



## CEMENT BOND INTEGRITY VERIFICATION USING CRUDE OIL FINGERPRINTING TECHNIQUE

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**Abstract:** Each source crude oil therefore has a unique fingerprint that can potentially be determined by varieties of instrumental and non-instrumental techniques which include gas chromatography (GC), gas chromatography flameionization detector (GC-FID), and gas chromatography mass spectrometry (GC-MS), among others. Geochemical fingerprinting is a rapidly expanding discipline in the earth and environmental sciences and is anchored in the recognition that geological processes leave behind chemical and isotopic patterns in the rockrecord. Many of these patterns commonly called geochemical fingerprints are slightly different from each other. In this study, GC was utilized in the analysis of commingled oils from well MS-2, to the extent to which it was believed that mixing occurred in the near wellbore owing to mechanical problems because of communication (cross flow from deeper and higher pressure reservoirs) other than the completion interval. Oil in deeper reservoirs, under higher pressure flowed into shallower pressure reservoir since communication between the reservoirs is believed to be present. The most likely cause of this communication is the cross flow due topoor cement bonding behind the casing as revealed by cement bond logs (CBL) from well MS-2.

Thefingerprints from an off-set well with good cement bonding was first identified then the wellhead samples of MS-2 streams can also be analyzed to determine if a channelling problem is indeed presentin the well. The finger printing analysis of the two samples suggest that the profiles of the wellhead sample taken from MS-2 is out-of-bounds or indicate a low probability of commonality for the oil sample pair to be from a common source.

**Key words:** Finger printing: gas chromatographv: Flame ionization detector: Radial plots: Carbon

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### 1. Introduction

Geochemical fingerprinting of hydrocarbon was developed in the petroleumindustry to develop an understanding of source rock and crude oil relationships.Fingerprinting of crude oil has received a considerable attention in recent yearsand the primary interests have been in

identifying the sources of oils spilled in water ways, allocating commingled fluids during production, reservoir fluid characterization, study of environmental pollution etc. (Charles & Jerry, 1989).

The overall methodology to identify a source of any oil is to compare properties of the oil in question to properties of known sources until a positive identification beyond a reasonable doubt is found or until the oils are demonstrated to be from other sources. Depending on the oil samples involved, the analytical requirements may range from only a GC analysis to an extensive assortment of tests (Charles & Jerry, 1989).

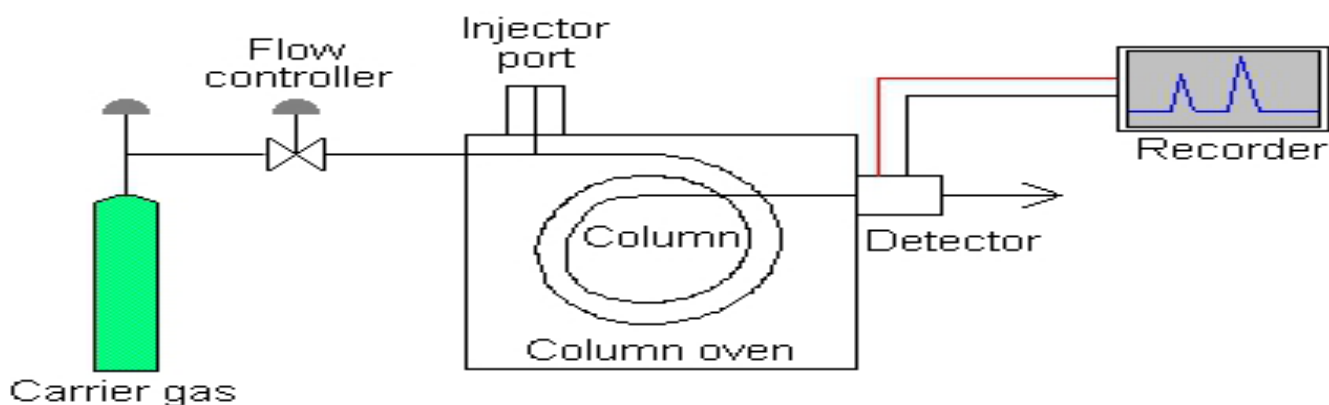
### 1.1 Objective of Study

In this case study of GC analysis, the normal paraffin and isoprenoids are analyzed and compared in the approximate range from C7-to-C35 for wellhead oil sample pair from well MS-2 and well CC-8. Well MS-2 is a dual string completion and has been identified to have poor-to average cement integrity behind the 9-5/8" production casing as indicated by recent cement bond log interpretations. The production profiles of the short string of MS-2 was out-of-bounds with in flow-outflow models and it is widely believed to be producing commingled oil from the deeper, higher pressured reservoir, hence the cement bond log investigations. Well

CC-8 is a single string completion for the deeper and higher pressured reservoir penetrated by well MS-2. Recent cement bond log interpretation has shown competent cement behind the production casing.

