

Comparative study of crude oils from the Machete area in the Eastern Venezuelan Basin by pyrolysis of asphaltenes

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Abstract

This work is an analysis of crude oil samples from the two most recent producing wells in the Machete area (Orinoco Tar Belt, Venezuela). The aim is to determine the type of environment in which the precursor organic materials were deposited. In spite of the fact that the degree of maturity and the biodegradation of the two crude oils are similar, their characterization leads us to conclude that they have very distinctive and different origins. The comparative study was performed by separating their main fractions, pyrolysis of asphaltenes, and further identification of several indicators (aromatic, polar and sulfur compounds, linear aliphatic hydrocarbons, and cadalene). Moreover, several biomarkers (terpanes, hopanoids and steranes) present in the saturated fractions obtained from the two crude oils were analyzed by using gas chromatography combined with mass spectrometry (GC–MS). The statistical study of geochemical indicator values and relative proportions of lipid and lipid-like biomarkers present in products from asphaltene pyrolysis shows a high probability of there being two distinct crude oil families from the Machete area.

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1. Introduction

The Eastern Venezuelan Basin (Fig. 1a) includes two major oil fields: El Furrial, which covers the northern part of the basin, and the Orinoco Tar Belt located on the southern boundary. The principal source rock is associated with the Guayuta Group [1], deposited during the maximum transgression in the late Cretaceous, and comprising the Querecual and San Antonio Formations. This group has a sequence of calcareous shales and sandstones formed by the deposition of organic sediments under anoxic conditions [2].

Several works based on biological markers have proven that most crude oils from the Orinoco Tar Belt have a marine origin (e.g. [3]). Using parameters such as total concentration of vanadium and nickel, V/Ni ratio, sulfur content, and a relative abundance of biomarkers from saturated fractions, numerous

researchers have established (after analysing 131 crude oil samples) the existence of four crude oil families in the Eastern Venezuelan Basin [4–6].

A previous study [7] determined that crude oils from the Machete area (the Orinoco Tar Belt) show different degrees of biodegradation and have specific gravity values between 6° and 10° API. In addition, it has been shown that numerous fresh and biodegraded crude oils may have a marine origin [2]. However, in this study we show that the extra-heavy crude oils from two wells (Mch 3-8× and Mch 3-9×) in the northern part of the Machete area may have been sourced by terrestrial organic matter.

The aims of this work are to characterize of the crude oil samples Mch 8-4× and Mch 3-9× through biomarkers and other geochemical parameters and to determine a marine and/or terrigenous origin [8]. The characterization was performed by flash pyrolysis of asphaltene fractions extracted from both samples, and the subsequent analyses of several geochemical indicators; at a later stage, biomarkers in saturated fractions of these crude oils were analyzed with a combination of gas

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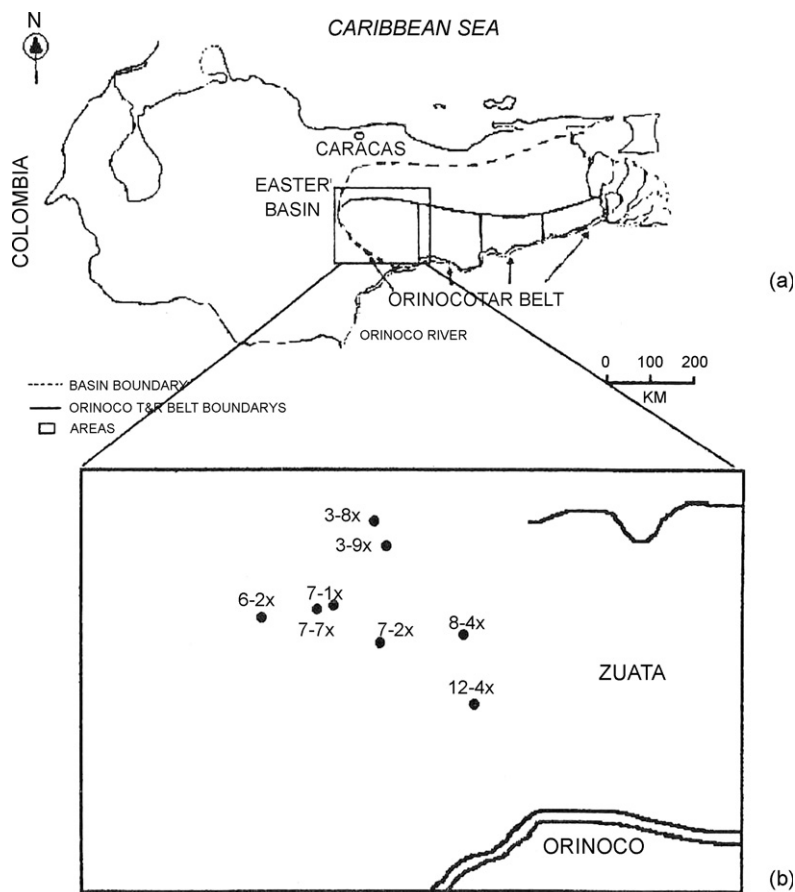


Fig. 1. (a) Location of Eastern Venezuelan Basin; (b) approximate situation of the eight study wells in Machete area (adapted, with changes, from Ref. [3]).

chromatography and mass spectrometry (GC–MS). We have also considered previous experimental data [5,6] on six other crude oils – one of them similar to Mch 3-9 \times oil and the rest to Mch 8-4 \times oil – from different wells in the Machete area that are currently non-producing (Fig. 1b): Mch 7-2 \times , Mch 7-7 \times , Mch 7-1 \times and Mch 6-2 \times wells in the south-central part; Mch 12-4 \times in the south-east, and another well, Mch 3-8 \times , situated in the north-central part zone.

