GEOCHEMICAL STUDY OF CRUDE OILS IN THE MACHETE AREA, EASTERN VENEZUELAN BASIN: EFFECTS OF BIODEGRADATION

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ABSTRACT – Eight extra heavy crude oils samples from the Machete area in the Eastern Venezuelan basin were analyzed to study the distribution of saturate and aromatic biological markers and the effects of biodegradation on these organic compounds. These crude oils have a marine source and were formed in association with their source rock's main phase of hydrocarbon generation and expulsion. The biomarkers analyses show two principal crude oil groups (A and B) according to different biodegradation levels. The group A shows higher degree of biodegradation than group B. For example, the group A shows depletions in the concentrations of the C_{27}-C_{29} steranes, presence of demethylated hopanes, the monoaromatic hydrocarbons are totally absent, alteration of methyl phenanthrene and methyl dibenzothiophenes compounds. The C_{27}-C_{29} steranes, methyl phenanthrene and methyl dibenzothiophene distributions are apparently untouched by bacterial alteration in the group B oils.

RESUMEN – Ocho muestras de crudos extrapesados provenientes del área de Machete, ubicada en la cuenca Oriental de Venezuela, fueron analizados para estudiar la distribución de los marcadores biológicos presentes en la fracción de hidrocarburos saturados y aromáticos, y los efectos de la biodegradación sobre estos compuestos orgánicos. Estos crudos fueron originados por una roca madre con materia orgánica marina y a un nivel de madurez equivalente a la fase principal de generación y expulsión de crudos. Los análisis de marcadores biológicos muestran dos grupos principales de crudos (A y B), de acuerdo a diferentes niveles de biodegradación. El grupo A muestra mayor grado de biodegradación que el grupo B. Por ejemplo, el grupo A presenta alteraciones en las concentraciones de los C_{27}-C_{29} esteranos, presencia de los hopanos demetilados, los hidrocarburos monoaromáticos están totalmente ausentes, alteraciones en la distribución de los metil fenantrenos y metil dibenzotiofenos. En los crudos del grupo B, los C_{27}-C_{29} esteranos, metil fenantrenos y metil dibenzotiofenos aparentemente no están alterados por la biodegradación.

INTRODUCTION

Two main petroleum provinces are described for the central part of the Eastern Venezuelan basin. These include the southern foreland platform near the Orinoco, with its heavy oil fields of the Faja Petrolifera, and in the north, the giant El Furrial and related traps in the frontal thrusts of the Serranía.The northern belt includes light to medium gravity as well as heavy biodegraded oils of the Maturin area (North Monagas oil fields), whilst the southern belt includes heavy and extra oils (Orinoco Oil Belt) and heavy and medium gravity oils of the areas to the north of Cerro Negro (Talukdar *et al.*, 1988).

The general geological and geochemical information of the Eastern basin can be found in Talukdar *et al.* (1988), Cassani & Eglinton (1986, 1991) and Parnaud *et al.* (1995). This study is concerned with the distribution of steranes, triterpanes, aromatic steroids, dibenzothiophenes and phenanthrenes in crude oils samples from the Orinoco Oil Belt and the effects of biodegradation on these organic compounds.

GEOLOGICAL SETTING

The Machete area is located in the Eastern Venezuelan basin within the Orinoco Oil Belt. Structural and stratigraphic development of the area has been described by Hedberg & Pyre (1944), Patterson & Wilson (1953), Dusembury (1960), Fiorillo *et al.* (1981) and Audemard *et al.* (1983). The west zone of Orinoco Oil Belt presents a pre-Cretaceous sequences with three formations: Hato Viejo, Carrizal and Espino, where Hato Viejo and Carrizal represent Orinoco Oil Belt's Paleozoic sequences (Fig. 1) The Cretaceous sequence is represented by the Temblador Group. It is divided into two formations Canoa and Tigre. In the west part of the area, a persistent dolomite divides the Tigre Formation in three members: La Cruz, Infante and Guavinita. From north to south, the section thickeness disappears due to the erosion. Additionally, an unconformity over the Espino Formation is present in this area. The Tertiary formations are represented for three sedimentary transgression-regression cycles. The oldest cycle from the Oligocene and the other two from the

