



Investigating Asphaltenes Composition in Crude Oil Samples using Iatroscan TLC-FID Method.

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ABSTRACT

This research was carried out to investigate the percentage composition of asphaltenes by Iatroscan analysis using Thin Layer Chromatography-Flame Ion Detection method (Iatroscan TLC-FID). The percentage composition of asphaltenes by Iatroscan TLC-FID method was compared with the weight% of asphaltenes precipitated. The results from the two methods nearly agreed with each other which revealed that the amount of asphaltene recovered by precipitation is analogous to Iatroscan analysis carried out prior to precipitation. The insignificant difference observed between the two results could be associated to some slight unavoidable experimental and analytical errors which were slightly encountered and instantly addressed. Based on the results obtained from Iatroscan analysis and % composition by weights of asphaltenes recovered, the non-degraded oil tagged 8676 was observed to comparatively have higher asphaltene composition (1125 mg, 11.22 %) than its counterpart which is very slightly degraded oil and tagged 6661 (608.5 mg, 6.085 %). This is not commonly reported in literature. Probably, this indicates that biodegradation may possibly not increase asphaltene composition of oil as widely reported.

Keywords: Asphaltenes, Biodegradation, Iatroscan TLC-FID, Oil

INTRODUCTION

The largest molecules found in crude oil are the Asphaltenes with many aromatic rings usually connected or bonded to a linear or cyclic saturated hydrocarbon structures and polar functional groups. Many authors have characterised and defined Asphaltenes by a C:H ratio close to one, specific gravities near to one, extremely aromatic, and friable, infusible solid component of crude oil (Mullins, 1990, Wolf & Alfani, 1982) respectively. Petroleum mixture comprises of four main classes of compounds, these classes of compounds are; Asphaltenes, Resins, Aromatic hydrocarbons and Saturated hydrocarbons (ARAS) making the acronym SARA when called via the reverse order. The percentage compositions of SARA in the crude oil samples were determined in this work using Iatroscan analysis with special consideration given to asphaltene content in each of the sample for selection purposes. Many researchers e.g. (Cebolla *et. al* 1995; Karlsen and Larter, 1991 *e.t.c.*) have used this technique in the past for the analysis of SARA constituents in crude oils and solvent extracts. However, lack of suitable standards for calibration was their major challenges. Some of these researchers relied on synthetic compounds as standards to achieve quantification. Although, (Bharati *et. al* 1997) have clarified that TLC-FID response factors are not

satisfactory when this type of materials are used to calibrate the Iatroscan Instrument.

Asphaltene is the heaviest and the most polar fraction of crude oil which is composed of conjugated polyaromatic ring systems. The aromatic fraction and number of aromatic cycles increases with boiling point. Evidences have shown that boiling point of this fraction increases with increase in molecular weight, density, viscosity, refractive index, polarity and structural complexity. The heavy oil fractions are usually enriched in resins and asphaltenes (Alboudwarej *et al.*, 2002; Aske *et al.*, 2001; Bearsley *et al.*, 2004; Buenrostro-Gonzalez *et al.*, 2004; Castro & Vazquez, 2009; Johansson *et al*, 2009; Kaminski *et al.*, 2000; Merdrignac & Espinat, 2007).

It has been reported that amount of Asphaltenes in light oil is less than 1% and the alkyl chains, hydroaromatic rings, heteroatoms, molecules of variable aromaticity, metals, and functional groups are all contained in the conjugated ring of asphaltenes' molecule (Merdrignac & Espinat, 2007).

In geochemical studies, important information about the origin, biological source material, and diagenetic history of the oil can be traced using the chemically bound biomarkers contained in the asphaltenes and other compounds

found in crude oil fraction Strausz *et al.* (1999) and Peng *et al.* (1999b).

Asphaltene Associated Problems in Refining and other Operations

Asphaltenes play a major role on the physical and chemical properties of crude oil. The presence of heteroatoms and high viscosity in crude oil is associated with asphaltene composition in the oil (Miller *et al.*, 1987). Headen *et al.* (2007) and Creek (2005) described asphaltene behaviour as like cholesterol in an animal tissue that precipitates and deposit to plug the pipeline. Therefore, the distinct propensity of asphaltenes to self-aggregate is one of their most likely features that are responsible for a large proportion of the problems observed during crude oil processing and refining (Maqbool *et al.*, 2011).