2. Geological setting

The main reservoirs in the Orinoco Tar Belt are in interbedded shales and sandstones present in Tertiary geological sequences. These reservoir rocks are lenticular-shaped due to their fluvial and alluvial origins (channels); average thickness from 300 to 1000 m, increasing from north to northwest [1]. Furthermore, the study area, the Machete, is located in the western part of the Orinoco Tar Belt and comprises sediments deposited in three distinctive cycles (see Fig. 2). The first cycle dates back to the late Palaeozoic and is in discordant contact with igneous-metamorphic rocks; it includes the Hato Viejo and Carrizal Formations. The second sedimentary cycle can be ascribed to transgression during the Cretaceous, as exemplified by the Temblador Group in the same area, composed of the Canoa and Tigre Formations. Lastly, cyclical events taking place during the late Tertiary led

to sedimentation processes at the Pascua, Roblecito and Chaguaramas Formations [1]. The above-mentioned reservoir rocks are at depths in the range of 300–400 m at the Roblecito and Chaguaramas Formations.

A previous work [6] has included average values corresponding to characteristics of the above-mentioned two oil families such as specific gravity and composition of the C_{14}^+ fraction, among others.

3. Experimental

The following techniques were used to analyze the two crude oil samples: precipitation of asphaltene fraction prior to separation of saturate fraction (SARA); later, pyrolysis of asphaltenes was first performed by gas chromatography coupled to flame ionization detection (Py-GC-FID) and then to mass spectrometry detection (Py-GC-MS); finally, the saturates were analyzed by gas chromatography–mass spectrometry (GC–MS).

3.1. Separation of crude oil fractions

Asphaltene fractions were separated from the two crude oil samples by precipitation from a solution containing a 40:1 volumetric excess of *n*-heptane [9]. The samples were kept through a batch-type reactor in constant agitation for 1 h at

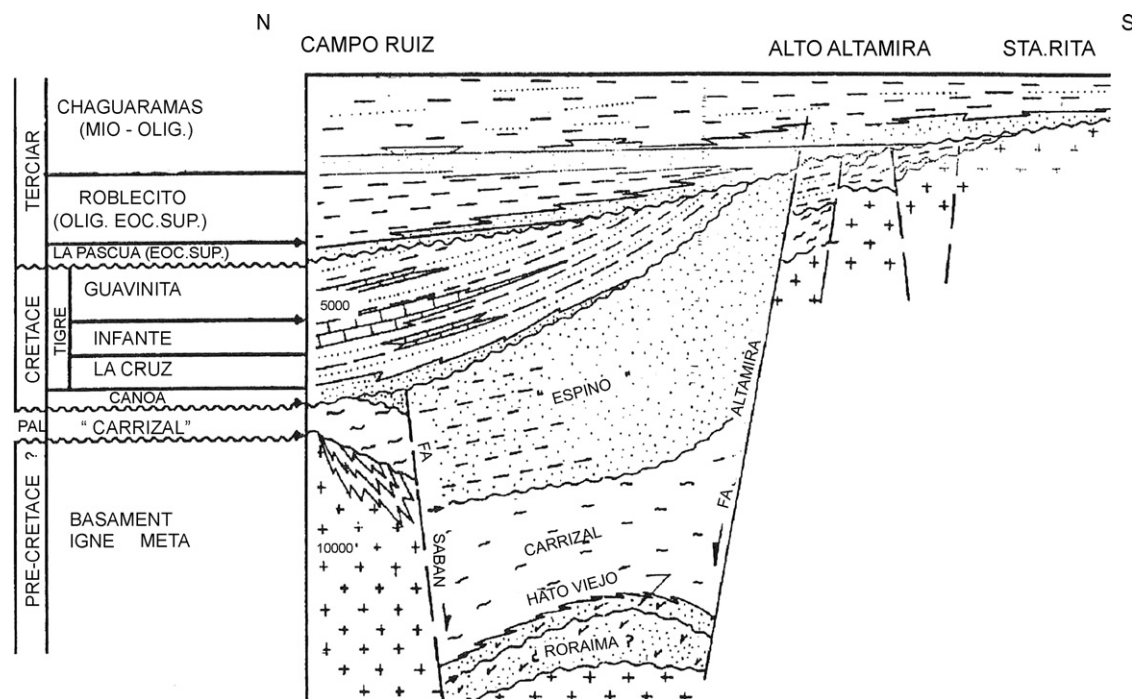


Fig. 2. North-south simplified stratigraphic cross-section of the geological intervals in the Machete area (adapted from Ref. [1]).

60 °C, followed by a 12-h inactive period [10]. The asphaltene material was adsorbed onto alumina. The asphaltenes were passed through a Soxhlet apparatus several times, using *n*-heptane until the liquid obtained in the filtration turned colourless. That liquid was later added to *n*-heptane solution. Likewise, the saturate fractions of the two crude oil samples were eluted by *n*-hexane using a column filled with activated alumina [11].

3.2. Pyrolysis of asphaltenes

Firstly, the asphaltenes were analyzed by combining flash pyrolysis and gas chromatography. These analyses were carried out with a CDS-100 unit – operated at 550 °C for 10 s intervals – and a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector at 300 °C and a splitless injector. A capillary column (60 m × 0.25 mm i.d.) model SE-52 was used. Experimental GC conditions were as follows: helium was the carrier gas and the oven temperature program was 40–300 °C at 3 °C/min. As a result, the mass ratios of *n*-alkanes and *n*-alkenes – corresponding to the studied crude oils – were obtained.