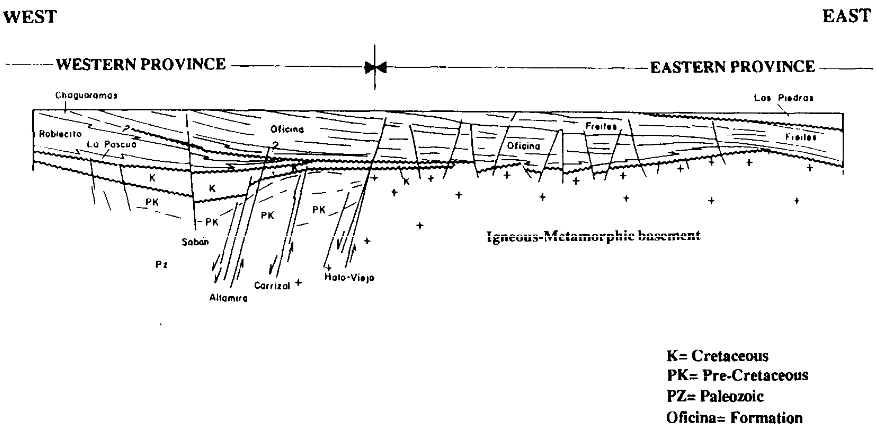

Fig. 1 - West-east cross section of Orinoco Oil Belt.

Miocene age. They are constituted by the La Pascua, Roblecito and Chaguaramas formations and Oficina and Freites formations, respectively (Fig. 1). The Oligocene cycle is discontinuous above older deposits (Cretaceous-pre-Cretaceous) or the basement. Infrayacent contact is unconformity with the Miocene sediments.

North of Machete area presents an igneous-metamorphic basement with active faulting during the Tertiary sedimentation and mainly it dislocated only at the bottom of the sequences, determining the boùndary between two tectonics provinces. Regional faults are characterized by rigid blocks without foldings where the normal faults (sintetics and antitetics) are present. In northeastern part of the Machete area, the Altamira fault system presents an inclination in the botton of the Cretaceous sequences toward the north, where it changes position to the northwestern.

EXPERIMENTAL

Eight crude oils from the Machete area were analized (Fig. 2). API gravity was determined by standard geochemical procedure. Capillary gas chromatography (GC) and capillary gas chromatography-mass spectrometry (GC-MS) were applied to characterize the saturated and aromatic fractions. The capillary GCs were run with a HP-5880 gas chromatograph using a 25m crosslinked methyl silicone column, temperature programmed from 115ºC to 275ºC at 8ºC per min. GC-MS analyses were carried out using the HP-5890 Serie II gas chromatograph coupled directly to an HP-5971 mass selective detector (MSD), a bench top quadropole mass spectrometer. The GC-MS was equipped with DB-5 and DB-1 columns for aromatic and saturated fractions analyses, respectively. The GC temperature was programmed from 100ºC for 2 min, then 100 to 280ºC at 4ºC/min and hold at 280ºC for 30 min. Biomarkers were determined in the MID (multiple ion detection) mode.

Vanadium, nickel and sulfur concentrations in crude oils were measured by x-ray fluorescence analyses, using a Phillips 1400 instrument.