Aggregation and precipitation of asphaltenes as revealed by many authors is the key factor causing a large variety of problems in production, refining and transportation operations, it is also found to be associated with, catalyst deactivation due to coke formation (Wolf and Alfani, 1982). These problems and incompatible refinable nature of asphaltenes have been linked to their high molecular weight. They tend to reduce oil flow in pipelines as deposits increase in thickness (Creek, 2005). Similarly, Wilhelms and Larter (1994) revealed that asphaltene are responsible for the formation of tar mats in petroleum reservoirs which in turn hinder crude oil recovery (Wilhelms and Larter, 1994). To deal with asphaltene deposits, involved huge amount of capital which raised the cost of production. The treatment costs increases from land to deep-water (Creek, 2005; Merdrignac and Espinat, 2007). The work of Maqbool *et al.* (2011) has re-affirmed that temperature, pressure and solvent conditions are the driving force that directs aggregation and precipitation of asphaltenes.

As a rapid screening tool, Iatroscan separates crude oil samples in to compound class fractions of various polarities (Karlsen and Larter, 1991). It was employed in this research to distinguish the asphaltene composition in the samples prior to the bulk geochemical work.

METHODOLOGY

Precipitation of Asphaltenes:

Deasphalting of the crude oil samples was firstly carried out prior to further analysis. This was done by a standard asphaltene precipitation by *n*-hexane. The sample oil associated asphaltenes were washed to remove waxes and impurities. The method was carried out in light of Alboudwarej *et al.* (2002) with little modification.

Procedure

200 ml of *n*-hexane was accurately added into a 250 ml conical flask containing about 10 g of

the crude oil sample with regular swirling. The mixture was stirred for 2 hours and was allowed to equilibrate for 24 hours. It was centrifuged at 3500 rpm per minute for 15 minutes and the asphaltene recovered. The hexane-solubles (maltene) is filtered without disturbing the whole mixture and kept in a vial. The asphaltene recovered was re-precipitated with another 40 fold of *n*-hexane per gram of the sample. The mixture was ultrasonicated for an hour and allowed to settle down for 24 hours and the asphaltene recovered by centrifugation again. The former and the latter procedures were repeated twice to boost recovery. The recovered asphaltene was transferred into a pre-weighed vial with small amount of Dichloromethane (DCM). Excess solvent was removed using stream of nitrogen and was allowed to stand at ambient temperature until evaporation ended. The amounts recovered were weighed respectively. The same precipitation procedure was repeated for another new 10 g of the same sample. The washing/cleaning of the precipitated asphaltenes was carried out by means of Soxhlet extraction technique for good 72 hours in order to remove co-precipitated maltenes.

TLC-FID (Iatroscan) Analysis of Whole Oils

An Iatroscan instrument (analysis) was used in this work to determine quantitatively how much asphaltene fraction contained in the crude oil samples. The method is quick, precise, and inexpensive (Karlsen and Larter, 1991). It was adopted in this work based on the procedure carried out by the latter as follows. About 10-10.8 mg of each crude oil sample is accurately weighed in a 2 ml GC glass vial and dissolved with 1 ml DCM. Before sample application, Chromarods were run five to six times through the flame ionization detector (FID) to remove contaminants, and activate the silica layer (stationary phase).

The development tanks containing the solvents (mobile phases) are lined with chromatographic paper on the inside back and side walls, from top to bottom. Each rod was spotted by 3 µl of the standard and the sample solution. It was applied drop wise manually by using a 5 µl syringe. Subsequently, the Chromarods were developed in *n*-hexane for 28 minutes and air dried for 3 minutes, developed again in toluene for 14 minutes and air dried for 6 minutes. It was further developed in another mobile phase made up of mixture of dichloromethane: methanol (97:3 v/v) for 3 minutes and oven dried for 90 seconds at 65°C. The samples were analysed and the data collected and interpreted using a spread sheet accordingly.

RESULTS AND DISCUSSION

TLC-FID Iatroscan Analysis of the Whole Oils

From the result in Fig. 1, oils 8676 and 6661 were observed to have higher asphaltenes compositions compared to their counter parts.

