OBAFEMI AWOLOWO UNIVERSITY

THERMAL MATURITY ASSESSMENT AND CHARACTERIZATION OF CRUDE OILS FROM EXXONMOBIL JOINT VENTURE AREA IN THE EASTERN NIGER DELTA, NIGERIA.

BY

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CERTIFICATION

This is to certify that OMOTOYE Sunday Joseph executed this research work in partial fulfillment of the requirements for the award of Master of Science Degree in Applied Geology, Geology Department, Faculty of Science, Obafemi Awolowo University, Ile-Ife, Nigeria.

……………………. …………………………

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DEDICATION

This research work is dedicated to the Almighty God, for His love, mercy and grace for the successful completion of this program and to my Late father Pa. M.O. Omotoye.

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ABSTRACT

Seventeen crude oil samples from producing Oil Wells in the Eastern Niger Delta were analyzed for their thermal maturity status. This was with a view to establishing maturity trends across the area and identifying maturity parameters that could reliably be used for maturity assessment of the area. Open Column Liquid Chromatography (OCLC) was used to separate the crude oil samples into saturate, aromatic and Nitrogen, Sulphur and Oxygen (NSO) compounds using n-hexane, methylene chloride and mixture of methanol and methylene chloride solvents respectively. The whole oil analysis with no prior preparation of the crude oil was done using gas chromatography (GC) with internal standard and helium (He) as carrier gas. Gas chromatography mass spectrophotometry (GC/MS) was used to evaluate compounds from saturate hydrocarbon such as tricyclic terpanes, pentacyclic terpanes, steranes and diasteranes. Also from the aromatic hydrocarbon, napthalenes, phenanthrenes and dibenzothiophenes as well as mono- and triaromatic steroids compounds were identified. Identification of each compound class was carried out using respective m/z values of 170, 191, 212, 217, 220, 231 and 253.

The value of pristine/phytane (Pr/Ph) ratio ranged from 2.3-5.1. Carbon Preference Index (CPI) value ranged from 1.03 to 1.09 with an average of 1.06. The average CPI value of 1.06 indicated that the oils were thermally mature. The values of $20S/(20S+20R)C_{27}$ and $\beta\beta/(\beta\beta+\alpha\alpha)C_{29}$, ranged from

0.23-0.47 and 0.20-0.24 respectively, while Tm/Ts ratio in the crude oil samples ranged from 1.33 to 2.23. Triaromatic-TA(I)/TA(I+II) ratio ranged from 0.03-0.20, while monoaromatic-MA(I)/MA(I+II) ratio ranged from 0.1-0.3. The value of methyl phenanthrene index- 3 (MPI-3) ranged between 0.9-1.0.The results showed that Sterane and hopane based maturity parameters were unreliable for oil maturity assessment.

The study concluded that the maturity of crude oils was found to increase from east to west in the study area. It also established new thermal maturity parameters for the correlation of oil samples.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Petroleum Geochemistry is an established science concerned with the utilization of chemical principles to the study of the formation, migration, accumulation and the alteration of petroleum and the application of this understanding in the exploration and recovery of oil and gas. Basically, petroleum geochemistry has its useful modern applications in exploration and production of "conventional" hydrocarbons and also supports the development of "unconventional" resources like shale gas. In petroleum exploration, petroleum geochemistry has been found to be an indispensable tool both at the initial and advanced stage in identifying source rocks and classifying crude oils into families (Ekweozor *et al*., 1979, Doust and Omotsola, 1990). Petroleum is generally considered oil and natural gases having various compounds, composed primarily of hydrogen and carbon. They are usually generated from the decomposition and/or thermal maturation of organic matter.

A biological marker, or biomarker, is a molecule synthesized by a plant or animal and unchanged, or having suffered only minor subsequent changes, with preservation of the carbon skeleton (Tissot and Welte, 1978). The biomarker is therefore representing a fingerprint of the geochemical input and the pH/Eh conditions of the paleodepositional environments that resulted in organic matter becoming incorporated into the sediment. Petroleum contains a small amount (1% and less) of biomarkers. The biomarkers can inform about the genetic relationship between petroleum, the quantity of petroleum expelled and the quality and maturity of the source rock from which the petroleum originated (Tissot and Welte, 1978).

From the point of view of exploration studies, crude oil thermal maturation may be considered as one of the most important geochemical effects. Maturation processes involve cracking, isomerization and aromatization reactions, as well as alkylation and dealkylation of aromatic rings. They commence in the source rocks; continue during migration and in the reservoir rocks. During a long geological time, they have been affected by heat, pressure and mineral catalysts, which resulted in the formation of thermodynamically more stable structural and stereochemical isomers or smaller molecules, as well as in transformation of saturated into aromatic hydrocarbons. The degree of maturity is most often estimated on the basis of parameters calculated from the distribution and abundance of saturated and aromatic hydrocarbons i.e., compounds which generally constitute 95−98 % of crude oils.

Isomerization processes at chiral centers or in rings were used in maturity estimation more often compared to cracking reactions, aromatization or alkylation–dealkylation processes.

1.1 PETROLEUM ORIGIN AND GENERATION

Petroleum is defined as a complex mixture of hydrocarbons derived from degradation of organic matter buried in sedimentary rocks. The organic matter in sediments was derived from the remains of extant organisms including algae, bacteria and higher plants. Sedimentary rocks are formed by accumulation, compaction, cementation and lithification of sediments. The potential petroleum source rocks are fine-grained sedimentary rocks rich in organic matter and have been empirically correlated with shales having >0.5% total organic carbon (TOC) content (Philippi, 1965). The transformation process of organic matter into petroleum (oil and gas) is divided into three main stages called process of maturation and includes; diagenesis, catagenesis, and metagenesis.

Diagenesis of organic matter refers to biologically, chemically, and physically induced changes in the organic matter composition that occur in the subsurface in sedimentary rocks at an equivalent vitrinite reflectance of 0.5% (Hunt, 1996; Peters *et al.*, 2005). Actually, these changes begin before organic matter reaches the sediments as organic matter sinking through the water column is fed upon by both the macrofauna and (aerobic) bacteria. Indeed, a significant proportion of the organic matter reaching the sediment does so in form of residues of the living organisms and/or higher plants. Decomposition occurs once the organic matter reaches the sediment surface. Burial by subsequently accumulating sediment eventually isolates it from water. Where the burial of organic matter is high enough, oxygen is eventually consumed