+ (Table 1). Von der Dick diagram (Figure 2) indicates that the source of generation of these gases is associated with hydrocarbon type condensate. In fact, production testing of both well shows gas and liquid hydrocarbon (condensate).

Bernard diagram confirms above information (Figure 3), these hydrocarbons were classified as a wet gas (thermogenic source), according to the $\delta^{13}C$ values obtained for CH_4 which range are between -44 ‰ and -69 ‰ (Hunt, 1996).

Table 1. Gas samples chromatography well 2 and well 3

Gases	**Well 2**	**Well 3 (sample 1)**	**Well 3 (sample 2)**
	% mol		
CH_4	90.08	89.79	89.84
C_2H_6	4.18	3.22	3.22
C_3H_8	1.69	1.25	1.25
i-butane	0.30	0.25	0.25
n-butane	0.55	0.42	0.42
i-pentane	0.177	0.153	0.151
n-pentane	0.143	0.124	0.121
Hexanes	0.108	0.113	0.106
Heptanes	0.094	0.124	0.111
Octanes	0.028	0.048	0.047
Nonanes	0.003	0.01	0.007
Decanes	0.001	0.000	0.000
Undecanes	0.001	0.000	0.000
N_2	0.43	0.59	0.56
CO_2	2.20	3.91	3.92

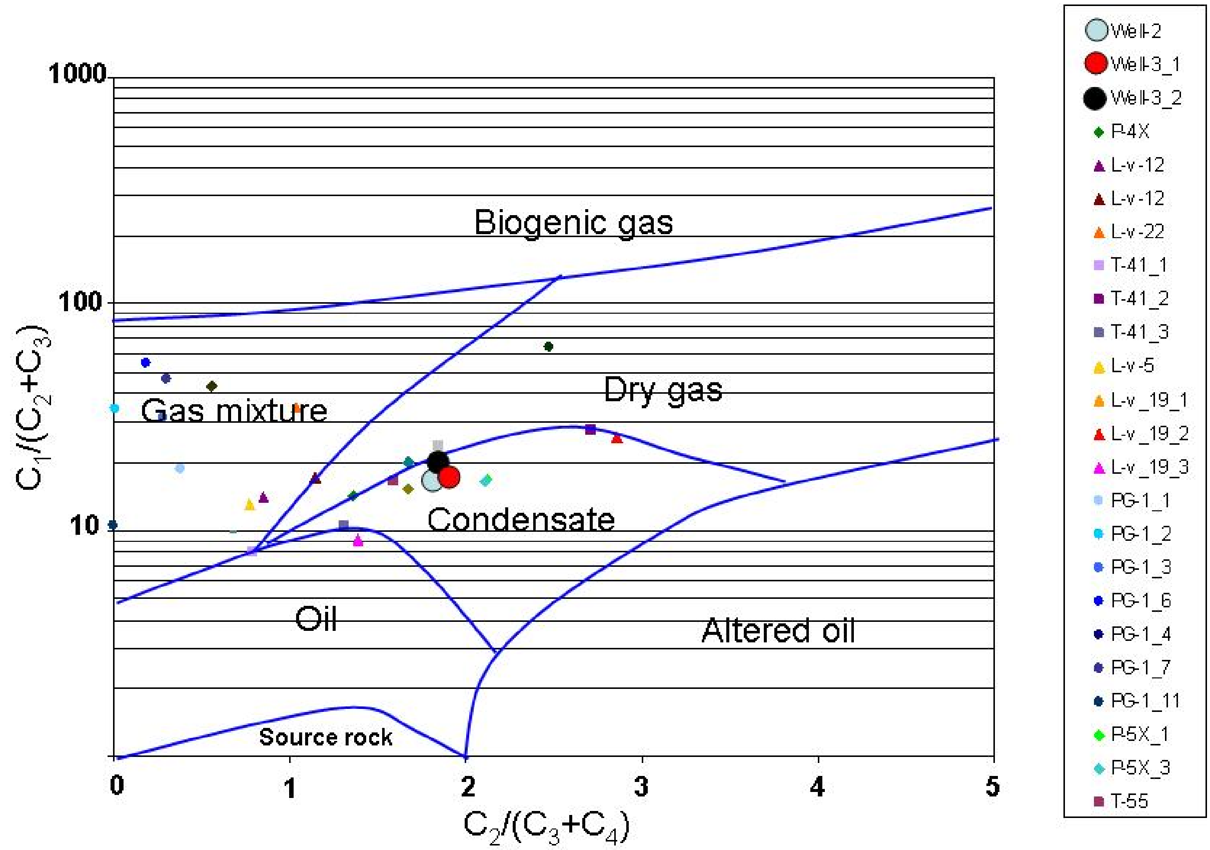


Figure 2. Identification of origin of the gases
(Modified after Von Der Dick et al., 1994)