Amount (weights %) of asphaltene recovered by precipitation:

The amount of asphaltene (wt. %) recovered after precipitation of the two oils in

$$wt\% = \frac{\text{weight of dry asphaltene}}{\text{weight of crude oil sample}} \times 100 \quad (1)$$

The Weight% of dried asphaltene recovered after precipitation and Soxhlet washing were 6.085% and 11.22% for the two oil samples that is 6661 and 8676 respectively. Similarly, the weights of the dry asphaltene in milligrams for these samples were found to be 608.5 and 1125 respectively.

Comparison between Iatroscan result and the amount recovered by precipitation (i.e. weights of asphaltenes):

In comparison between the TLC-FID Iatroscan result shown in Fig. 1 with the calculated weight of the asphaltene (which is the amount recovered after precipitation) after the bulk geochemical processes Fig. 2. The two results were very close to agreement. The slight difference observed between Fig. 1 and Fig. 2 could be attributed to experimental and analytical errors. Moreover, the result of Iatroscan analysis is also in agreement with the studies conducted by Karlsen and Larter (1991) and proved that Iatroscan is rapid screening tool, precise, and inexpensive technique.

question (i.e. those with a relatively higher Asphaltenes content) was calculated using equation (1) and presented in Fig. 2.

From Fig. 2 it is clearly shown that sample 8676 which is a fresh none degraded oil according to Peters and Moldowan (1993) scale presented in Fig. 5, Table 1 and plots in Fig. 3 to 4 had higher asphaltene composition than that of its counterpart which is slightly degraded.

Concurrently, the difference and level of degradation between the samples as investigated were found to be insignificant with minor or no loss of *n*-alkanes or any other biomarkers in the samples. Although, samples 6661 and 8673 were slightly degraded and ranked “1” in the Peters and Moldowan (1993) scale, still none of the sample appeared to have lost their isoprenoids, hopanes and steranes. This indicates that the samples were slightly biodegraded. Concomitantly, oils (8672 and 8676) were ranked “0” on the same scale demonstrating that they are not degraded. At the same time, the % composition of asphaltenes by Iatroscan analysis was similar to the weight (%) of asphaltenes precipitated.