Lastly, the asphaltene fraction was also analyzed using combined flash pyrolysis and gas chromatography with a mass spectrometer detector (GC–MS). The same pyrolysis unit was employed and experimental conditions were not modified. The settings for the VG autospec brand mass spectrometer were: electron photomultiplier 2000 V, filament current 220 mA, electron energy 70 eV, a split injector and source temperature at 250 °C. The samples were analyzed by selected ion monitoring (SIM) and full scan modes: 84, 95, 98, 107, 111, 134, 148, 183, 184 and 198 *m/z* ions were analyzed. The amounts of pyrolyzed products are reported from the relative intensities of different

compounds in the mass fragmentograms as an area divided by the weight of asphaltenes measured in milligrams for each sample [12–14].

3.3. Analysis of saturates

Saturated hydrocarbons from each crude oil sample were separated using combined gas chromatography and mass spectrometry employing the above-mentioned conditions and records. A capillary column (60 m × 0.25 mm i.d.) model SE-52 was used: 191, 217 and 218 *m/z* ions – corresponding to terpanes and steranes, respectively – were analyzed through mass spectrometry. To verify repeatability both samples were injected twice [15].

4. Results and discussion

Geochemical indicators commonly used in the characterization of oil seeps, crude oils and bitumens include concentrations of vanadium and nickel, among other trace elements. Despite the fact that the concentrations of these metals can be influenced by processes of thermal alteration, deasphalting, biodegradation and washing water or during migration, the V/Ni ratio itself tends to be constant due to the structural similarities among organometallic compounds that contain vanadium and nickel. This trait means the ratio is one of the most useful parameters for determining both the origin of precursor organic materials and oil–oil or oil–source rock correlations [16].

V/Ni ratios and vanadium and nickel concentrations (Table 1) are very similar for the Mch 3-9× and Mch 3-8× crude oils. Also note the very low variations among these parameter values for crude oils from the Mch 8-4× well and the

Table 1
Amounts (area/mg asphaltenes) of aliphatic hydrocarbons, cadalene, thiophenes, phenolic and organosulfuret compounds present in pyrolysis' products from all studied crude oils

Sample	Alkenes C ₈ –C ₁₄	Alkenes C ₂₅ ⁺	Alkanes C ₈ –C ₁₄	Alkanes C ₂₅ ⁺	Polar compounds	Thiophenic compounds	Sulfuret compounds	Cadalene	V (ppm)	Ni (ppm)	V/Ni rate
Mch 3-9×	962	1003	1098	1975	2007	65	300	70	0.6	0.5	1.20
Mch 8-4×	1338	201	2687	659	219	2243	3354	7	621	110	5.55
Mch 7-2×	1332	211	2387	499	225	1976	2936	6	679	118	5.75
Mch 12-4×	1409	202	2322	495	298	1965	3014	7	727	140	5.19
Mch 7-7×	1630	227	2623	444	243	2139	3246	6	806	145	5.92
Mch 6-2×	1704	248	2698	765	281	1950	3003	6	783	130	5.68
Mch 7-1×	1788	275	2725	780	275	2275	3388	7	798	135	5.91
Mch 3-8×	966	1112	1030	1989	2000	60	285	68	0.4	0.5	0.80

other five wells [5]. These geochemical data seem to indicate that these eight crude oils can be grouped into two clearly distinct families [17]; consequently, six of these crude oils must have come from the same source rock.

4.1. Asphaltene pyrolysates

Since asphaltenes that have been removed from different crude oil constituents contain correlation information [18], Table 1 displays the amounts of pyrolysed products generated from the asphaltene fractions extracted from the Mch 8-4× and Mch 3-9× samples; as well as previously published data corresponding to each of the other six crude oils [6]. C₈–C₁₄, C₂₅⁺ homologues aliphatic hydrocarbons (*n*-alkanes and *n*-alkenes) were studied, in addition other geochemical parameters: polar compounds (phenols, cresols, dibenzofurans and others), sulfur substances, aromatic molecules, and cadalene.

The gas chromatographic profiles corresponding to samples Mch 8-4× and Mch 3-9× obtained after asphaltene separations and their pyrolysis are shown in Fig. 3. Both gas chromatograms display the aliphatic hydrocarbon fraction distribution. The Mch 8-4× crude oil sample reveals maximal values around C₈ and C₁₄ for the relative abundance of hydrocarbons shows and a steady decrease with retention time for C₂₅–C₃₃ homologues. However, the asphaltene fraction extracted from the Mch 3-9× crude oil sample shows a very different pattern and an abundance of *n*-alkenes and *n*-alkanes, with C₂₅–C₃₃ homologues predominating, and a small relative abundance of low molecular weight C₈–C₁₄, *n*-paraffins. Furthermore, the Mch 3-9× crude oil shows considerable high molecular weight alkanes and alkenes and C₂₅⁺ homologues about three times higher than the Mch 8-4× sample. It can also be noted that the relative abundance of C₈–C₁₄ aliphatic hydrocarbons in the Mch 3-9× sample is about two times lower than in the Mch 8-4× crude oil.

A high proportion of the low-chain *n*-paraffins ranging between C₈ and C₁₄ is characteristic of lipids associated with algal material [19,20], and therefore is typical of crude oils deriving from source rocks with marine organic matter. However, the second gas chromatogram displays a distribution associated to source rocks with high contents in terrigenous organic matter [21].