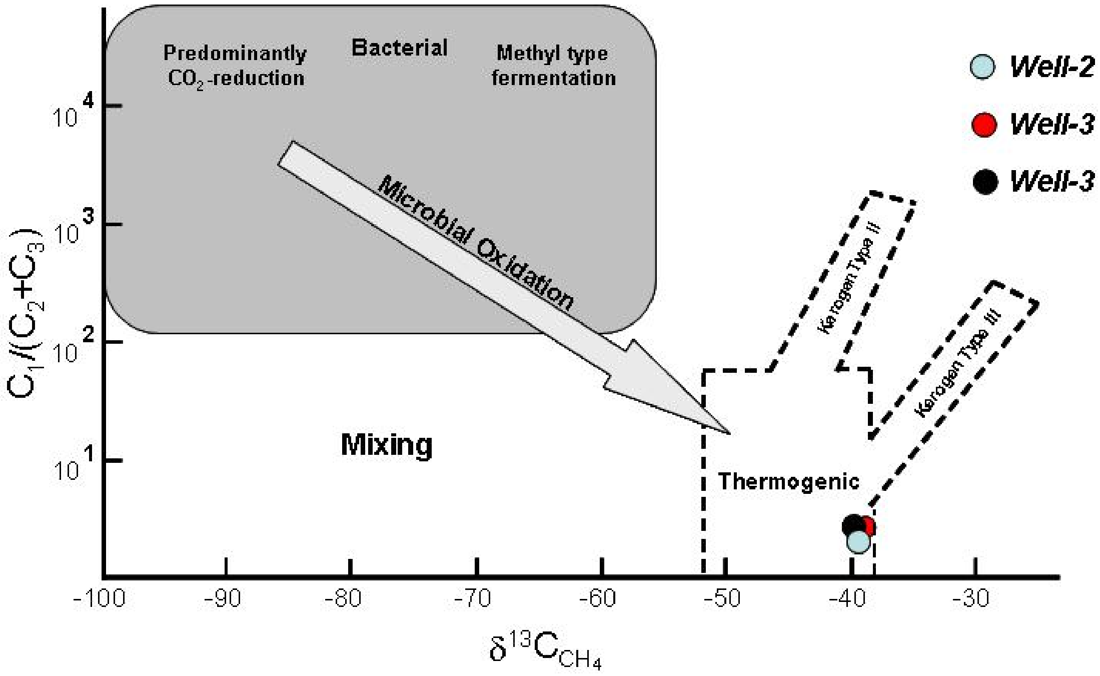


Figure 3. Bernard diagram
(Modified after Whiticar, 1994)

In relation to the value obtained for $\delta^{13}C_{CO2}$ close to -6 ‰, this represents a ^{13}C-enriched gas relative to CO_2 gas associated with oil (values δ between -25 ‰ to -28 ‰), suggests a contamination source, possibly air (Javoy et al., 1986, Whiticar, 1994). Air contamination occurred during sampling, probably due to the presence of trace atmospheric gas (air) inside the sample equipment, which alters the initial values of the gas. Nevertheless, the effect caused by this contamination is negligible for characterization of gas due low percentage value obtained for CO_2 (Table 1).

On the other hand, despite the predominance of methane in natural gas, reliability and unambiguous information from the source rock from the data of this compound by itself is complicated. Therefore, it is necessary to use the information provided by other hydrocarbons and gaseous species to coexist such as ethane, propane, butane and carbon dioxide. Unlike methane, carbon isotope ratios of the gaseous components C_2+ might show differences between different gases, due to the close association of ethane isotopic with their counterparts.

In this sense, were obtained values of δ^{13}C isotope ratios of hydrocarbon gases with more carbon than methane, specifically the number of C_2-C_5 alkanes including iso-butane. Figure 4 shows the δ^{13}C isotope ratio of methane and ethane to predict the type of organic matter which is associated precursor gas. The results of Well 2 and Well 3 suggests that the gas was originated from the thermal cracking (thermogenic gas) of a type III-II kerogen consists of a mixture of terrestrial and marine organic matter, dominated by the first (Huang et al., 2003).

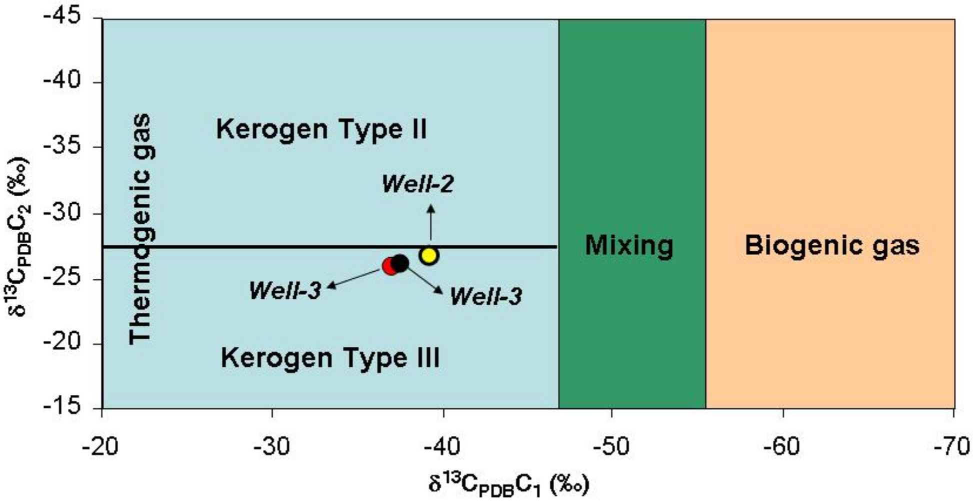


Figure 4. Organic matter type from δ13CCH4 and δ13CC2H6
(Modified after Huang, 2003)

Moreover, the difference between ethane and propane isotope plotted in the Figure 5, shows that the gas in the reservoir has been generated by primary cracking of organic matter in source rock, and its maturity is equivalent in terms of values of vitrinite reflectance % Ro near to 1.1 (mature area within the window generation). According to isotopic differences found for the gases methane, ethane and methane-propane, the temperature required for the generation of gas was about 180°C, at which organic matter remains on catagenesis stage, generation zone of wet gas (Figure 6) (Rooney et al., 1995).