RESULTS AND DISCUSSION

The Machete crude oils are extra heavy oils. API gravities range from 5 to 14.7º API, with the majority in the 6-10º API range (Table 1). API gravity is a bulk parameter which caracterizes the whole oil and is affected by many variables. Table 1 lists the vanadium, nickel and sulfur concentrations. The vanadium/vanadium+nickel ratio (V/V+Ni) varies between 0 to 0.85 and the sulfur content varies between 0.8 to 6%. The API gravities, V/V+Ni ratios and the sulfur percent, are affected by the biodegradation process. Biodegradation reduces oil API gravity and increase sulfur and other heteroatoms concentrations in the crude oil, by selectively

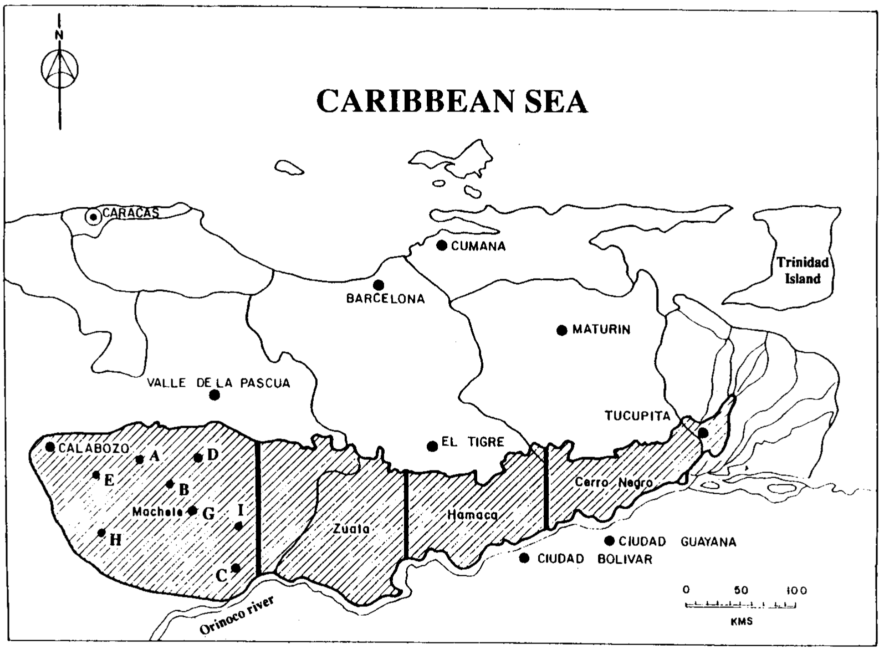

Fig. 2 - Map of Orinoco Oil Belt, showing crude oil samples localizations.

removing saturates and aromatics compared to NSO-compounds and asphaltenes (Peters & Moldowan, 1993). Thus, related oils can show different API gravities, V/V+Ni and sulfur content if some they have been biodegraded to different degree. Variations of the crude oil biodegradation levels are shown in Fig. 3. Different degrees of biodegradation transform oils from low to medium and finally to high specific gravity, resulting in some cases in heavy oil accumulations, such as the Orinoco Oil Belt.

Unresolved humps, due to naphthenic compounds, and the absence of n-alkanes and isoprenoid hydrocarbons are common features of most of the gas chromatograms (Fig. 4). Biodegradation results in depletion of n-alkanes prior to significant alteration of any other compounds class, including the acyclic isoprenoids pristane and phytane. Many authors have suggested a sequence of alteration of the different types of hydrocarbons, based on laboratory and field results (Bailey *et al.*, 1973b; Rubinstein *et al.*, 1977; Connan *et al.*, 1980; Connan, 1984; Rowland *et al.*, 1986). According to these results, the normal alkanes are removed first, starting with C_1 to C_{15} members, followed by their higher homologues. The branched alkanes are more resistant to biodegradation but are also destroyed eventually.

Sample	Groups	Formation	º API	V(ppm)	Ni(ppm)	S(%)	V/V+Ni
B	A	Tigre	6.3	1022	181	5.7	0.85
C	B	Chaguarama	7.5	626	124	4.6	0.83
D	B	Chaguarama	14.7	<1	8	0.8	<0.10
E	A	Tigre	5	853	170	5.6	0.83
G	A	Roblecito	6.3	2700	310	6	0.9
H	B	La Pascua	6.3	795	140	4.5	0.85
I	B		9.8	727	140	4.6	0.84

Table 1 - Geochemical data for oils analized, showing API gravity, vanadium (V), nickel (Ni), vanadium/vanadium+nickel ratio (V/V+Ni) and sulfur content (S).