Gas chromatography technique has been used successfully in the determination of hundreds of hydrocarbons and other organic compounds. It is an ideal tool for analyzing gas and liquid samples, thus allowing the researcher to identify both the molecular species present, their concentrations, and also to obtain information from hydrocarbon samples (free product) by determining the compositions of the hydrocarbons present (Oforka, Osuji, & Onojake, 2012). It allows the ability to respond quickly in improving production and appropriately allocating commingled fluids and spills. It also allows engineers to have an effective well reservoir management by solving integrity problems such as leaks and tubing failures (Kaufman, R.L., et al., 2002). This study therefore seeks to demonstrate the suitability of geochemical fingerprinting technique for fingerprinting appropriately reservoir fluids in mature and marginal fields as a means of identifying failed cement bond competencies.

### 1.2 Background of study



**Fig. 1.1: A schematic diagram of Gas Chromatograph**

Chromatography is the separation of a mixture of compounds into their individual components primarily according to their volatilities. There are numerous chromatographic techniques but gas chromatography (GC) is the most important one. It has a number of advantages over other separation techniques. It can identify (qualitate) and measure the amount (quantitate) various sample components.

Since the introduction of fingerprinting, gas chromatography has been widely used as an important method in the analysis of petroleum hydrocarbon which has complex compositions, although newer techniques have extended the applications of GC in the petroleum composition analysis. Such techniques are being briefly reviewed which include high temperature gas chromatography (HTGC), one

dimensional gas chromatography (1D-GC), two dimensional (2DGC), gas chromatography mass spectrometry (GC-MS), amongst others (Huang *et al.*, 2012). Although some of these techniques such as 2D-GC and GC fingerprinting are still very young, it is expected that, with the advance of research work, they will be used more routinely to give more precise composition in a broader range and also to forecast the near future compositions of fluids (Huang *et al.*, 2012). Also since the inception of fingerprinting, the evolving rates of gas chromatography techniques have risen with respect to their effectiveness ranging from traditional methods to the novel methods. And, due to the safer, faster and less costly method of this technique, its importance and application has greatly increased. However, it's quite necessary to note that the combined GC techniques yield better result than when used individually.

Crude oil or petroleum is a naturally occurring mixture, consisting pre-dominantly of hydrocarbons (alkanes (paraffins), alkenes (olefins), and aromatics) with other elements such as Sulphur, Nitrogen, and Oxygen etc. appearing in the form of organic compounds which in some cases form complexes with metals. The mixture of crude oil is highly complex, and the complexity increases with boiling range. The instrumental techniques of chromatography, ultraviolet and infra-red spectroscopy together with mass spectrometry facilitate knowledge of the detailed hydrocarbon type composition, concentrations and molecular species of crude oil. For this reason, the approach of fingerprinting requires analytical data of high precision and accuracy. It is therefore not surprising that the advancement of geochemical fingerprinting occurred along side progress in analysis techniques. For real world

applications of GF, in which large sample through put, reasonable cost, and fast turnaround are key requirements, combined geochemical techniques are employed, in this study, Gas Chromatography-Flame Ionization Detector (GC-FID) and Radial plots.

Application of GC-FID, being a relatively new technology as highlighted above may come with a few technical constraints. Surface variability of crude oil, contaminations from chemicals or effects of multiphase systems may introduce some limitation to this technique. It is important for all operators of GC technique to understand the limitations of this technology. Experimental errors introduce further in accuracies in the level of components analyzed. GC fingerprints are largely a qualitative practice and is dependent on the skills and experience of the people involved in the analysis.

## 2.0 Materials and Methods

The methods employed in this study will be based on identification of crude oil properties by GC-FID and radar plots, and the analytical method will be based on the physical and chemical properties.

Gas Chromatographic (GC) technique was used for the analysis of the oil samples. This was done using the Hewlett Packard 6890 GC equipped with a 50m x 0.25mm x 0.5µm film thickness PONA (Cross-linked Methyl Siloxane Capillary Column). A flame ionization detector (FID) detects and separates the components. The carrier gas was helium flowing at a rate of 40ml/s and the oven was programmed from 35°C to 320°C at 3.00°C/min. The initial and final temperatures were held for 5 min and 20 min respectively. The peak areas were electronically integrated and identification was based on retention times and comparison with authentic standards. The peak integration was achieved using the HP Chem Station software.



Fig 2.0: Hewlet-Packard – HP 6890 GC System

## 2.1 Steps and Procedures

1. Physiochemical Properties: Determination of the following physical and chemical properties of crude oil samples following well established procedures which are specific gravities, API, flash points etc.