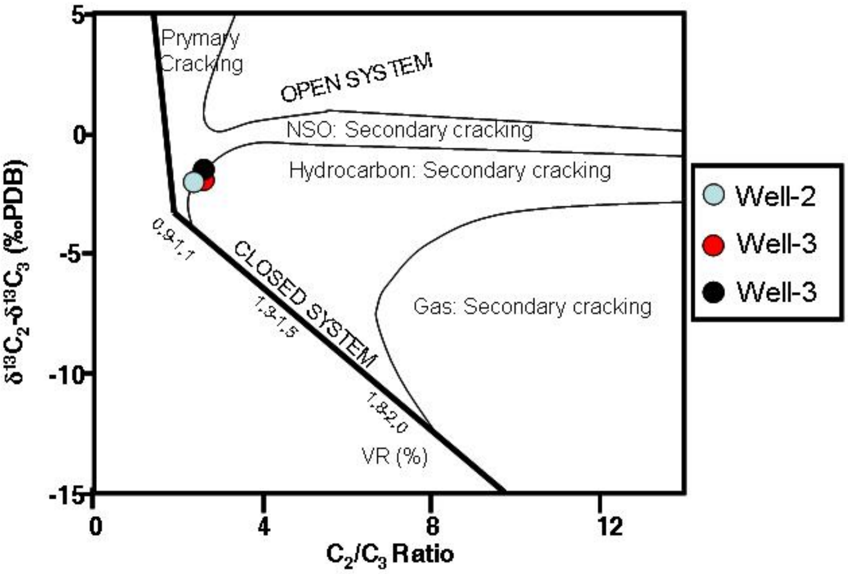


Figure 5. Maturity of the natural gases and degree of opening and closing on the system (Modified after Gürgey et al., 2005)

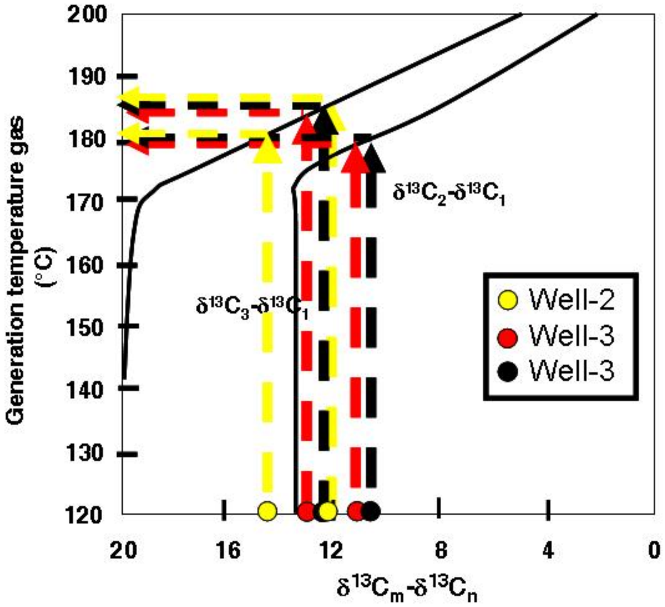


Figure 6. Generation temperature gas vs. isotopic differences (Rooney et al., 1995)

4.2. Geochemical condensates characterization

Liquid petroleum present in the same reservoir showed values for ° API (≈ 49 ° API) that indicate it corresponds to a light hydrocarbon type, close to condensates (Hunt, 1996). This value correlates with SARA composition: saturated hydrocarbons (70 wt%) and aromatics (30 wt%), with no concentration for asphaltenes and resins fractions. Figure 7 shows certain correspondence between both wells and indicates type crude oil paraffin.