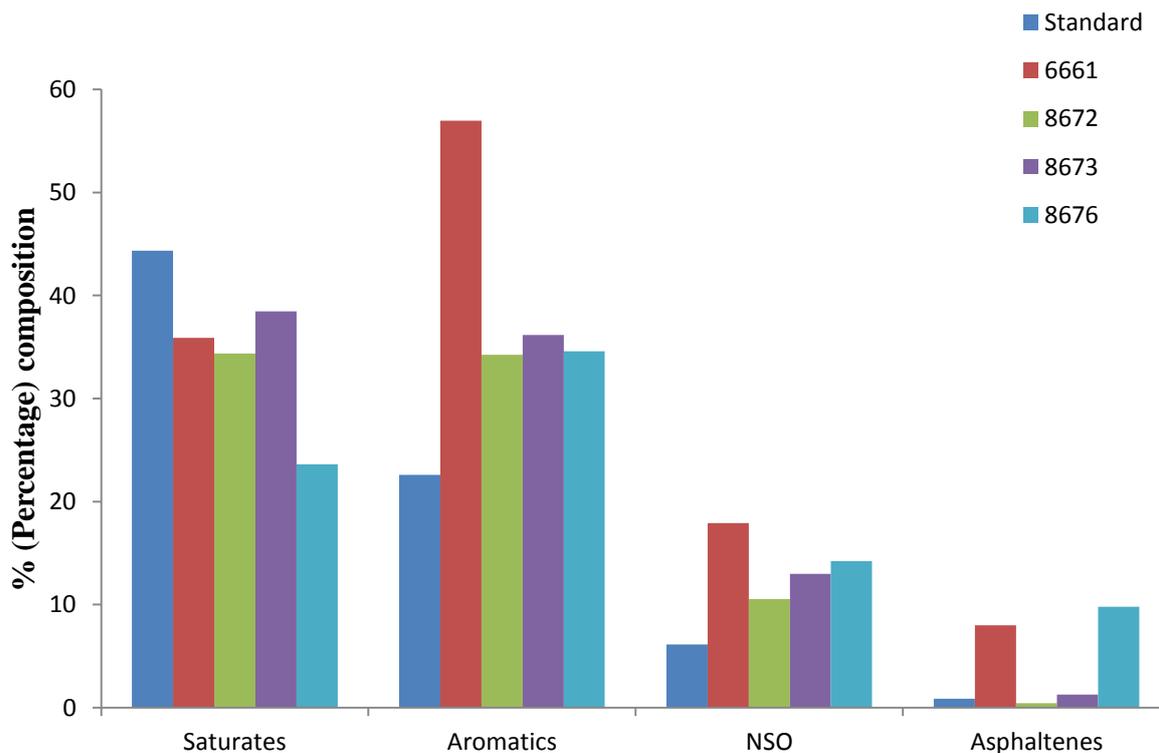


Fig.1. Iatroscan TLC-FID Result of Saturates, Aromatics, Resins and Asphaltenes (SARA) Compositions of the Oil Samples

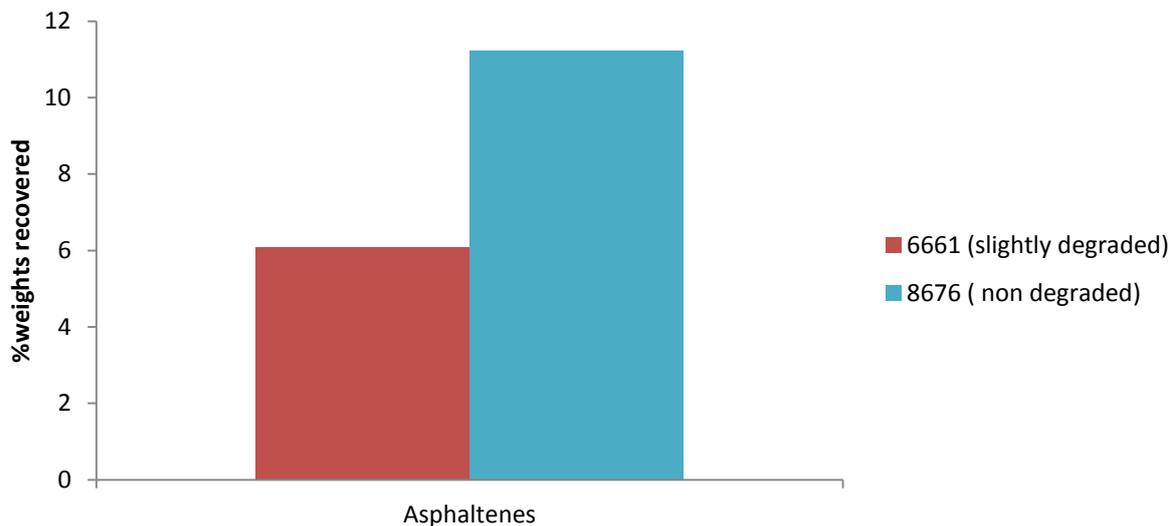


Fig.2. Weight (%) of Dried Asphaltene Recovered After Precipitation and Soxhlet Washing.