2. Fractional Distillation: Distillation of each sample of the different crude oils. The fractions obtained are analyzed by GC-FID to obtain the chromatograms which are then visually identified or differentiated by the use of specific peak ratios.

3. Hydrocarbon Fingerprinting: GC fingerprints are created by injecting a small portion of the sample into a gas chromatography. Once injected, the product is heated into a capillary column by a flow of an inert gas (helium). After injection, the

temperature of the column is raised. As the temperature rises, the compounds begin to move through the column. Generally the more volatile but lower boiling compounds start moving first. A Flame Ionization Detector (FID) connected to the end of the column detects the components of the products as they elute from the column. The time taken for individual components to travel through the column is dependent on the column characteristics, prevailing temperature, length of the column, and the character of the compound itself.

## 3.0 GC Results

Two (2) oil samples from MS-2 and CC-8 wells were analyzed for whole oil Finger Printing using GC-FID. The GC chromatograms represent the total Hydrocarbon makeup of the oil samples.

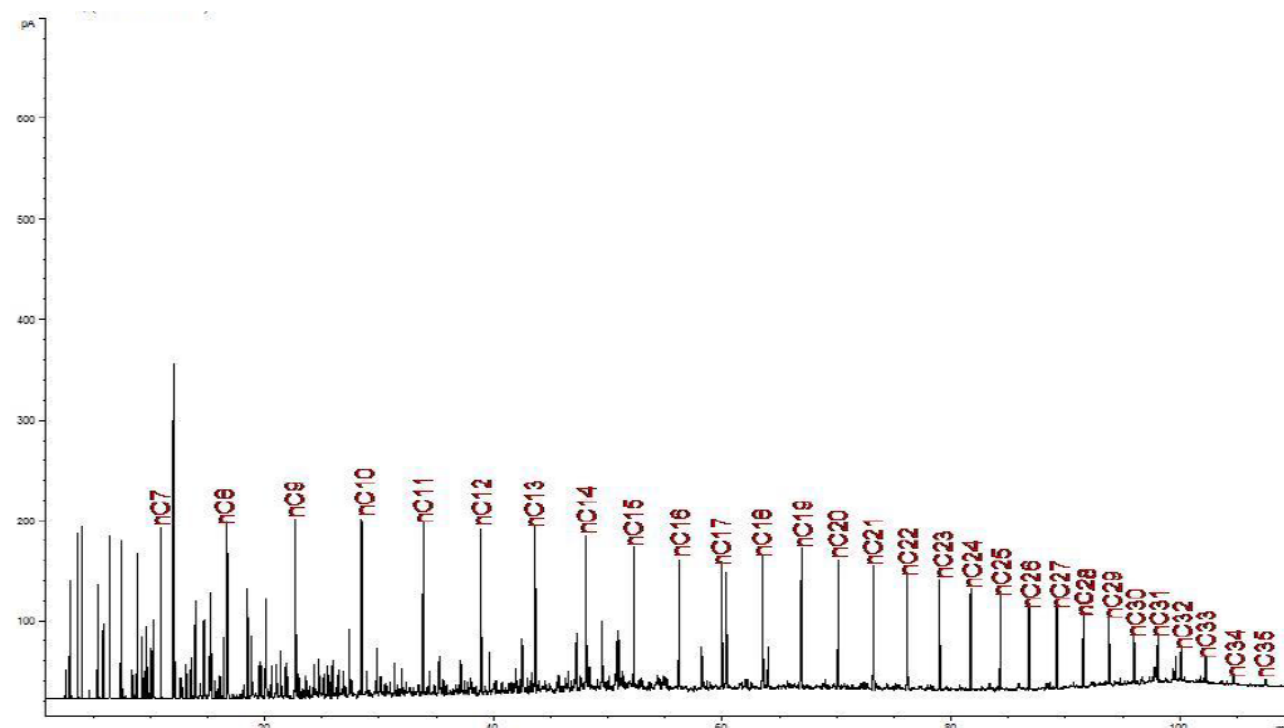
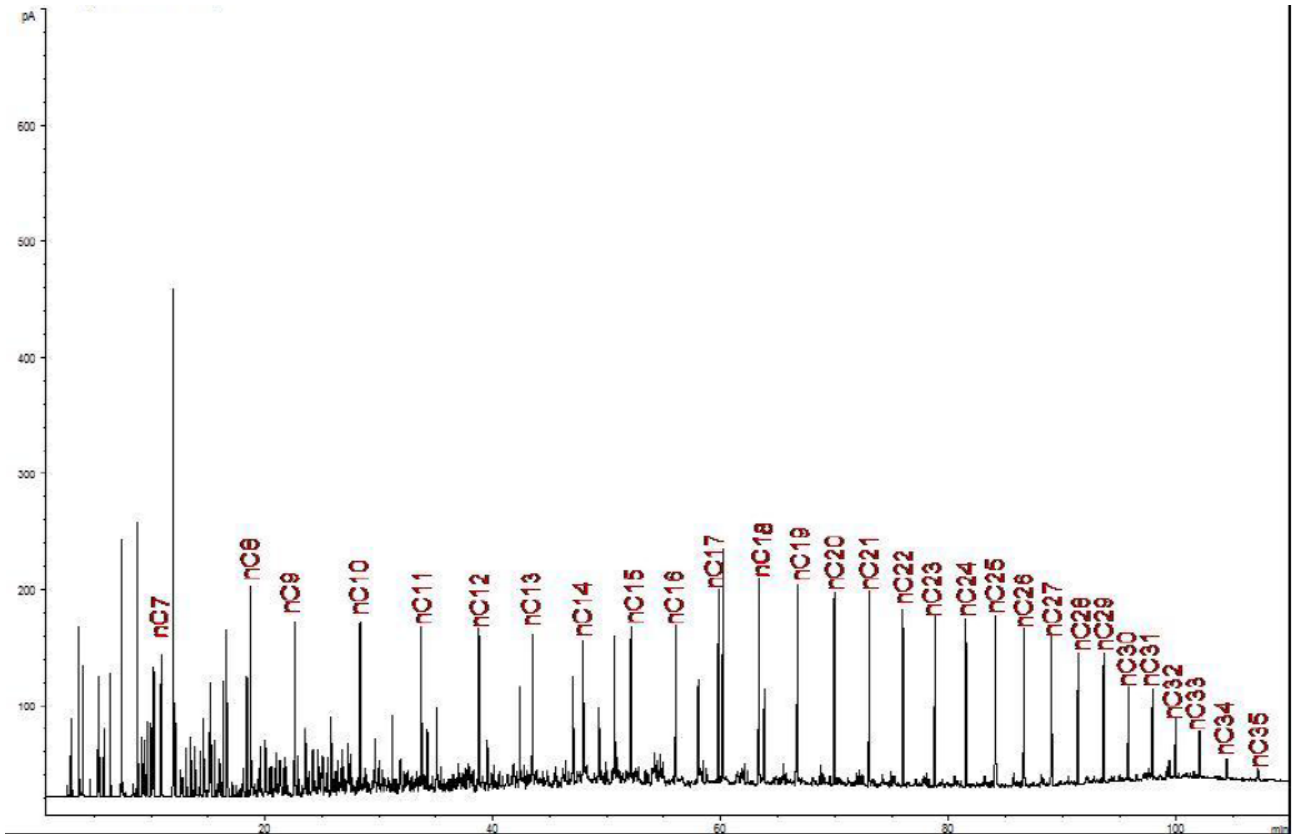