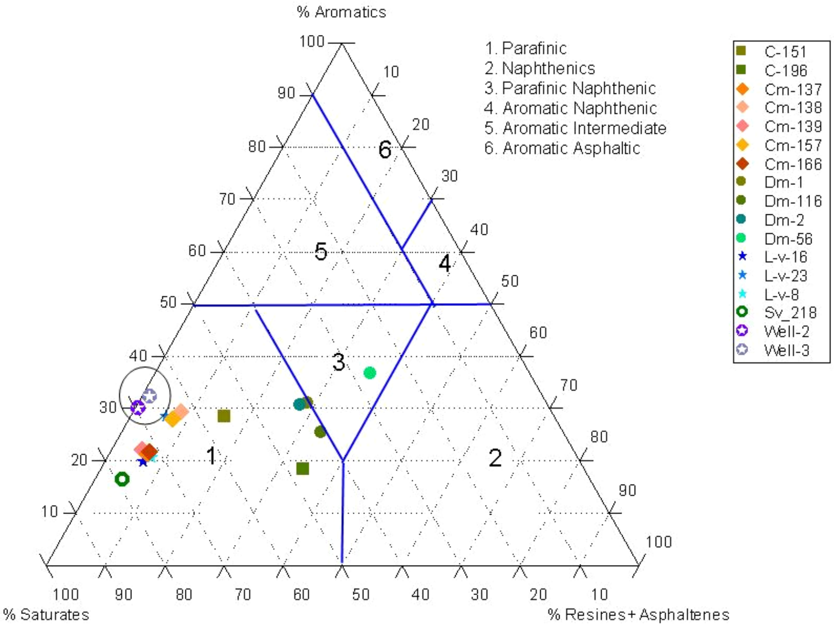


Figure 7. SARA composition

Different elements concentrations were determined to infer crude origin such as S, V and Ni, in oil from Well 2 and Well 3. The value of the sulfur concentration was low 349 ± 30 ppm (mg / kg). The proportion of this element in the oil is correlated with siliciclastic source rock type. V and Ni relation suggests that these elements are in low proportions in relation to other wells in the study area (Falcón area), including oils present in Hombre Pintado, Tiguaje and Cumarebo fields (Figure 8).

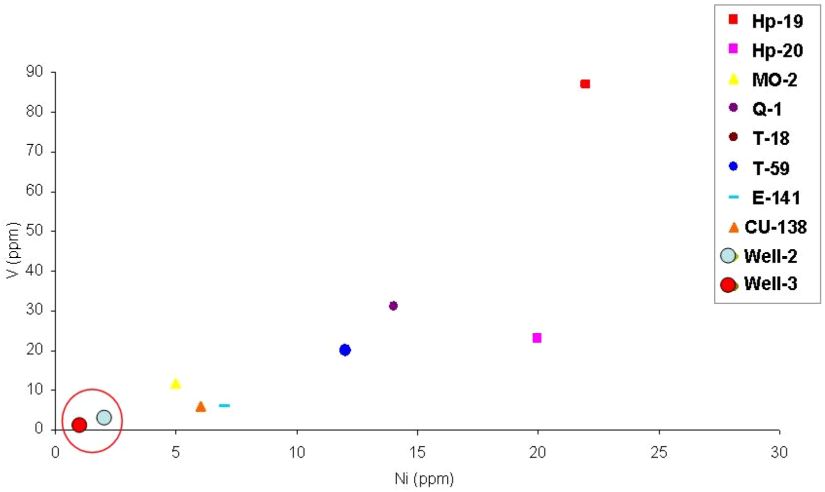


Figura 8. V and Ni correlation between oil from Well-2, Well-3 and different wells on the study area

By the other hand, Figure 9 shows the chromatogram obtained for the total crude of Well 2 and Well 3 well. Distribution pattern obtained suggests a greater prevalence of lower molecular weight compounds <C_{15}. This type of distribution is typical of light crude and can be associated with a high level of maturity.