Table 1 also shows the amounts of other pyrolysed products from asphaltenes (expressed as area/mg asphaltene): phenols and C₁–C₂ cresols; thiophenes, methylthiophenes, dimethylthiophenes, benzothiophenes and dibenzothiophenes, all of them considered together, in addition to the whole organosulfur compounds.

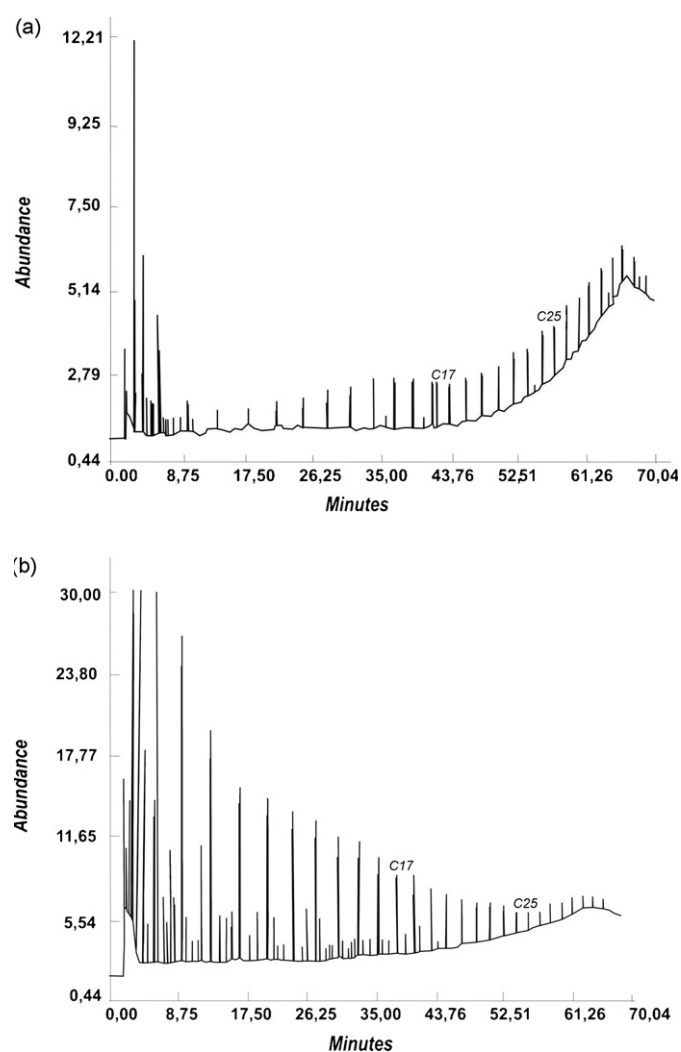


Fig. 3. Gas chromatographic profiles showing the compositions of asphaltene fractions obtained by pyrolysis of Mch 3-9× (a) and Mch 8-4× (b) samples. Note: numbers refer to carbon number chain.

Experimental results indicate that the lowest proportions of thiophenes, benzothiophenes and their alkyl derivatives can be found in samples from the Mch 3-8× and Mch 3-9× wells, with levels about ten times lower than in the other six crude oils. Most sulfur compounds present in crude oils were generated during early diagenesis, through the reaction between sulfydric acid and inorganic polysulfides with unsaturated organic molecules and other unstable organic compounds, hydrogen sulfide being produced by the microbial reduction of natural sulfates. In clastic environments, detrital iron reacts with sulfydric acid to produce mineral phases such as pyrite; in that respect, the amount of sulfur organic compounds formed is minimal. However, in pelagic biogenic deposits such as carbonates, diatoms and bedded cherts, detrital iron is rare, thus leading to the existence of sulfur compounds. Therefore, crude oils with high contents in sulfur compounds tend to be associated with marine carbonatic sequences; in contrast, crude oils with low contents are usually related to land-derived siliciclastic series [22–24].

The proportion of polar compounds in asphaltene pyrolysates is about ten times higher in the Mch 3-8× and Mch 3-9× crude oils, and the values of triaromatic substances are five times higher than in the other six crude oils. Variations found in the above-mentioned samples have been reported by several researchers attempting to determine the quantity of organic material deriving from higher plants in crude oils and in coals [25,26]. Phenols and alkyl-phenols probably derived from the diagenetic alteration of lignitic precursors in vitrinite and inertite. In addition, some liptinitic macerals (esporinite) can produce phenolic substances. The presence of these compounds indicates a higher plant origin, in particular conifers [27]. Triaromatic and naphthalene compounds are also related to precursors, such as tricyclic terpenes from conifers, which were aromatized through a thermal maturity process [28,29].

Finally, significant amounts of cadalene (C₁₅H₁₈) were only observed in the Mch 3-8× and Mch 3-9× crude oils; this molecule is an aromatised cadinane structure. Such hydrocarbons mainly derives from continental organic matter (resinite) by means of the rearrangement and dehydrogenation of unsaturated sesquiterpenoids [25,27].