Fig. 3.1 CC-8 Crude Oil Chromatogram

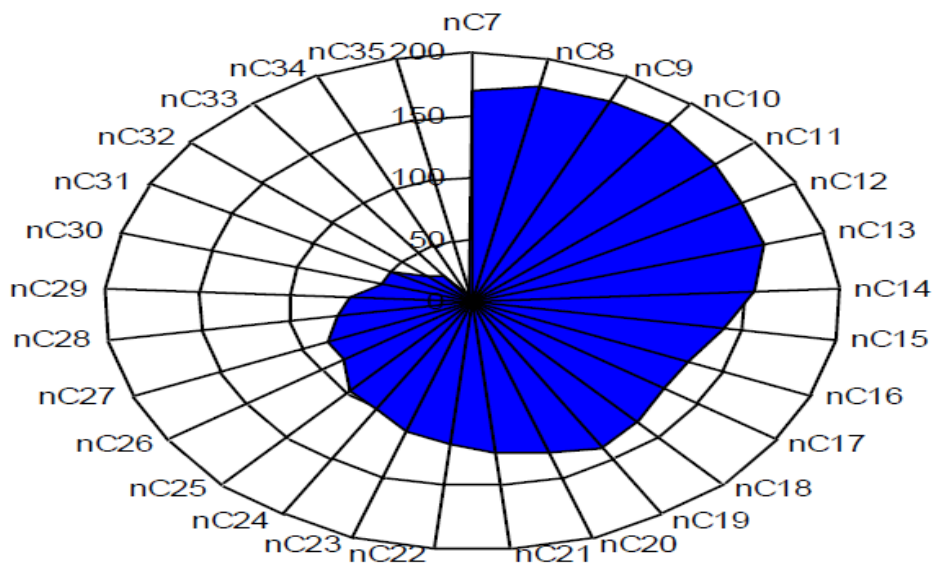


**Fig. 3.2 MS-2 Crude Oil Chromatogram**

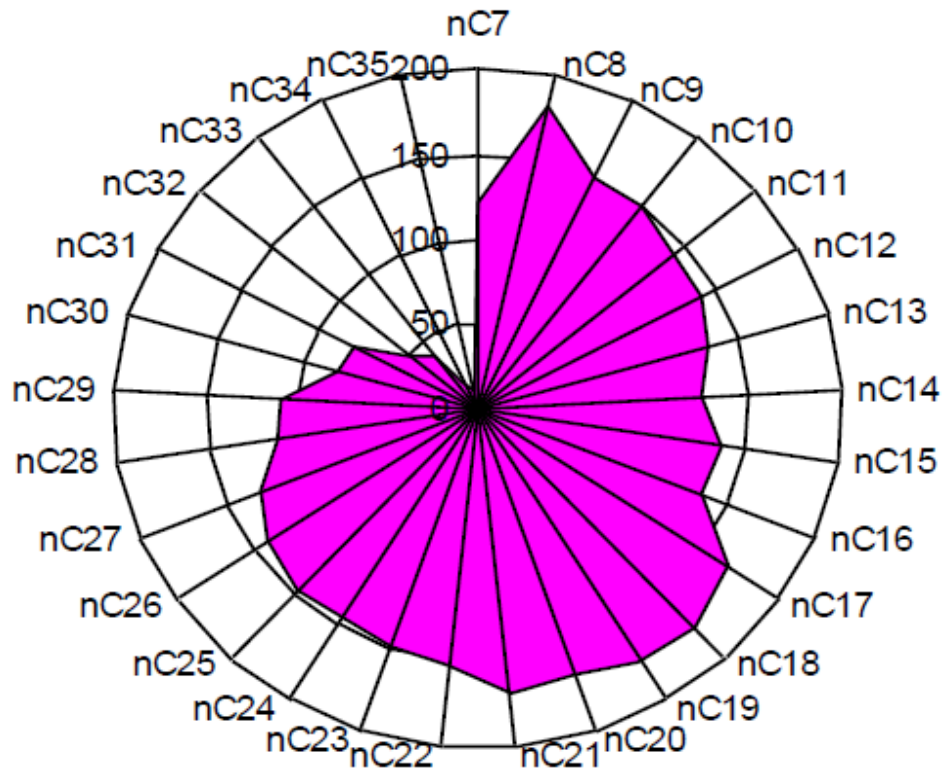
The analysis results above show that the crude oils from MS-2 and CC-8 wells contain field detectable hydrocarbons with chain length of 35 carbon atoms. Visual inspection of the

chromatograms (Fig. 3.1 & 3.2) shows that they have similar profiles, although their physical appearances were a bit different.

**3.1 Radar Plots**



**Fig 3.3 Radial Plot for MC-2 Crude Oil**



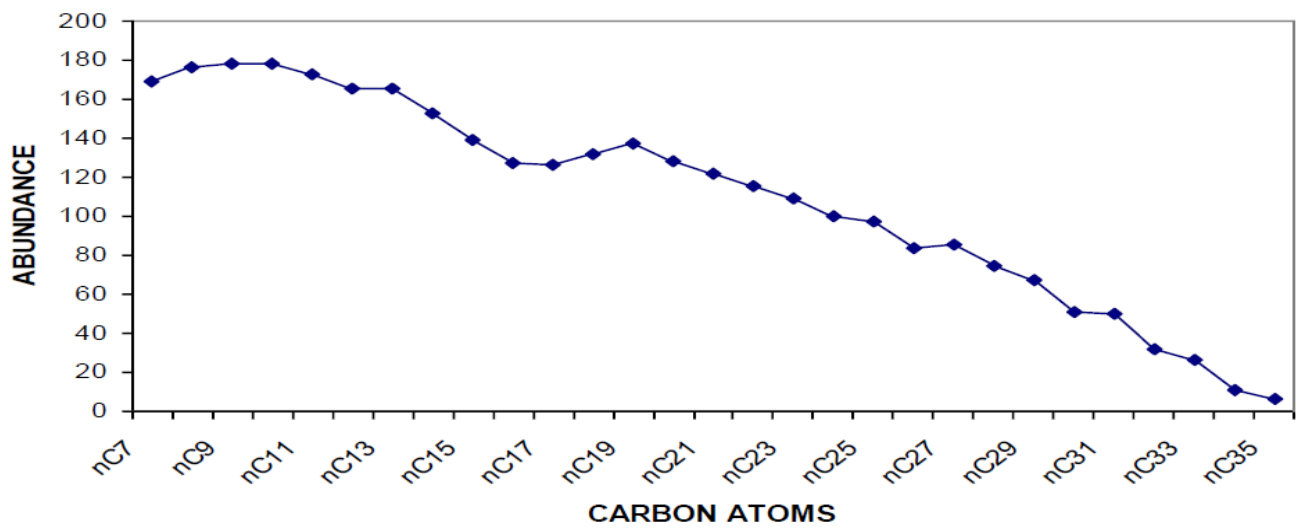
**Fig. 3.4: Radial Plot for CC-08 Crude Oil**