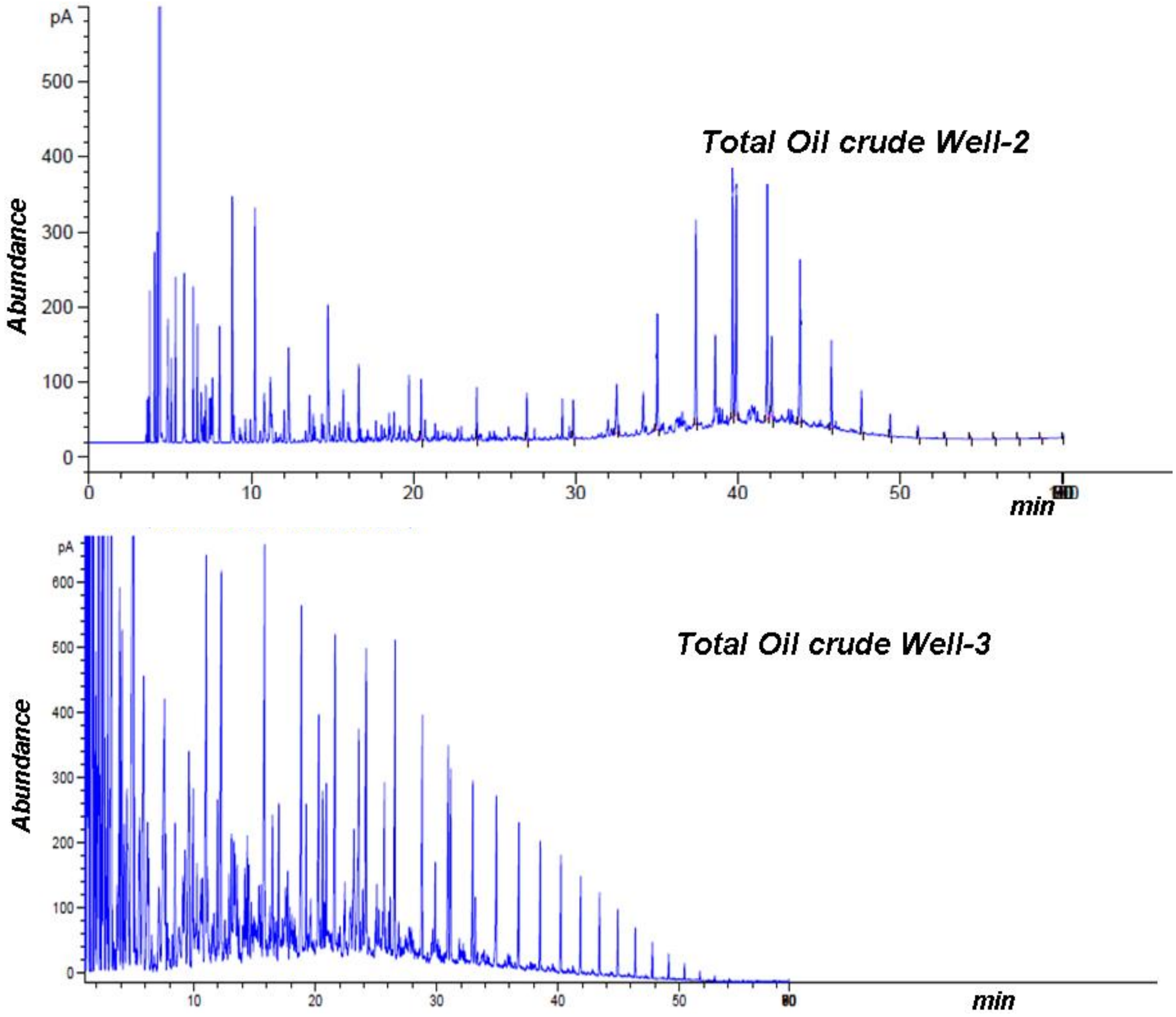


Figure 9. Well 2 and Well 3 total oil crude chromatogram

The values obtained for the ratio of paraffin (0.44) and aromaticity (2.18) suggest that there has been slightly affected by evaporative fractionation processes (Thompson 1987; 1988) while the ratios for heptane isomers of branched and unbranched parameters assessed by P1 (compound unbranched), P2 (mono branched) and P3 (poly-branched) suggest that oil has been slightly altered by biodegradation (Figure 10).

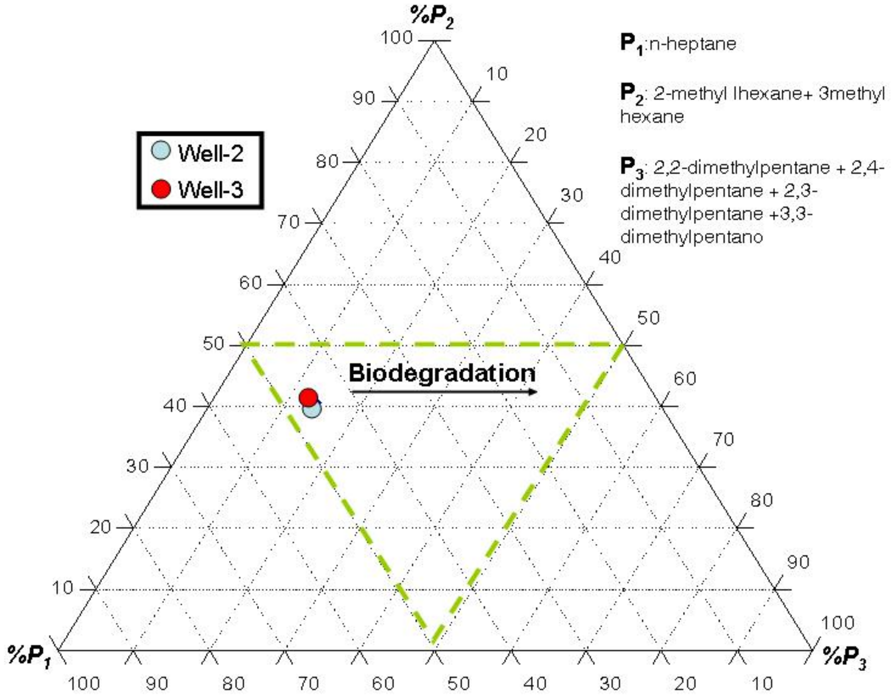
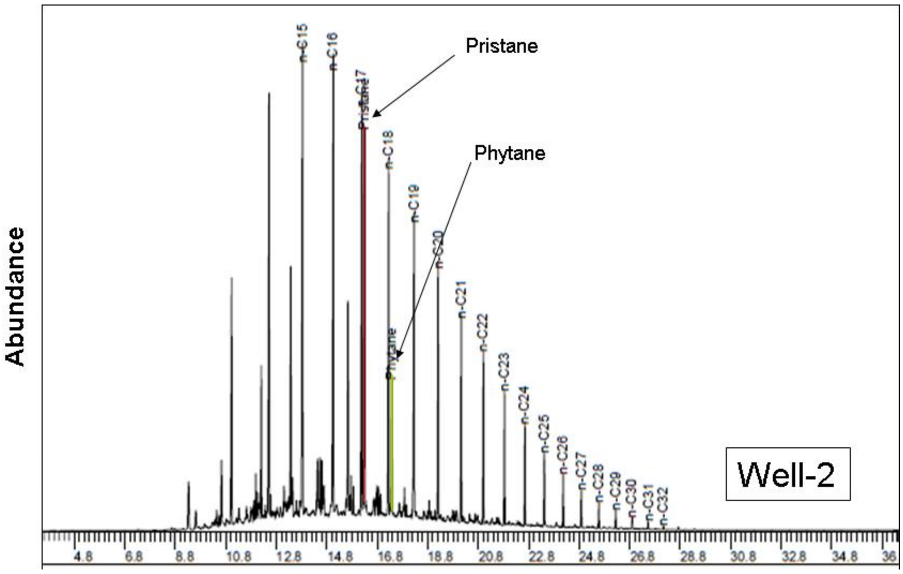