The study of biological markers from the satured and aromatic fractions, by GC-MS, is necessary to obtain further information on these oils. Biodegradation of biological markers destroys molecular information useful in maturity and correlation assessments of some crude oils. In these altered crude oils, marked changes were observed in the distributions of certain biomarkers (Table 2). GC-MS mass fragmentograms shown in Figure 5 support a marine source for the Machete crude oils. The predominance of C_{27} steranes and high concentrations of tricyclic terpanes in the m/z 191 fragmentogram, suggest a marine component within the organic matter which generated these oils. A marine source is also indicated by the low hopane/sterane ratios (0.6-1.6, table2).

Various parameters in Table 2 indicate that all Machete crude oils are at similar levels of maturity. Narrow ranges for the %22S (53.6-58.8),

Sample	Groups	C27%	C28%	C29%	Hop/ste	%20S	%22S	PP-1
A	B	36	32	32	1.6	45.7	58.8	n.d.
B	A	36	34	30	bio.	bio.	bio.	1.26
C	B	39	33	28	1.2	43.7	57.1	1
D	B	16 bio.?	22 bio.?	62 bio.?	1.1	n.d.	53.6	bio.
E	A	bio.	bio.	bio.	bio.	bio.	bio.	1.18
G	A	bio.	bio.	bio.	bio.	bio.	bio.	bio.
H	B	37	31	32	0.6	44.5	55.6	bio.
I	B	36	32	32	0.8	44	58.8	0.8

C27 (%), C28 (%), C29 (%): C27-C28-C29 steranes
Hop/ste: hopane C30/sterane C29
%20S: sterane isomerization (20S/20S+20R)
%22S: homopane isomerization (22S/22S+22R)
PP-1: 3+2 methyl phenanthrene/9+1 methyl phenanthrene
bio: biodegradation
n.d.: no determinate

Table 2 - Chemical parameters of Machete crude oils.

%20S (43.7-45.7) and relatively uniform values for alkyl phenanthrene maturity parameter PP-1 (0.80-1.26) are observed. Taking into account the stage of hydrocarbon generation associated with the mean values for these various maturity parameters (Radke *et al.*, 1982; Mackenzie, 1984), these crude oils were formed in association with their source rock's main phase of hydrocarbon generation and expulsion.

The effects of biodegradation on triterpanes, steranes and polynuclear aromatic compounds have been described by several researchers (Seifert & Moldowan, 1979; Volkman *et al.*, 1983; Connan, 1984; Lin *et al.*, 1989; Peters & Moldowan, 1991; Cassani & Eglinton, 1991; Peters & Moldowan, 1993). According to these studies, the normal alkanes are removed first, starting with C_1 to C_{15} members followed by their higher homologues, then by the removal of iso- and anteiso-alkanes, steranes, diasteranes and the alteration and removal of hopanes followed by moretanes. For some aromatic hydrocarbons it has been established that there is an order of susceptibility to biodegradation which is, in general, monoaromatics >diaromatics>triaromatics.

The sterane, triterpane and aromatic mass chromatograms corresponding to these crude oils show two principal oil groups according to different biodegradation levels (Fig. 6 and 7).

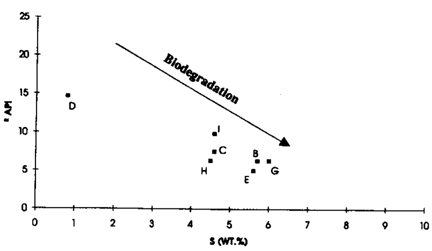

Fig. 3 - API gravity versus sulfur content plot.