The radial plots of the Straight Chained Hydrocarbon Composition (SCHC) versus Abundance (Fig. 3.3 & 3.4) from oils from the wells show the following distribution

**Table 3.0: SCHC Distribution Table**

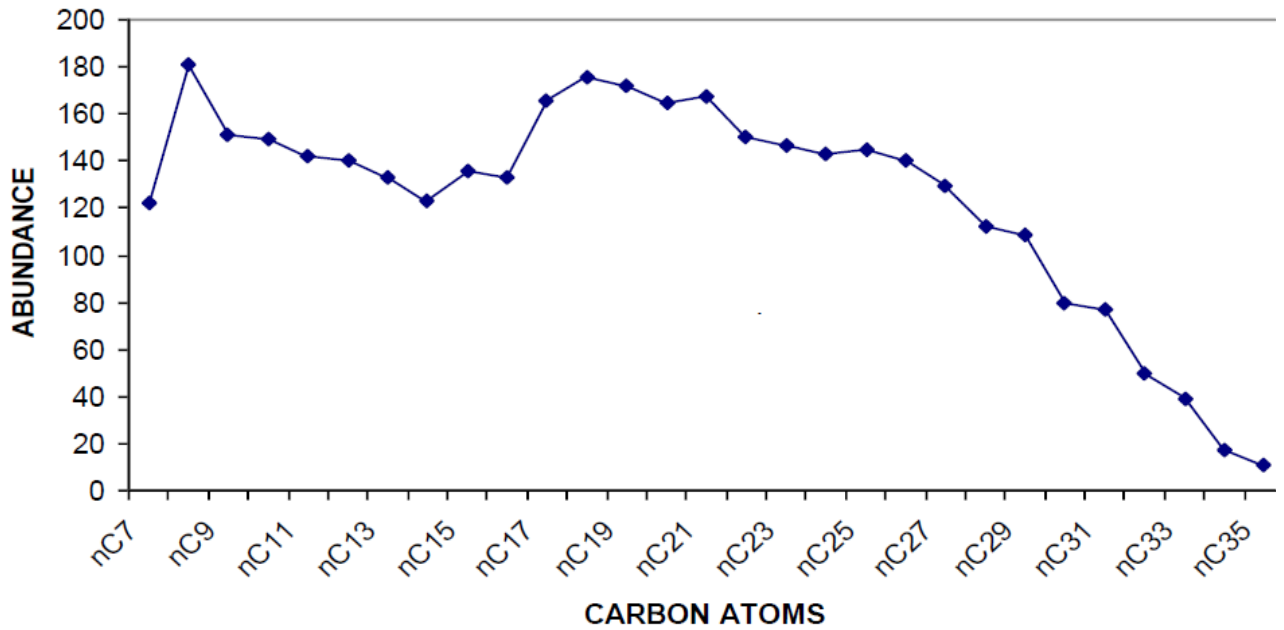
Wells	SCHC Distribution
CC-8	C7 and C35
MC-2	C7 and C35