Figure 10. P1, P2 and P3 ternary diagram

Moreover from GC analysis of the saturated fraction oil sample corresponding to the fraction C_{15}^{+} presented a unimodal distribution pattern, typical of oil associated to organic matter of marine origin (Figure 11). That distribution shows predominance between n-C_{14} paraffins and n-C_{16}, and odd paraffins. However, this pattern of distribution could be affected due to not or low proportion of heavier hydrocarbons showing a pattern associated to marine organic matter. Pristane / Phytane ratio (3.367) indicates a contribution of terrestrial organic matter deposited under oxic conditions (Peters et al., 2005), which correlates with Figure 12, indicating a mixed origin of organic matter with a predominance of type III organic matter associated with less reducing environments (oxic-suboxic type). This environment according to Figure 12 is transitional type.



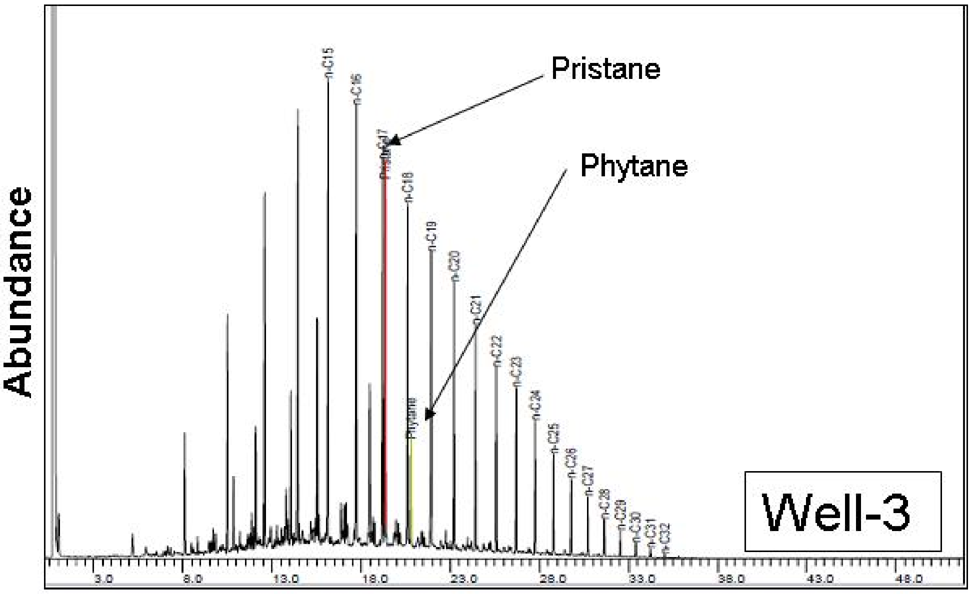


Figure 11. C$_{15}^{+}$ fraction saturated hidrocarbons.