4.2. Biological markers

It is known that hopanes and steranes are more readily biodegraded than *n*-alkanes and isoprenoids [30]. Both samples were affected by biodegradation, but in all samples hopanes and steranes were detected. Therefore, biodegradation appears to

have only slightly altered the molecular composition of the samples. Microbial alteration and removal of the regular steranes and four α -methylsteranes from petroleum occurs after the complete removal of C₁₅–C₂₀ isoprenoids and before or after the hopanes depending on conditions; the susceptibility of regular steranes to biodegradation decreases in the following order: $\alpha\alpha\alpha 20R \gg \alpha\beta\beta 20R \geq \alpha\alpha\alpha 20S \geq \alpha\beta\beta 20S$. These relative susceptibilities vary depending on circumstances, types of bacteria and chemical characteristic of crude oils [30]. The use of these compounds as the only indicators of thermal maturity can lead to interpretate wrongly that the decrease of $\alpha\alpha\alpha 20R$ sterane is due to the increase of thermal maturity [30]. Fig. 4 shows that the proportion of $\alpha\alpha\alpha 20S$ relative to $\alpha\alpha\alpha 20R$ sterane is consistent with that expected for the thermal maturity of an oil. Therefore, steranes within the oil samples do not appear to have been altered by biodegradation.

Furthermore, the 20S sterane and 22S hopane percentages (Table 2) for these crude oils indicate they reached similar levels of maturity. These similar levels of thermal maturity indicate that differences between Mch 8-4× and Mch 3-9× crude oils are due to the distinctive origin of each of them. Consequently, analyses of biomarkers can lead to the determination of the corresponding types of precursor organic matter (because it will not reflect latter alteration by thermal or biological processes).

Hopane and regular sterane distributions for the Mch 8-4× and Mch 3-9× oil samples are shown in Fig. 4. These hydrocarbons were identified by comparison with their *m/z* 191 and 217 mass fragmentograms. Mch 8-4× sample has high contents in C₁₉–C₂₆ tricyclic compounds (maximal value around C₂₃), a hopane/sterane ratio lower than three, abundance of C₂₇, C₂₈ and C₂₉ steranes ($\alpha\alpha C_{27} > \alpha\alpha C_{29}$). This sample has also low amounts of 28,30-bisnorhopanes, homopregnane (C₂₁) and methylpregnanes (C₂₂). In contrast, data from sample the Mch 3-9× display a hopane/sterane rate higher than five, an absence of tricyclic terpenoids and the presence of 18 α (H) oleanane. The presence of tetracyclic terpanes (C₂₄₋₄) must also be taken into account, as well as a higher relative abundance of C₂₇, C₂₈ and C₂₉ steranes ($\alpha\alpha C_{29} > \alpha\alpha C_{27}$).

The C₂₃/C₃₀ rates corresponding to both crude oil groups (Table 2) also suggested different types of precursor organic matter. Tricyclic terpanes show a C₂₃ maximum peak and a lower abundance of C₂₄, since they are algal or bacterial lipids from the prokaryotic membranes [30]. These compounds are very abundant in crude oils and source rocks of marine or lacustrine origin and commonly correlate with tasmanites-rich rocks, suggesting an origin from these algae [31]. However,

Table 2

Values for biomarkers and indices corresponding to crude oils coming from Mch 8-4× and Mch 3-9× crude oils, respectively

Sample	C ₃₅ homohopane index (%)	Oleanane index (%)	22S hopane rate (%)	20S sterane rate (%)	Homopregnane/methylpregnane C ₂₁ /C ₂₂ ratio	C ₂₃ /C ₃₀ rate (%)
Mch 8-4×	15.9	0.00	54.0	46.0	2.11	82.6
Mch 3-9×	0.00	25.0	58.0	42.0	1.11	8.00

C₃₅ homohopane index: C₃₅ homohopanes (20S + 20R)/C_{31–35} homohopanes (22S + 22R); oleanane index: 18 α H-oleanane/C₃₀ $\alpha\beta$ hopane; 22S hopane rate: C₃₂ hopane (22S)/C₃₂ hopane (22S) + C₃₂ hopane (22R); 20S sterane rate: C₂₉ $\alpha\alpha$ sterane (20S)/C₂₉ $\alpha\alpha$ sterane (20R) + C₂₉ $\alpha\alpha$ sterane (20S); C₂₃/C₃₀ rate: (C₂₃-3 tricyclic terpanes/ α - β C₃₀ hopane).