### 3.2 Carbon Abundance



**Fig. 3.5: Plot of Carbon Atom versus Abundance for CC-8 Crude Oil**





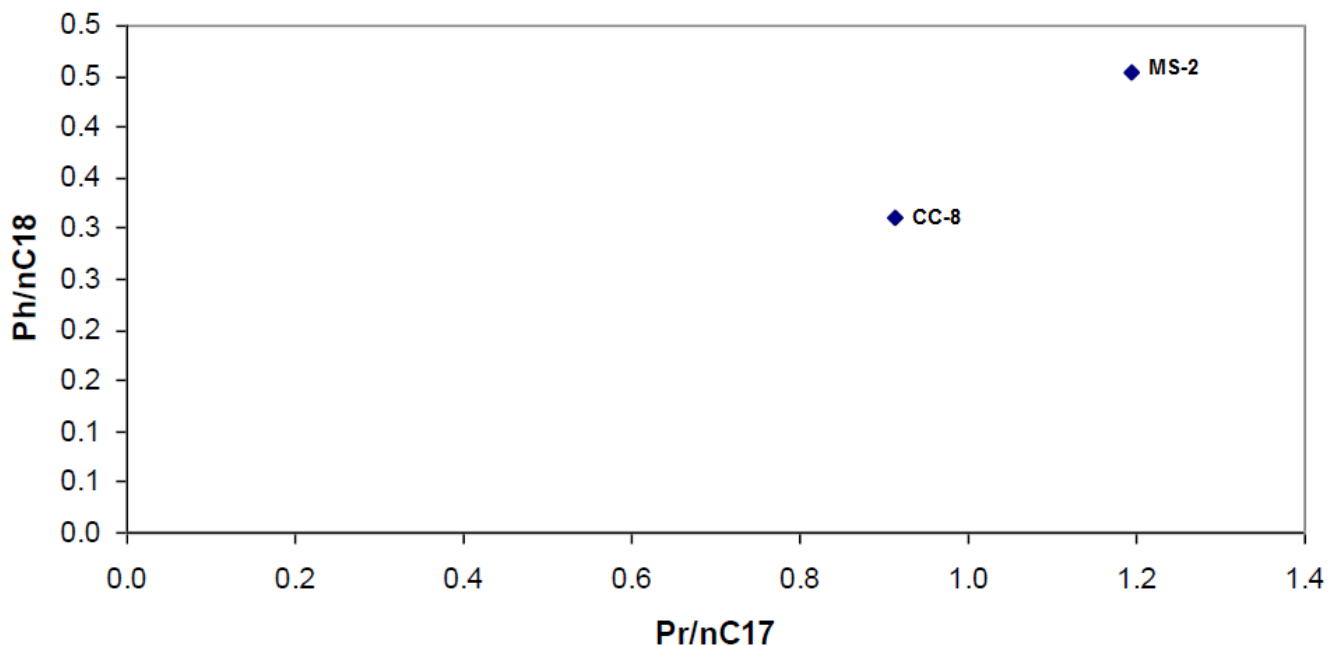
**Fig. 3.6: Plot of Carbon Atom versus Abundance for MS-2 Crude Oil**

The plots of the Carbon Atoms versus Abundance (Fig. 3.5 & 3.6) show oils from MS-2 & CC-8 wells have high abundance of the light ends (C7 to C15) than the heavy ends (C16 – C35).

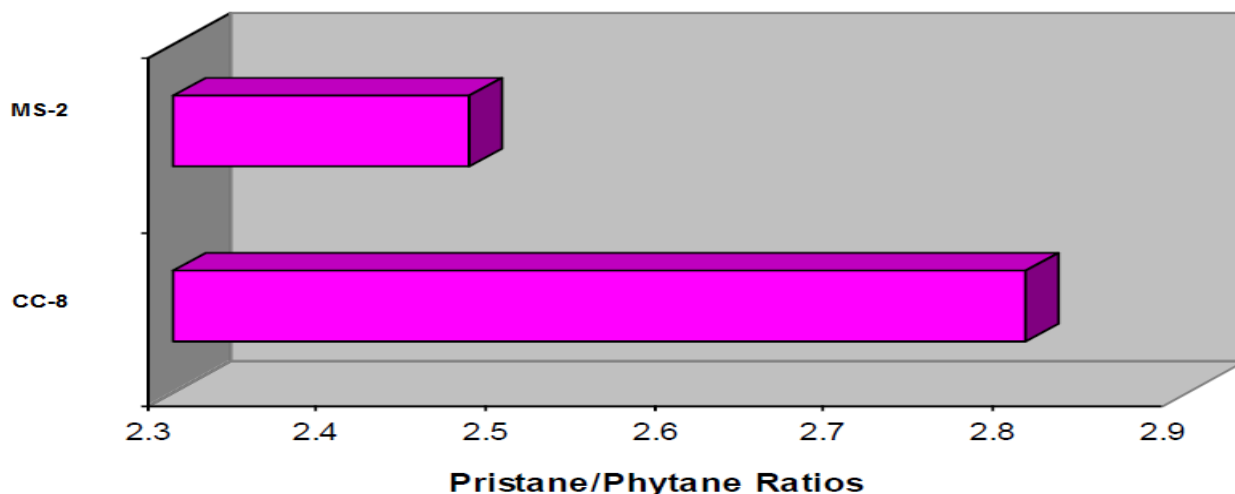
### 3.3 Pristane / Phytane Ratio

The pristane/phytane (Pr/Ph) ratio is one of the most commonly used correlation parameters

which have been used as an indicator of depositional environment. Accordingly, isoprenoids/n-alkanes (Pr/n-C17 and Ph/n-C18) ratios provide valuable information on biodegradation, maturation and diagenetic conditions.