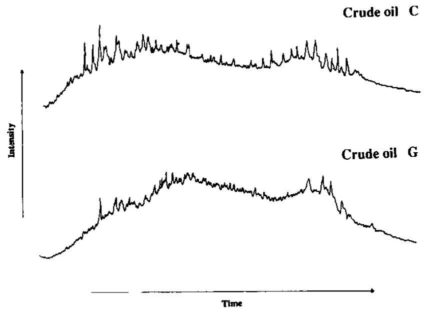

Fig. 4 - Gas chromatograms of Machete crude oils.

Group A: the m/z 217 and 218 mass fragmentograms show a depletion in the in the concentrations of the C_{27}-C_{29} 14α(H), 17α(H)-20R,S and 14β(H), 17β(H)-20R,S steranes. These compounds have almost completely disappeared while the lower-molecular-weight steranes (C_{21}-C_{22}) are relatively more abundant (Fig. 6). Similar observations have been reported previously by several authors (Rullkötter & Wendish, 1982; Mckirdy *et al.*, 1983; Volkman *et al.*, 1983; Connan, 1984; Cassani & Eglinton, 1991). The m/z 191 mass fragmentogram illustrates the degree of biodegradation of hopanes for these oils determined by the presence of demethylated compounds (Fig. 6). An indication of the neoformation of demethylated hopanes by biodegradation is that the 17α(H), 18α(H), 21β(H)-25, 28, 30- trisnorhopane is practically absent. The tricyclic terpanes are apparently more resistant to biodegradation and do not seem to be affected in these samples.

Aromatic hydrocarbons are very resistant to biodegradation according to Volkman *et al.* (1984) and Wardroper *et al.* (1984). However, in extreme cases of alteration there is a preferential depletion of the 20R configuration in the mono- and triaromatic steroids species in the high-molecular-weight range (Wardroper *et al.*, 1984). In these oil samples the monoaromatic hydrocarbons are totally absent (Fig. 6). The absence of these compounds is