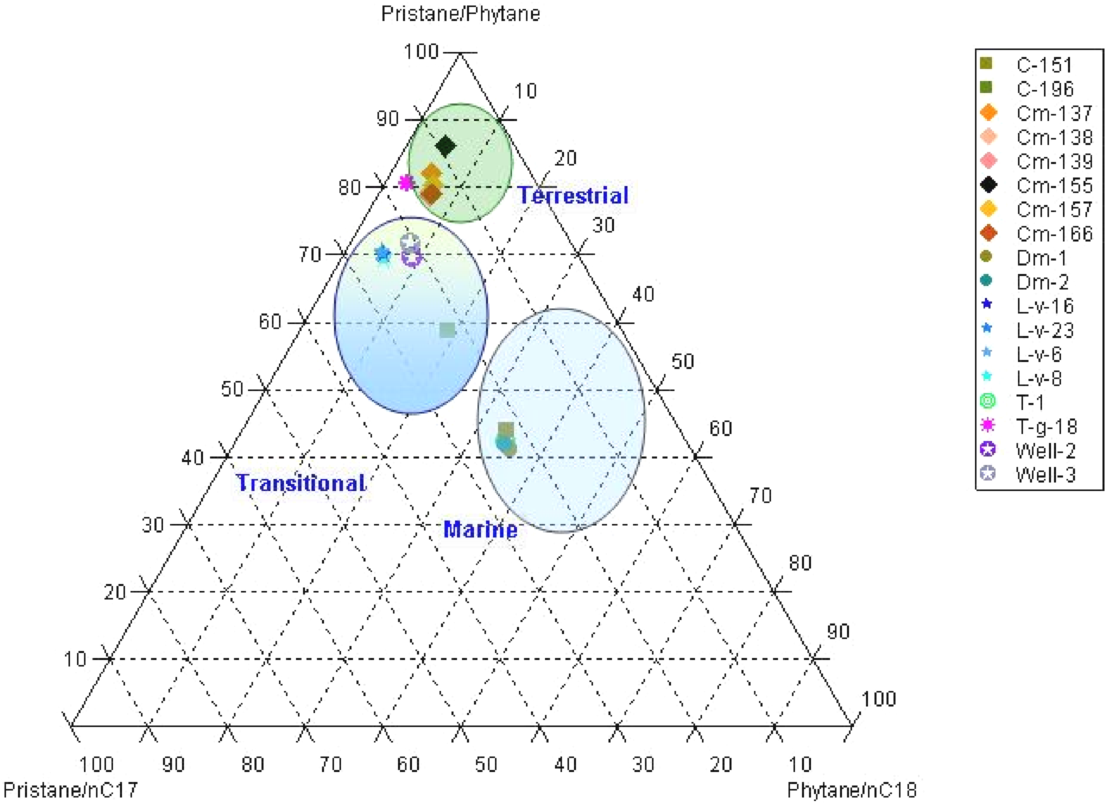


Figure 12. Ternary diagram pristane, phytane and n-C$_{17}$, n-C$_{18}$ alcanes

According to above, C$_{27}$, C$_{28}$ and C$_{29}$ ββ steranes identified in saturated biomarker m/z 218 ion, showed a higher prevalence of C$_{27}$%>% C$_{29}$ associated with lacustrine origin crude (Peters and Moldowan, 1993; Peters et al., 2005). However, Figure 13 shows a ternary diagram of C$_{27}$, C$_{28}$ and C$_{29}$ steranes of various crude oils in Falcon and Maracaibo area showing source classification based on the proportion of each compound and reflecting marine origin for crude oil from Well-2 and Well-3, similar to those obtained in the field Cumarebo and Mara.

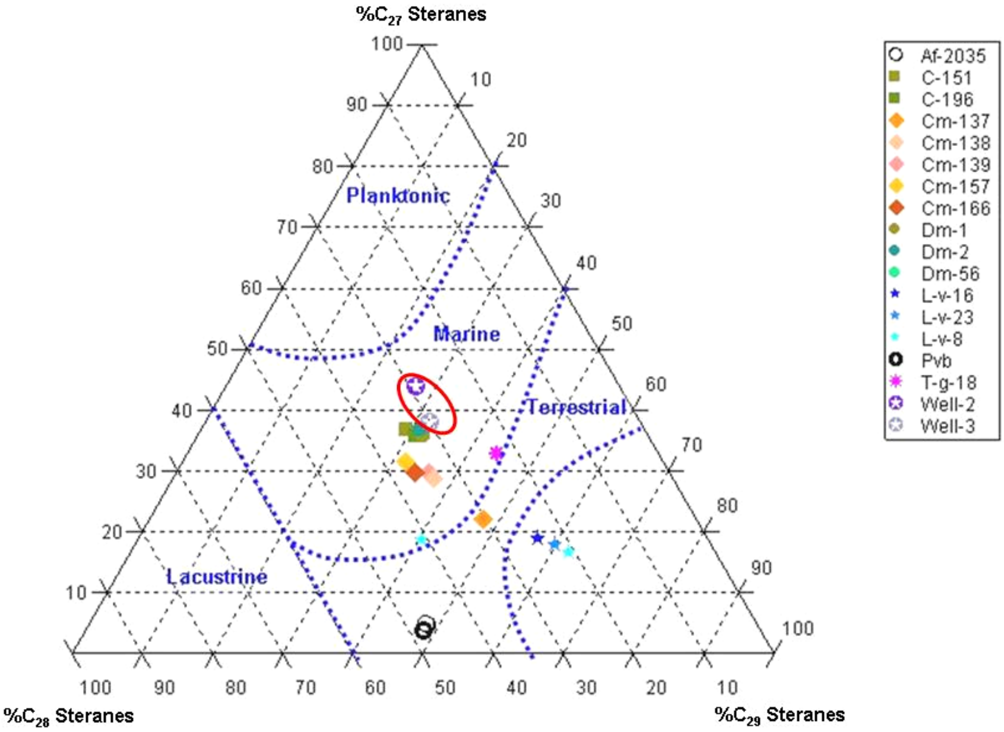


Figure 13. Ternary diagram steranes (ββ) C_{27}, C_{28} y C_{29} for oils from Golfo de Venezuela, Falcón and Maracaibo areas

On the other hand in relation to maturity of oils, diamondoids suggest maturity equivalent to vitrinite reflectance value between 1.3 - 1.6% Ro, obtained by the Index Methyl Adamantene (IMA) was within the range of wet gas window, consistent with the generation region obtained for gas samples. The origin of these hydrocarbons assessed by the steranes (Figure 13) seems to be associated with a source rock type III-II with predominantly terrestrial organic matter (Peters and Moldowan, 1993, Peters et al., 2005). Even though, isotopic correlations between the saturate and aromatic hydrocarbons suggest a marine origin (Figure 14), (Peters et al., 2005). Lithology associated is siliciclastic deposited under marine conditions with some oxygen availability. Age source rock reported from isotopic data (total $^{13}C_{oil}$ δ-23 ± 0.3 ‰) suggests that it is Miocene (Peters et al. 2005).