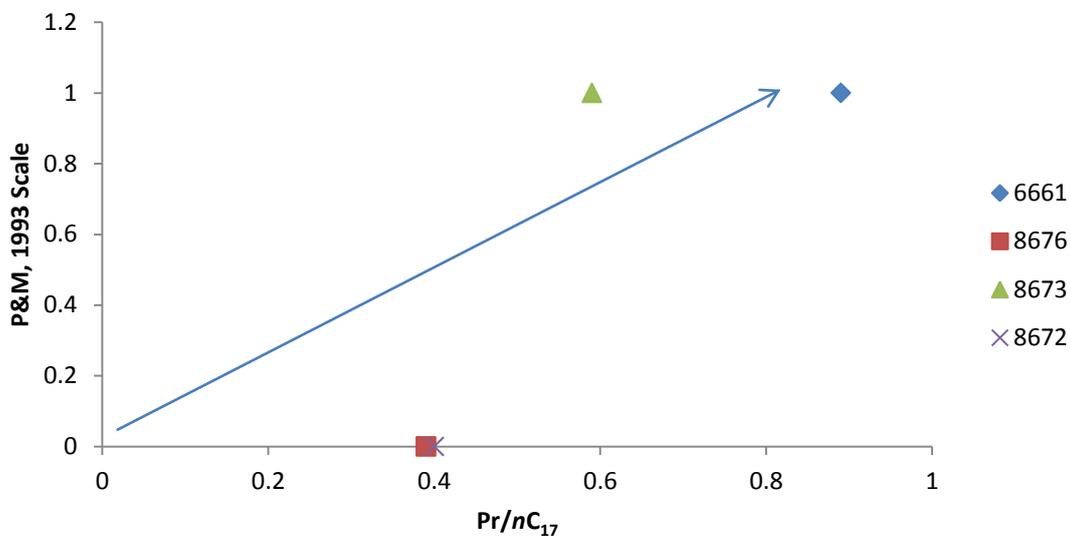


Fig.3. Ratio Pristane/nC₁₇ against the level of biodegradation on Peters and Moldowan (1993) Biodegradation Scale.

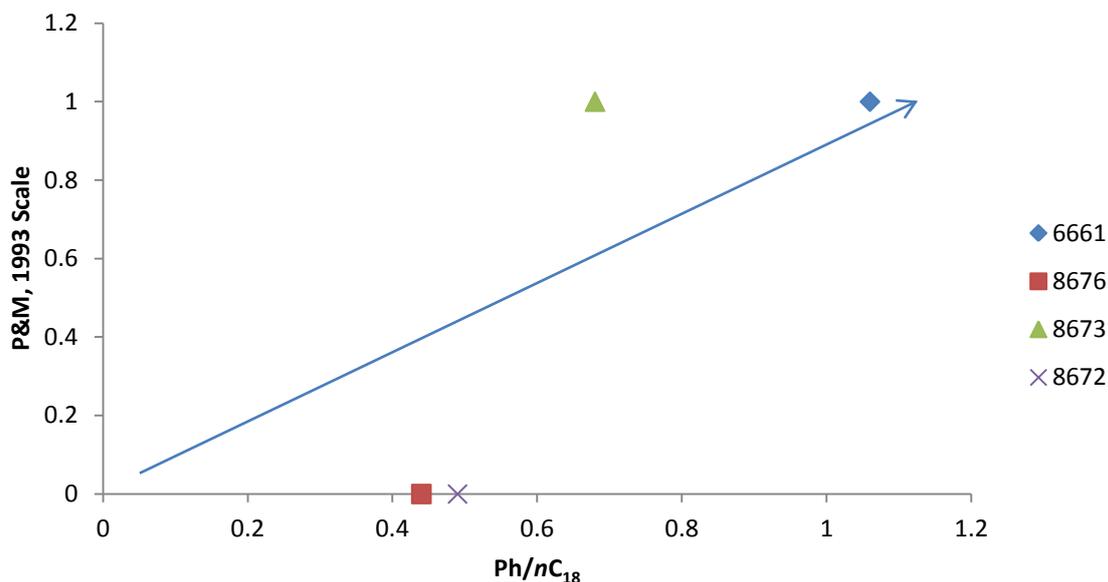


Fig.4. Level of biodegradation against Phytane/ nC_{18} ratio. There was systematic increase of Pristane/ nC_{18} ratio among the oils with increasing biodegradation

Table 1 Ranking of biodegradation in the crude oil samples. It was done in the light of Peters and Moldowan (1993) Biodegradation Scale.

S/N	Sample	P&M (1993) Ranking	Chemical composition
1	6661	1	Lower homologous <i>n</i> -alkanes depleted
2	8676	0	Presence of abundant <i>n</i> -alkanes
3	8673	1	Lower homologous <i>n</i> -alkanes depleted
4	8672	0	Presence of abundant <i>n</i> -alkanes