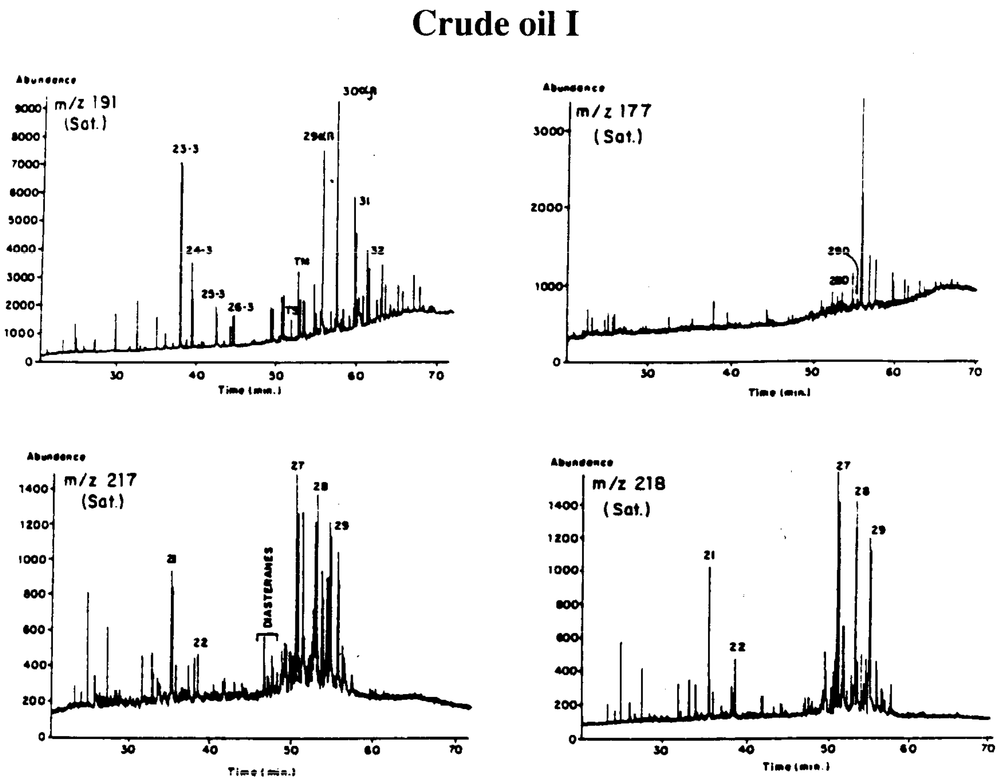

Fig.5 - Mass chromatograms (m/z 191, m/z 177, m/z 217, m/z 218) from a representative crude oil of Machete area (crude oil I).

Group A

Crude oil G

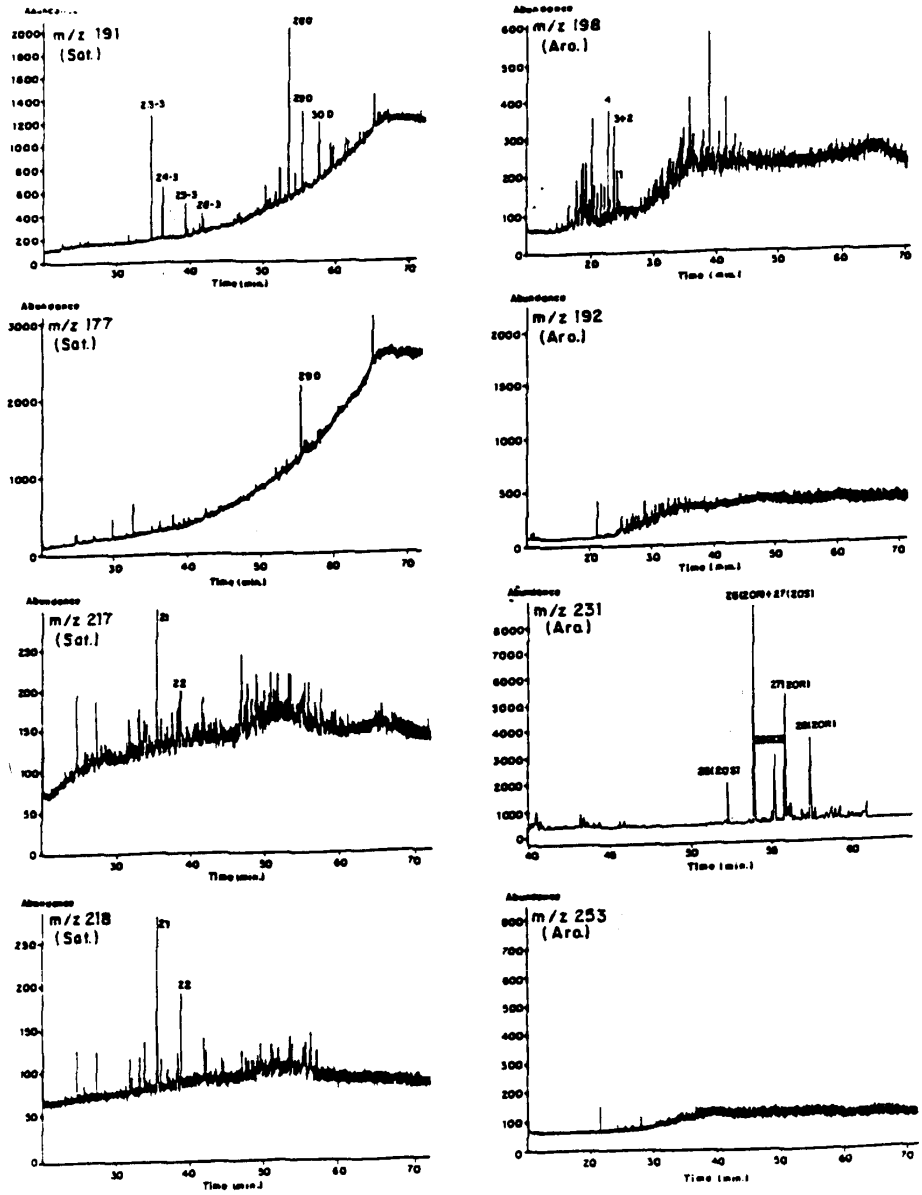

Fig. 6 - Mass chromatograms (m/z 191, m/z 177, m/z 217, m/z 218, m/z 192, m/z 198, m/z 231, m/z 253) from saturated and aromatic fractions of a representative crude oil (G) from group A.