**Fig. 3.7: Plot of Pr/nC17 versus Ph/nC18 ratios for CC-8 and MS-2**



**Fig. 3.8: Bar Chart Showing Pr/Ph Ratios for CC-8 and MS-2**

The cross plots of the Pr/nC17 versus Ph/nC18 and the Pr/Ph ratios for CC-8 & MS-2 are shown in Fig. 3.7 & 3.8. The plots confirm the observed profile of the chromatograms. Considering the crude oils from MS-2 & CC-8, the Pristane/Phytane (Pr/Ph) ratios of these oils ranged from 2.5 for MS-2 to 2.8 for CC-8. The average Pr/Ph is 2.7. The Pr/nC17 ranged from 0.9 for CC-8 to 1.2 for MS-2 and averaging 1.1. The Ph/nC18 ratio ranged from 0.3 for CC-8 to 0.5 for MS-2 with an average of 0.4.

**Table 3.1: API Gravity Data Table**

Wells	API Gravity
CC-8	30.2
MC-2	29.3

**4. Discussions of Results.**

The gas chromatography of the crude oil samples from both wells showed close similarities. They showed high concentrations of low molecular weight hydrocarbons. N-alkenes from n-C7 to n-C35 are seen in the chromatograms of both oil samples. However, the distribution pattern of Well CC-8 oil sample chromatograms is unimodal, while that of the Well MS-2 sample is a bimodal distribution (Fig. 3.6) indicating an input of mixed marine and terrestrial organic matter. Low molecular weight hydrocarbons (< n-C7) were not observed. This phenomenon could be as a result of evaporative loss while sampling.

In crude oil correlation, the ratios of Isoprenoids to n -paraffin are often used for oil source

correlation, maturation and biodegradation studies (Oforka, Osuji, & Onojake, 2012). Various ratios of isoprenoids to n-alkanes were computed such as the Pr/Ph; Pr/n-C17; Ph/n-C18; n-C25/n -C18; (Pr + C17)/ (Ph + C18). The crude oil samples have low Pr/Ph ratios which range from 2.5 to 2.8. Pr/Ph ratios were used to assess the depositional environment of the crude oils. The low Pr/Ph ratios suggest oils derived from source rock with a significant marine contribution. Plot of Pr/n-C17 versus ph/n-C18 can be used to classify oils and rock extracts into different groups. Source, maturation, migration and biodegradation are the major factors responsible for differences in crude oil composition. Values that are less than 1.0 serve as a sign for non-biodegraded oils. Both Pr/n-C17 and Ph/n-C18 decrease with maturation due to increasing prevalence of the n - paraffin (Oforka, Osuji, & Onojake, 2012). The values of Pr/ph, Pr/n-C17 and Ph/n-C18 for analyzed crude oils are given above. These samples have Ph/n- C18 less than one (<1.0) suggesting that they are non-biodegradable.

**5. Conclusion and Recommendation**

Petroleum hydrocarbon fingerprinting of crude oils from the two wells under study has provided an insight into source signature of the hydrocarbon materials under investigation. The molecular hydrocarbon composition of these crude oils revealed that the oils from Well MS-2 were formed in source rocks containing mixed kerogen (marine and terrestrial) deposited in an



oxicpaleoenvironment. This is a slight departure from the oil samples from Well CC-8 believed to be from a source rock with marine contribution, there by suggesting comingled production due to poor cement bond. The distribution of n - alkanes / isoprenoids and the low pr/ph ratios suggest that the oils were derived from source rock with a significant marine contribution, deposited in an oxicpaleoenvironment, while the Ph/n-C18 values less than one (<1.0) indicate that the samples were non biodegraded. n-alkanes are generated faster than isoprenoids in contrast to biodegradation. Accordingly, isoprenoids/n-alkanes (Pr/n-C17 and Ph/n-C18) ratios provide valuable information on diagenetic conditions, biodegradation and maturation. The very first effects of microbial degradation can be monitored by the ratios of biodegradable to the less degradable compounds. Isoprenoid hydrocarbons are generally more resistant to biodegradation than normal alkanes. Providing a rough indication to the relative state of biodegradation is the ratio of the pristane to its neighboring n-alkane C17. Thus as weathering continues, this ratio ultimately decreases. Reservoir geochemistry has already established itself as an extremely useful tool in the reservoir engineering domain. Although, the GC-FID technique being used in this research runs on a low cost, low maintenance requirement, relatively resistant to misuse, and can measure concentrations at very high and low levels, it is only limited to the basic hydrocarbon information and degree of weathering, can't detect inorganic substances and oxidizes all compounds that pass through it. Other detection methods can therefore be employed for better identification. Such detection techniques may include gas chromatography mass spectrometry (GC-MS), or Electrospray Ionization Mass Spectrometry (ESI-MS) etc.

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