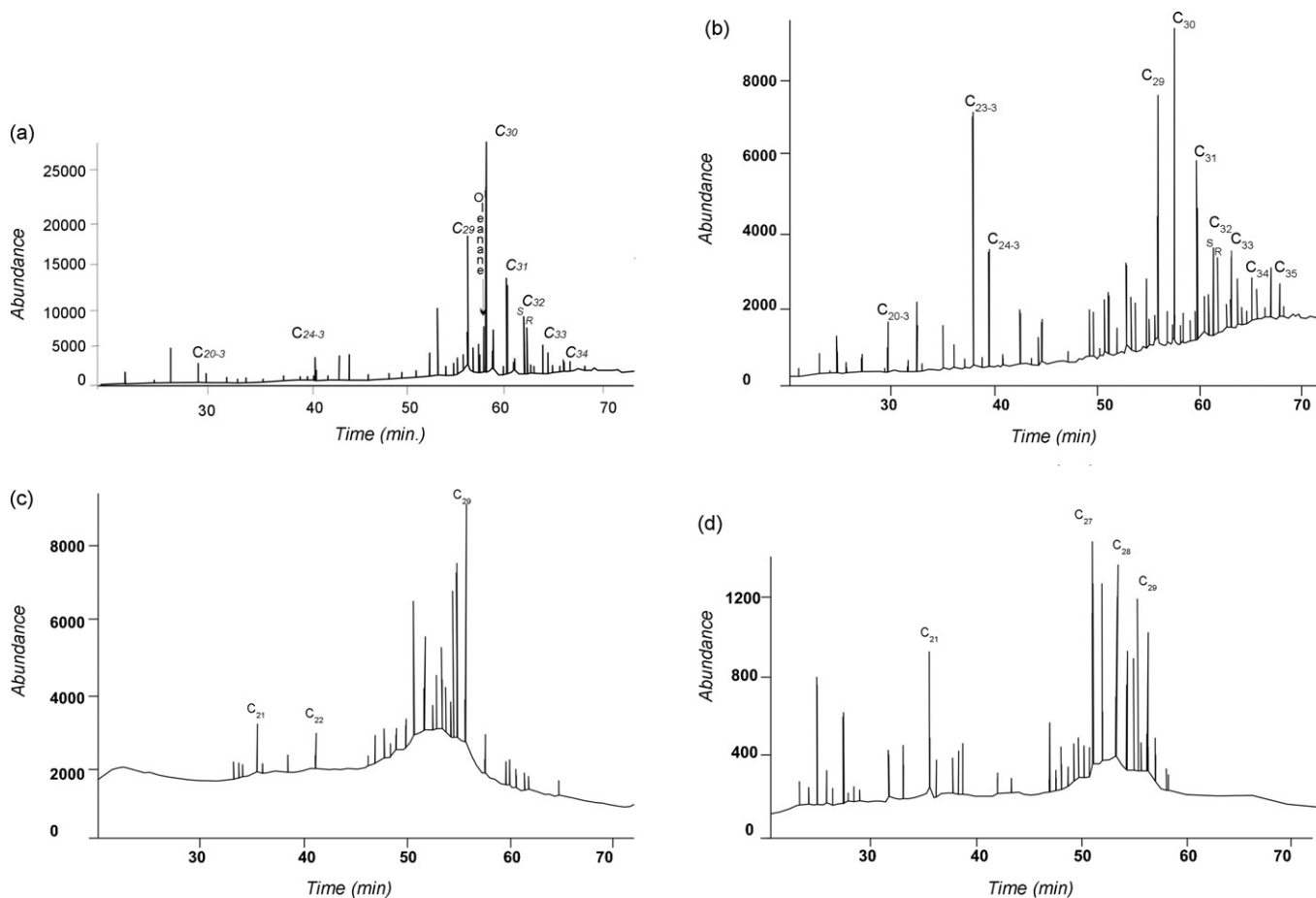


Fig. 4. (a) and (c), respectively, m/z 191 and 217 ion fragmentograms for saturated fraction from Mch 3-9 \times oil; (b) and (d), respectively, the same ion fragmentograms for the saturates from Mch 8-4 \times oil.

other researchers [32] noted tricyclic terpanes in crude oils originated in moderate salinity conditions and suggested that these lipids are bacterial-origin biomarkers. Likewise, tetracyclic terpanes are originated by degradation of pentacyclic triterpenoids [24].

The C₂₇–C₂₉ sterane distribution makes it possible to determine the type of organic matter more commonly present in any source rock, since cholesterol – the C₂₇ homologue precursor – is found in Rhodophytae or red algae; by contrast, C₂₉ sterol is characteristic of higher plants and Phaeophytae or brown algae [24]. Therefore, the greater proportion of C₂₉ steranes in sample Mch 3-9 \times indicates that the organic matter that sourced this oil contained a greater proportion of plant sterols than the organic matter that sourced oil Mch 8-4 \times .

As shown in Table 2, C₂₇ homohopane and oleanane indices, 20S sterane and 22S hopane ratios, as well as C₂₁/C₂₂ pregnane ratios were determined for both samples. The side chain of homohopane precursor molecules is degraded to originate lower homologs under sub-oxic to oxic conditions. Conversely, C₃₅ hopanepolyols are preserved under anoxic conditions, thus high homohopane indices can be observed [33]. Several researchers [34] determined that the sulfur addition at the end of the side chain of C₃₅ hopanopolyols is responsible for the preservation of homohopane precursors; hopanoid sulfides are formed by reaction of inorganic sulfur species with a terminal

double bond of the above-mentioned side chain or, for example, thiophene compounds with D or E ring of C₃₅ hopanopolyols. Homohopane is commonly originated by sulfurization of C₃₅ hopanopolyols and subsequent desulfurization of the side chain during early thermal maturity process. Sample Mch 8-4 \times has a C₃₅ homohopane index of 15.9%, suggesting a C₃₁–C₃₅ homologues distribution characteristic of calcareous, carbonatic shale or limestone deposits under anoxic conditions. By contrast, sample Mch 3-9 \times has a C₃₅ homohopane index value of zero, common to clastic environments under oxic conditions.

Another important biomarker when comparing the two samples is the oleanane index, which stands at 25% for sample Mch 3-9 \times and 0 for Mch 8-4 \times . The oleanane is an indicator of crude oil's age and type of precursor organic matter. The precursors of oleanane are pentacyclic triterpenoids – associated with angiosperms – from the Triassic or older times, thus a high oleanane content is commonly reported in crude oils from the Tertiary [30]. The absence of oleanane does not prove that a crude oil was originated during the Cretaceous or older times and does not indicate a marine precursor organic matter, as it has been reported that the preservation of this biomarker in deltaic rocks prevents the aromatization of oleanane precursor molecules [35]. Therefore, the absence of oleanane in sample Mch 8-4 \times only provides evidence for a different source type, and not for a source rock of a different age.