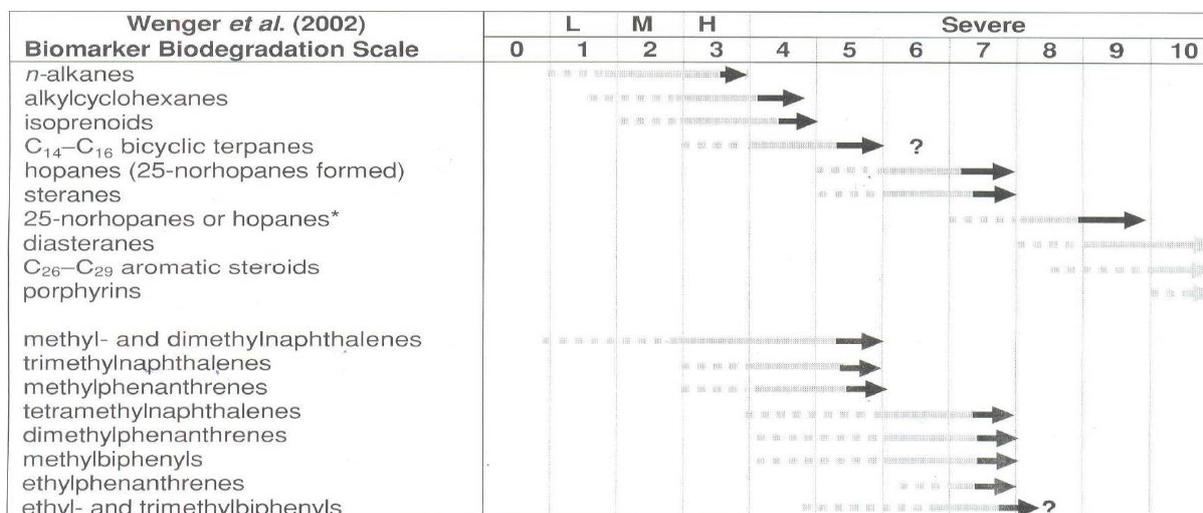


Fig. 5. Peters and Moldowan (1993) biodegradation scale modified by Wenger *et al.* (2002).

It is based on the differing resistance of different compound classes to microbial attack. Arrows indicate where compound classes are first altered (dashed lines), substantially depleted (solid grey),

and completely eliminated (black). Degree of biodegradation from Wenger *et al.* (2002) reflects changes in oil quality (L, lightly biodegraded; M, moderately biodegraded; H, heavily biodegraded)

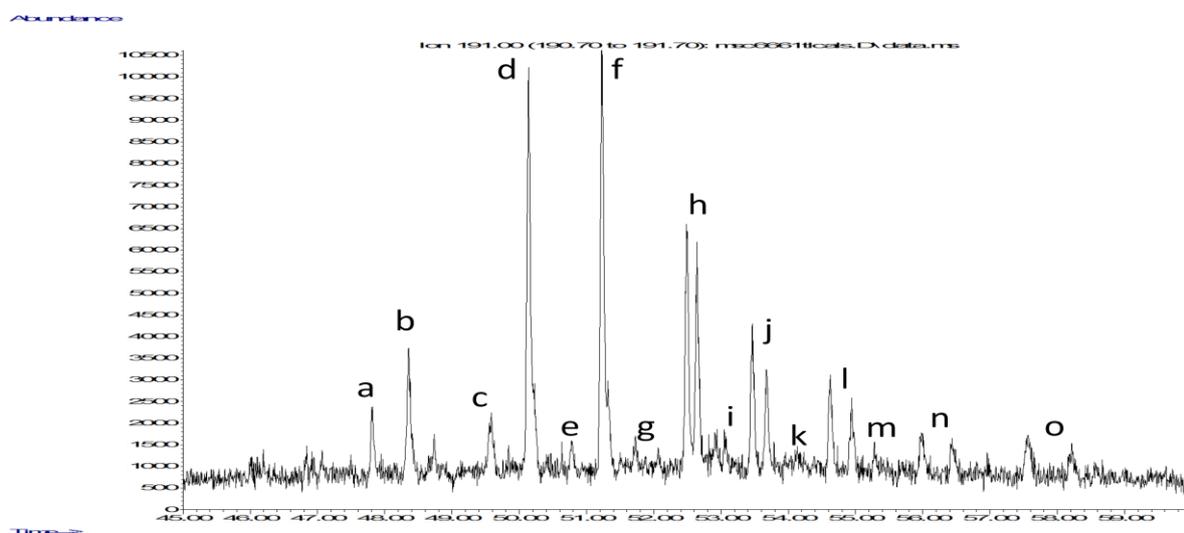


Fig. 6 Chromatogram (ion 191) of the saturate fraction of sample 6661 obtained after the TLC of the whole oil fraction of the sample and analysed by GC-MS. The Biomarkers (Hopanes) are marked with alphabets above the peaks.