Group B

Crude oil C

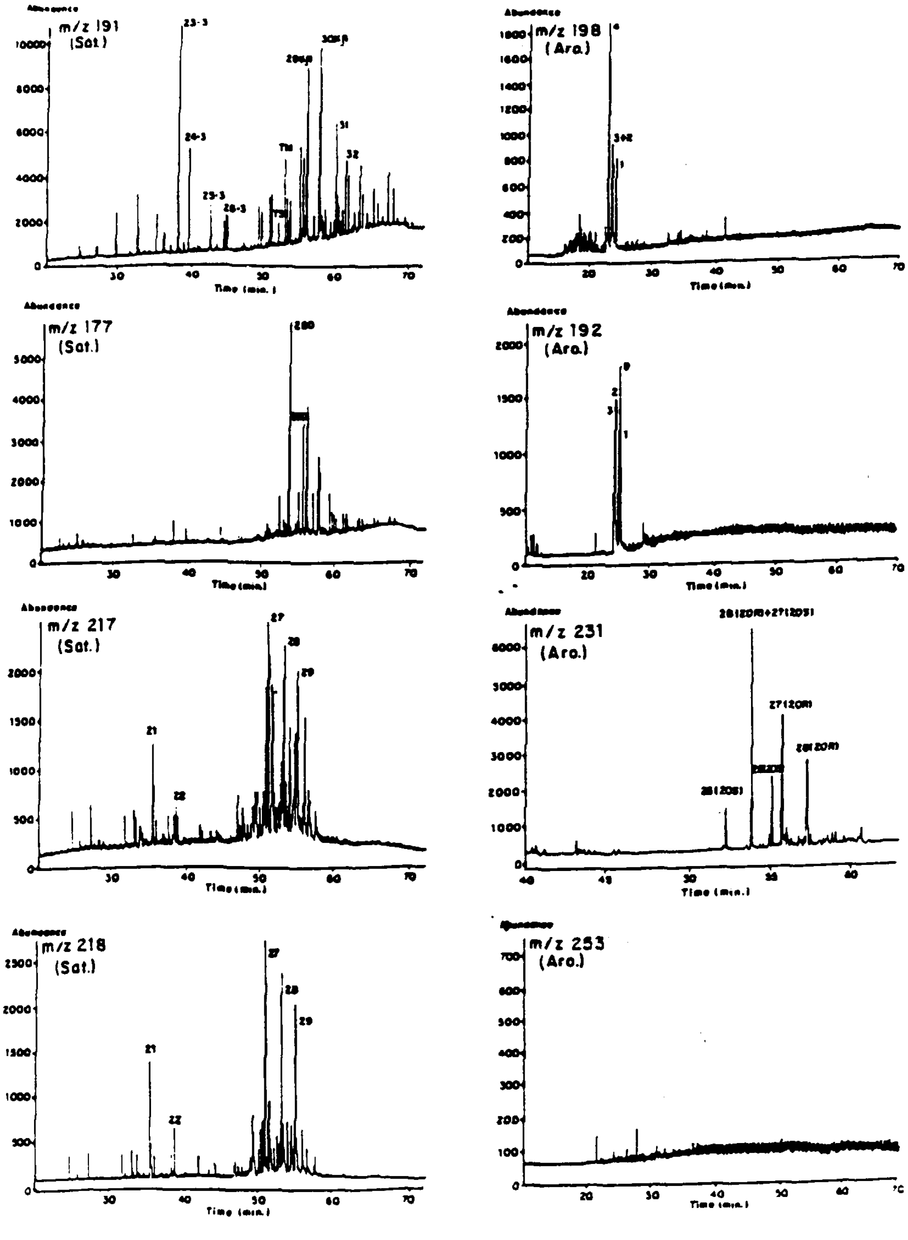

Fig. 7 - Mass chromatograms (m/z 191, m/z 177, m/z 217, m/z 218, m/z 192, m/z 198, m/z 231, m/z 253) from saturated and aromatic fractions of a representative crude oil (c) for group B.