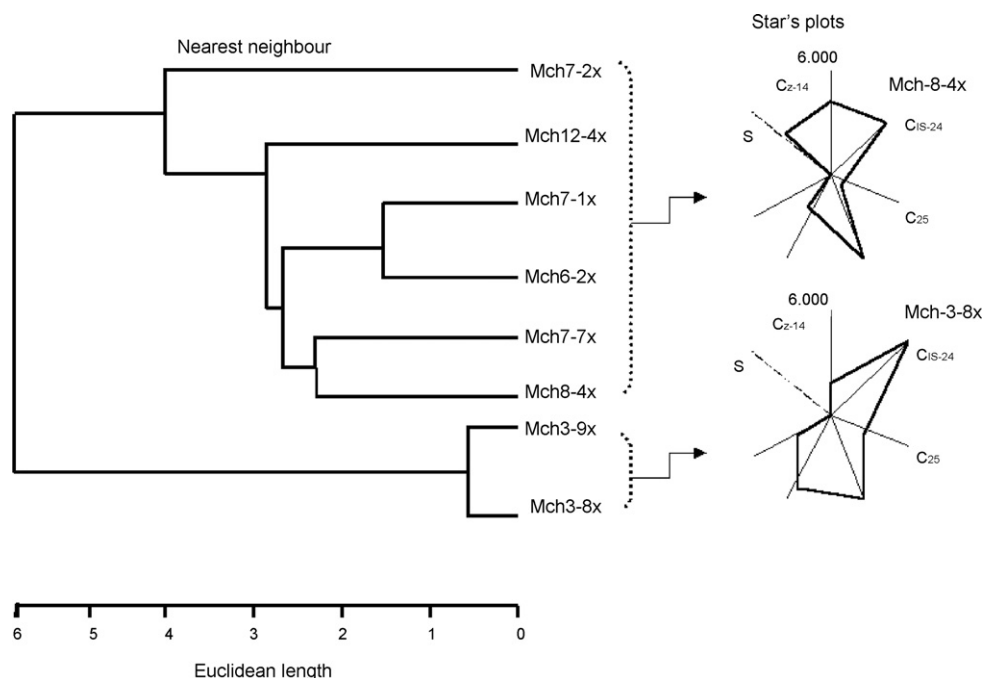


Fig. 5. Results from multivariate statistical analysis and graphic representation of data through star plots.

The C_{21}/C_{22} pregnane ratio for sample Mch 8-4 \times is 2.1, whereas it is 1.1 for sample Mch 3-9 \times . These values confirm the existence of two distinctive precursor environments: a marine origin for crude oil Mch 8-4 \times and a terrestrial origin for Mch 3-9 \times [24]. An examination of all data obtained from the crude oil fractions seems to rule out, first, the hypothesis proposed by some authors [2] regarding the mixture of several crude oils from a marine origin and, second, the very low probability that some of the eight crude oils studied, corresponding to distinctive precursor environments, have been mixed.

4.3. Statistical analysis

Statistical treatment was made with the Hierarchical Cluster Analysis for the dataset with continuous and categorical-level variables; as a consequence, a number of groups have automatically been formed so that records within a cluster are similar [36]. The dendrogram plot shown in Fig. 5 only displays two clusters taken from previous information [6] and data – linear hydrocarbons, polar compounds, sulfur substances, mono-, di- and triaromatics – obtained after asphaltene pyrolysis and later use of GC–MS techniques, as well as a graphic representation of data using a star plot. As expected, the two clusters have a high degree of dissimilarity between them, quantified through very different values taken from the respective euclidean lengths calculated through the centroid method. This Cluster Analysis was performed using the SPSS 13.0 package for Windows.

Measurements of similarity within the cluster formed by crude oils Mch 7-7 \times , Mch 7-1 \times , Mch 6-2 \times , Mch 12-4 \times , Mch 7-2 \times and Mch 8-4 \times indicate that they all have very dissimilarities among them. Crude oils Mch 3-8 \times and Mch

3-9 \times also show very high similarity to each other, using the proximity procedure [37].

Therefore, the statistical analysis confirms the experimental results obtained from analysing the fractions of asphaltene and saturates, respectively, indicating the most probable existence of two crude oil families.

Star plots allow a better visualization of the variations found in the multivariate statistical analyses, graphically representing the composition of each crude oil corresponding to the above-mentioned families, expressed by the yield of pyrolysed products (peak area/mg). The two resulting diagrams clearly show the compositional differences between the two types. The Mch 3-8 \times and Mch 3-9 \times crude oils, for instance, are known for having a high proportion of C_{15} – C_{24} *n*-paraffins, an abundance of cadalene, C_1 – C_2 cresols and phenols, as well as low contents in thiophenic compounds and other sulfur compounds; by contrast, the other six crude oils have high concentrations of C_8 – C_{14} *n*-alkanes, monoaromatic molecules and sulfur compounds.

5. Conclusions

Geochemical indicator values obtained during this study allow the eight crude oils to be classified into two families of very different characteristics. The first family comprises crude oils from the two wells in the north-central part of the study area, whereas the second family includes the six crude oils from other parts of the Machete area.

The first group is characterized by presence of cadalene, phenols, C_1 – C_2 cresols, as well as the greater abundance of higher carbon number *n*-alkanes (C_{25}^+) in asphaltene pyrolysates, the presence of $18\alpha(H)$ -oleanane, the absence of tricyclic terpanes, a low homohopane index and a high proportion C_{29}

sterane (a biomarker for higher plants). These geochemical data suggest that the crude oils from wells Mch 3-8× and Mch 3-9× originated from a terrestrial allochthonous organic matter kerogen deposited during the Tertiary in a clastic environment under oxic conditions. The second group has a high C₃₅ homohopane index (indicative of an anoxic depositional conditions), an oleanane index value of zero, and a high relative abundance of sulfur compounds (benzo and dibenzothiophenes) and tricyclic terpanes. It is probable that the crude oils in this second group from the wells (Mch 8-4×) in the southern part of the Machete area originated from marine or lacustrine autochthonous organic matter under anoxic conditions.