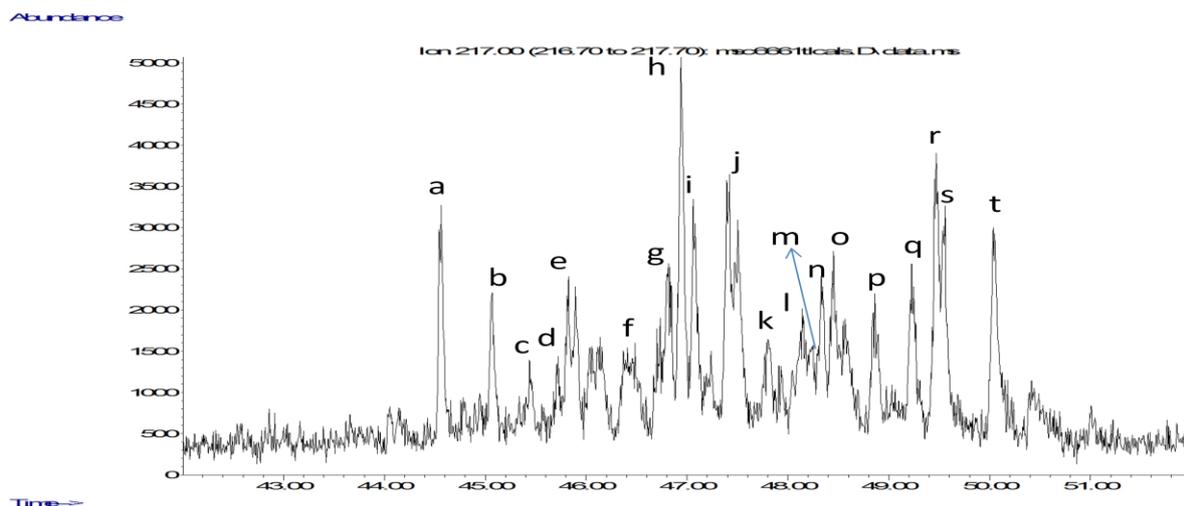


Fig. 7 Chromatogram (ion 217) of the saturate fraction of sample 6661, it was obtained after the TLC of the whole oil fraction of the sample and analysed by GC-MS. The Biomarkers (Steranes) are marked with alphabets from a-t above the peaks.