probably the result of severe biodegradation in the reservoir. Methylated phenanthrenes are resistant to biodegradation in the reservoir with susceptibility to biodegradation decreasing in the trend $C_1>C_2>C_3>C_n$; where n represents the total number of carbon atoms in the salkyl substituents (Connan, 1984; Volkman *et al.*, 1984). These biodegraded samples show alteration of methyl phenanthrene compounds, indicating the high degree of biodegradation.

Sulphur-bearing aromatics have been reported to be partially attacked by bacteria (Connan, 1984). Micro organisms belonging to the genus Pseudomonas were proved to be capable of converting dibenzothiophene into sulfur-containing oxygenated compounds under aerobic conditions (Kodana, 1970; *in* Connan, 1984). In these oils the partial removal of methyl dibenzothiophenes series has been confirmed by GC-MS analysis (m/z 198, Fig. 6). This fact reflect the severe biodegradation of this crude oils group.

Based on pressure data and formation water composition distributions combined with the integration of new structural data, a hydrodynamic model was proposed by Parnaud *et al.* (1995) for the Maturin subbasin. Along the Orinoco heavy oil belt, meteoric waters still migrated in each aquifer from the Mesa highs to reach their exsurgence along the Orinoco River banks. The oil probably migrated rapidly toward the Orinoco fields due to the large freshwater flow arising from the uplifted ranges to the north. The heavy biodegraded oils found in the traps of the basin are regarded as evidence for such a process.

Group B: Steranes are the first high-molecular weight biomarkers to be alterated. Our results indicate that this stage of biodegradation has not been attained in any of the group B oils (Fig. 7) The m/z 177 mass fragmentogram is also shown. In these crude oils, demethylated hopanes were found to be present. Assuming that demethylated hopanes are formed by biodegradation of hopanes, this situation indicates that reservoir biodegradation probably affects the hopanes before the steranes. Comparison of these results with the literature forces us to conclude that possibly the specificity and sequence of reactions that occur during biodegradation are highly dependent on reservoir conditions and the types of bacterial populations which alter oil. Probably partial biodegradation of homopanes can occur without alteration of the steranes (Peters & Moldowan, 1991).

The triaromatic, methyl phenanthrene and methyl dibenzothiophene distributions are apparently untouched by bacterial alteration, but the monoaromatic hydrocarbons (m/z 253) are affected in these crude oils (Fig. 7). In this case it is difficult to affirm whether this is due to alteration by bacteria or to water washing process.

These observations demonstrate that biodegradation could be locally controlled by the population of microbes, nutrient supply and oxygen content and probably pH, Eh and temperature of the water in contact with the petroleum in a reservoir (Philp, 1983). The relative extents of biodegradation described in the literature is not necessarily applicable to all situations.

CONCLUSIONS

The Machete crude oils are extra heavy oils. These oils show different API gravities, V/V+Ni and sulfur content due to different biodegradation levels. The study of biological markers in the saturated and aromatic fractions indicates that these crude oils have a marine source and were formed in association with their source rock's main phase of hydrocarbon generation and expulsion. The sterane, triterpane and aromatic mass chromatograms corresponding to these oils show two principal crude oil groups (A and B) according to different biodegradation levels. The group A shows higher degree of biodegradation than group B. This work demonstrate that the relative extents of biodegradation described in the literature does not neccesarily applicable to all situations.

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