The maturity of crude evaluated from various geochemical parameters show no clear definition as to this aspect is concerned, some parameters suggest that these hydrocarbons have a high level of thermal evolution (diamondoids, isoprenoids relations and n-paraffins) and others do not show clearly this maturity level (n-heptane and iso-heptane indexes). Considering the range of maturity values reported, the level of thermal evolution of these hydrocarbons must be located in a range of maturity of 0.9% ≤ Ro ≥ 1.3 - 1.6.

This width range in maturity levels may be reflecting a possible mixture of hydrocarbons with different levels of maturity; however this aspect, from the point of view of organic matter there are not variations, so that, if this hypothesis is true, the mixture corresponds to hydrocarbons associated with same source rock. To check this, is important to verify by 1D modelling, which of the possible sequences that can be hydrocarbon source rocks could be generated with different stages of maturity.

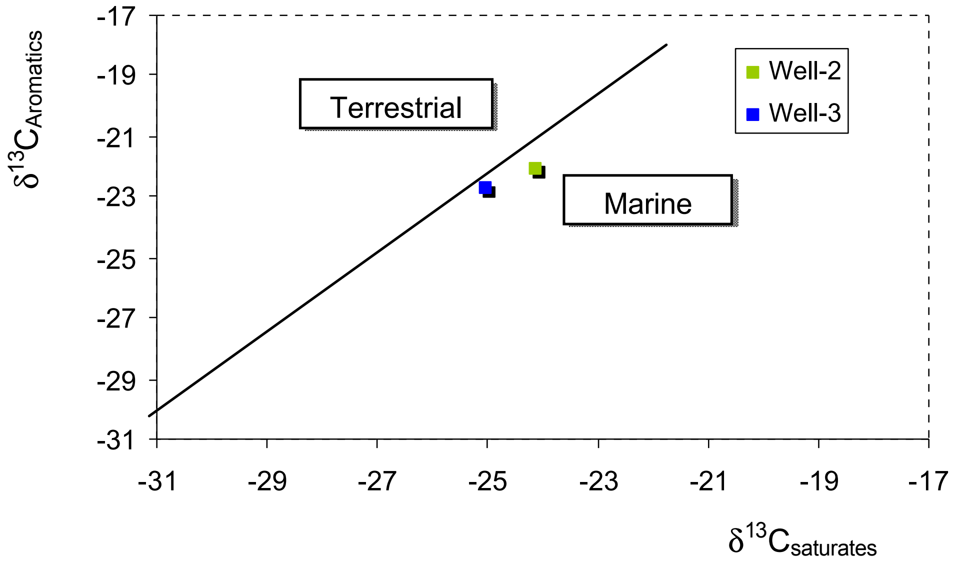


Figure 14. Isotopic correlations between the saturate and aromatic hydrocarbons

5. Conclusions

- Geochemical characterization made to fluids found in Well 2 and Well 3, shows similar characteristics, suggesting that these fluids are genetically correlated and correspond to the same family.

- According to isotopic data, gas has been generated from the thermal cracking of a kerogen type III-II, consisting of a mixture of terrestrial and marine organic matter dominated by terrestrial organic matter.

- Thermogenic origin for gas correlated with origin found for liquid fraction in reservoir; besides suggest that both have been generated at higher maturity levels in the oil window, and slightly above 1% reflectance of vitrinite.

- The maturity showed two different tendencies. However, considering the range of maturity values δ or obtained for the parameters evaluated, the level of thermal evolution of these hydrocarbons should be located in a range of maturity of ≤ 0.9% Ro ≥ 1.3 to 1.6. Another hypothesis that could be representing these varying levels of maturity is a possible mixture of hydrocarbons with different degrees of thermal evolution, but further studies are required to give further support to this hypothesis.

- As for the origin of hydrocarbons, evaluated from the liquid fraction, they show a trend associated with a mixed source rock, deposited in transitional type environments, where organic matter was deposited in suboxic conditions. The associated lithology type is siliciclastic (shale).

- The thermal evolution level determined in the liquid fraction show no clear definition as parameters suggest that these hydrocarbons have a high level of thermal evolution (diamondoids, CPI, relations of the isoprenoids and n-paraffins) and other not clearly show the level of maturity (n-heptane and iso-heptane index values). Considering the average maturity values or ranges obtained for the parameters evaluated, the level of thermal evolution of these hydrocarbons should be located in a range between 0.9% ≤ Ro ≥ 1.3 to 1.6. However, this aspect should be evaluated in greater detail, and that these differences in maturity values may be possible to represent a mixture of hydrocarbons with different degrees of thermal evolution, but further studies are required to give further support to this hypothesis.

- Well-3 and Well 2 hydrocarbons showed good correlation between them, which suggests that these hydrocarbons are genetically correlated and should be associated with the same rock. These hydrocarbons show a positive correlation with crude oil fields evaluated in La Vela, Mara, La Concepción, Tablazo Tiguaje, among others. Only in the case of Campo Cumarebo there was some similarity in the depositional environments of source rocks.