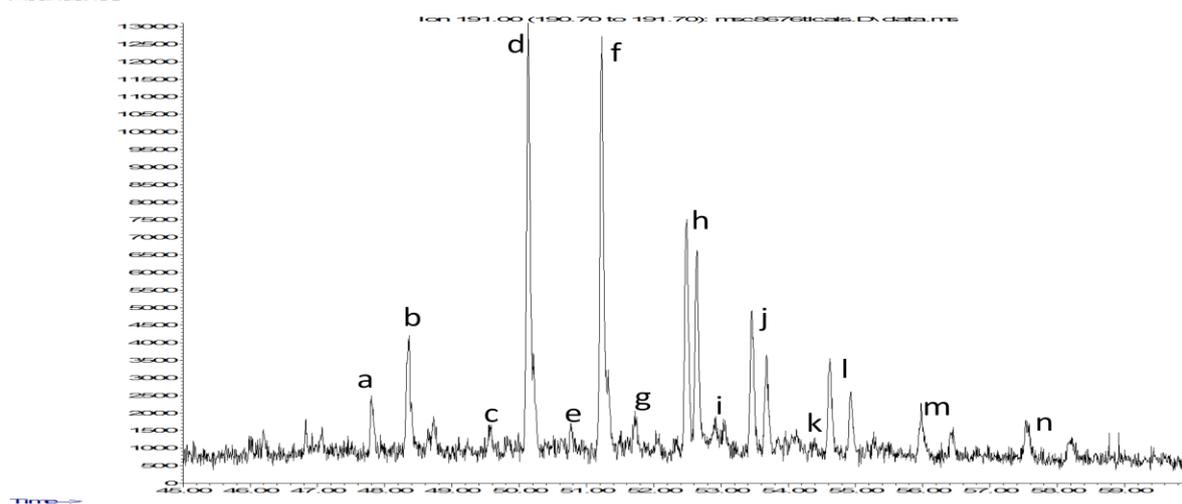


Fig. 8 Chromatogram (ion 191) for the saturate fraction of sample 8676 obtained after the TLC of the whole oil fraction of this sample and analysed by GC-MS. The Biomarkers (Hopanes) are marked with alphabets above the peaks.

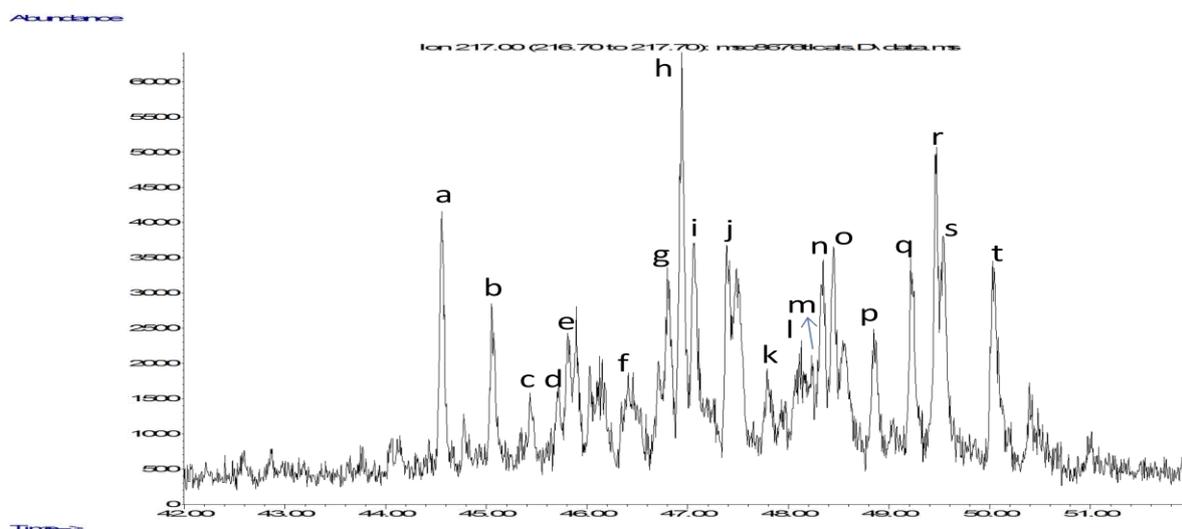


Fig. 9 Chromatogram (ion 217) for the saturate fraction of sample 8676, it was obtained after conducting TLC on the whole oil fraction of this sample and analysed by GC-MS. The Biomarkers (Steranes) are marked with alphabets from a-t above the peaks.

In general, the hopanes and steranes are abundant in the oils and their distributions were very similar as presented in Fig. 6 to 9 indicating that the oils were from same source rock. However, information about biodegradation cannot be inferred from these compounds due to the fact that biodegradation is at initial stage and has not reached them. Therefore assessment of biodegradation level in this study was limited to Ph/nC₁₇ and Ph/nC₁₈ ratios only as illustrated in Fig. 3 and 4.

CONCLUSION

Based on Iatroscan analysis and weights% composition of asphaltenes recovered, the non-degraded oil (8676) was observed to have higher asphaltene when compared to its corresponding

slightly degraded oil (6661). This variance was not commonly reported in previous literatures. Probably, this indicates that biodegradation may possibly not increase asphaltene composition of oil as widely perceived and reported.

The amount of asphaltene recovered by precipitation was found to be similar to Iatroscan analysis carried out prior to precipitation. The slight difference between the two results was associated to experimental and analytical errors which were very minimal.

The results of this research could be used to augment exactness in modelling asphaltene's physical properties in solution and their nature in refinery processes. Conversely, this could in turn be helpful in creating and scheming ways to

unravel production, transport and refinery problems associated with them.

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