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References

- [1] C. Gonzalez de Juana, J. Iturralde de Arozena, X. Picard, *Geology of Venezuela, Its Petroliferous Basins*, Foninves, 1980, pp. 5–300.
- [2] F. Cassani, PhD Thesis, Bristol University, 1985, pp. 65–78.
- [3] F. Galarraga, PhD Thesis, Maryland University, 1986, pp. 56–90.
- [4] R. Simoza, N. Carrión, J. Torres, E. López, in: *Proceedings of the Sixth Venezuelan Geological Conference*, vol. 3, 1985, pp. 2087–2116.
- [5] M. Alberdi, Dr. Sci. Thesis, Venezuelan Central University, 1987, pp. 182–192.
- [6] M. Alberdi, C. López, F. Galarraga, *Venezuelan Geol. Soc. Bull.* 21 (1996) 7–21.
- [7] T.R. Occo, M. Méndez, C. Ceccarelli, *Rev. Latinoam. Geoquím. Org.* 2 (1996) 5–14.
- [8] S. Wakeham, C. Lee, J.I. Hedges, P.G. Hernes, M.L. Peterson, *Geochim. Cosmochim. Acta* 61 (1997) 5363–5369.
- [9] J.G. Speight, S.E. Moschopedis, in: M.J. Comstock (Ed.), *Advances in Chemistry Series*, 1981, pp. 195–196.
- [10] J.G. Speight, *The Chemistry and Technology of Petroleum*, Marcel Dekker, 1998, pp. 23–29.
- [11] F. Prah, L.A. Pinto, *Geochim. Cosmochim. Acta* 51 (1987) 1573–1582.
- [12] F. Behar, R. Pelet, *J. Anal. Appl. Pyrol.* 8 (1985) 173–187.
- [13] R. Pelet, F. Behar, J.C. Monin, *Org. Geochem.* 10 (1986) 481–498.
- [14] C.J. Boreham, T.G. Powell, *Org. Geochem.* 17 (1991) 723–733.
- [15] M.J. Fabianska, G. Bzowska, A. Matuszewska, M. Racka, U. Skret, *Poland Chem. Erde* 63 (2003) 63–91.
- [16] M.D. Lewan, *Geochim. Cosmochim. Acta* 48 (1984) 2231–2238.
- [17] L. Lopez, S. Lo Mónaco, F. Galarraga, A. Lira, C. Cruz, *Chem. Geol.* 119 (1995) 255–262.
- [18] F. Behar, R. Pelet, J. Roucache, *Org. Geochem.* 6 (1984) 587–595.
- [19] D. Van de Meent, S. Brew, R. Philip, B. Somonet, *Geochim. Cosmochim. Acta* 44 (1980) 999–1013.
- [20] B. Horsfield, in: J. Brooks, D. Welte (Eds.), *Advances in Petroleum Geochemistry*, vol. 1, Academic Press, 1984, pp. 47–298.
- [21] B. Horsfield, *Geochim. Cosmochim. Acta* 53 (1989) 891–901.
- [22] R. Berner, *Geochim. Cosmochim. Acta* 48 (1984) 605–615.
- [23] J.S. Sinninghe Damste, W.I. Rijpstra, J.W. De Leeuw, P.A. Schenk, *Geochim. Cosmochim. Acta* 53 (1988) 873–889.
- [24] J.M. Hunt, W.H. Freeman (Eds.), *Petroleum Geochemistry and Geology* 1996, 30–39.
- [25] J. Bendoraitis, in: B. Tissot, F. Bienner (Eds.), *Advances in Organic Geochemistry*, vol. 3, Technip ed., 1974, pp. 209–224.
- [26] M. Ioppolo, R. Alexander, R. Kagi, *Org. Geochem.* 18 (1992) 603–609.
- [27] S.C. Teerman, R.J. Hwang, *Org. Geochem.* 17 (1991) 749–764.
- [28] S.E. Moschopedis, S. Parkash, J.G. Speight, *Fuel* 57 (1978) 431–434.
- [29] M. Radke, D.H. Welte, H. Willsch, *Org. Geochem.* 10 (1986) 51–53.
- [30] K.E. Peters, C.C. Walters, J.M. Moldowan (Eds.), *The Biomarker Guide, vol. 2: Biomarkers and Isotopes in the Petroleum Exploration and Earth History*, Cambridge University Press, 2005.
- [31] B.R. Simoneit, M. Schoell, R.F. Dias, F.R. De Aquino-Neto, *Geochim. Cosmochim. Acta* 57 (1993) 4205–4211.
- [32] S.M. De Grande, F.R. Aquino Nieto, M.R. Mello, *Org. Geochem.* 10 (1993) 1039–1047.
- [33] K.E. Peters, J.M. Moldowan, *Org. Geochem.* 17 (1991) 47–61.
- [34] J. Köster, H. Van Kaam-Peters, M. Koopmans, J. De Leeuw, J. Sinninghe Damste, *Geochim. Cosmochim. Acta* 61 (1997) 2431–2452.
- [35] A. Murray, I. Sosrowidjojo, R. Alexander, R. Kagi, *Geochim. Cosmochim. Acta* 61 (1997) 1261–1276.
- [36] H.C. Romesburg, *Cluster Analysis for Researches*, Lifetime Learning Publications, 1984, pp. 45–54.
- [37] B.S. Everitt, *Cluster Analysis*, Arnold, 1993, pp. 42–50.