OBAFEMI AWOLOWO UNIVERSITY

CHARACTERIZATION OF THE PARAFFINIC HYDROCARBON FRACTION OF NIGERIAN BITUMEN USING MULTIVARIATE ANALYTICAL TECHNIQUES

BY

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CERTIFICATION

This research work carried out by Akhigbe, Godswill Ehimengbale has been read and approved as meeting part of the requirements for the award of M.Sc. Degree in Chemistry offered in the Department of Chemistry, Faculty of Science, Obafemi Awolowo University, Ile-Ife, Nigeria.

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DEDICATION

This work is dedicated to the Almighty God, who is the Author of Creativity, Science and Technology, my all in all and my Source; for His favour, mercy, grace and hand upon my life.Also to my parents Mr. and Mrs. S.O. Akhigbe for their love.

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ABSTRACT

Analyses of organics, metals and physical properties of the paraffinic hydrocarbon fraction of Nigerian bitumen were carried out with the view to establishing the characteristics which will aid the exploitation and exploration of this natural resource.

Bitumen samples were extracted from the oil sands obtained from Southwestern Nigeria using toluene and then deasphalted using *n*-pentane, while paraffinic hydrocarbons were eluted by column chromatography using *n*-hexane as eluents. The organic components of the paraffinic hydrocarbon fraction were investigated using Fourier transform infrared (FT-IR) spectrometry and Gas chromatography. The metal concentrations were determined usingAtomic absorption spectrophotometer. The physical properties (flash point, carbon residue, refractive index and colour) were determined using standard methods.

The results revealed that paraffinic hydrocarbons in the bitumen had a mean value percentage of 35.128 ± 2.729. The Infrared spectra of the paraffinic hydrocarbon fraction showed mainly the presence of C-H (CH_3) and C-H (CH_2) functional groups, indicating high purity of the saturate fraction. Thirty-one different organic compounds which were mainly saturates of high molecular weight (> C9) were identified and quantified by Gas Chromatograph. Pentadecane had the highest concentration with a mean value of 3369.744 ± 1375.669 mg/l, while undecane had the least concentration (7.541 ± 4.057 mg/l). The concentration of total organics was highest in B2 (26747.448 mg/l), while B1 (13121.459 mg/l) was the least. The paraffinic fraction had a mean carbon preference index (CPI) value of 1.035, indicating high maturity of the fossil fuel. The principal component analysis using the organic concentrations as variable showed close clustering, and correlation with close eigen values, indicating that the paraffinic hydrocarbon compounds had similar chemical properties, common sources, and/or maturation age. This study revealed that Mn had the highest mean concentration (4.746 ± 1.096 mg/l), while Co (0.394 ± 0.859 mg/l) had the least. The concentrations of Mn, Cu, Co, Zn, Fe, V, Cr and Ni in the paraffinic hydrocarbon fraction were generally low compared to other fractions of Nigerian bitumen. The *t*-test values for the metal concentrations indicated no significant difference (except Mn) for all the bitumen fractions, while concentrations of the metals in the paraffinic fraction and Nigerian crude oil showed significant difference except Mn, Cr and Fe. The cluster analysis of the metals showed two groups which are fairly well correlated indicating similar sources and/or chemical affinity. It was observed that V/Ni ratio of the paraffinic hydrocarbon fraction was 0.10 – 1.88 (1.12 ± 0.685), indicating that Nigerian bitumen matures with the age of the producing field. The V/Ni ratio of the paraffinic fraction was close to that of Nigerian bitumen 0.45 – 2.28 (1.12) which was higher than the average value (0.16) obtained for Nigerian crude oil. The V/(V+Ni) ratio 0.09 – 0.65 (0.50 ± 0.226) obtained in this study is also similar to 0.31 – 070 (0.50) obtained for Nigerian bitumen. The colour of the paraffinic hydrocarbon fraction ranged from colourless to off-white.

This study concluded that the paraffinic hydrocarbon fraction of Nigerian bitumen was a useful source of petrochemicals, refineries feedstock and fuel.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Until recent years; conventional, light crude oil has been abundantly available and has easily met world demand as a source of energy. However, due to increase in the demand of crude oil worldwide,there is continues depletion of this natural resource, and decrease in the supply of the fossil fuel. This has led to consideration of alternative or insufficiently utilized energy sources, among which natural bitumen is perhaps the most readily available to supplement short-term and long-term needs. Exploitation of bitumen as a source of refinery feedstock has been long ago, because of its low quality relative to conventional crude oil and the cost of refining; its price is usually lower than that of conventional crude oil.

Natural bitumen is the remains of very large volume of conventional oil that has been generated and subsequently biodegraded.It is a highly viscous oil that may be immobile in the reservoir. Chemically and texturally, it resembles the residuum produced by refinery distillation of light oil (Attanasiand Meyer, 2007). Its constitutes are important energy resource that must be thoroughly treated in order to convert it to an upgraded crude oil (refinery feedstock) before it can be used in refineries to produce gasoline and other fuels.

Oil sands are naturally occurring mixtures of sand or clay, water and a heavy and viscous form of crude oil called bitumen (Adebayo and Kazim, 2011).Strausz*et al.* (2010) described bitumen as the heaviest form of petroleum which is viscous, black and sticky. It is a complex mixture of high boiling point range

of hydrocarbon compounds and molecules withrelatively low hydrogen to carbon ratio (Yoon *et al.,*2009).

World oil reserves are estimated at 1.292 trillion barrels, in which the Organization of Petroleum Exporting Countries (OPEC) accounts for 70%. According to the Energy Information Administration (EIA), the Middle East accounts for 58 % of world oil reserves, which also lead in reserve growth and undiscovered potential (Enu, 1985; 1990). Oil sand deposits are found in many countries throughout the world, but are found in extremely large quantities in Canada and Venezuela. In African, substantial amounts oil sand has been found to exist in the Democratic Republic of Congo and Nigeria (Adegoke*et al.,* 1980; Adebiyi *et al.,* 2005).

The economy of Nigeriais highly dependent on the petroleum industry, it accounts for about 90% of the country's foreign exchange earnings, about 20 per cent of the Gross Domestic Product (GDP), and about 85% of the Federal Government Collectable Revenue (Adedimila, 2000). Oil sand deposit of Southwestern Nigeria is believed to be one of the largest in the world (Adegoke, 2000) and it has been estimated to be the second largest in place deposit, it occurs over a 120 km by 6 km belt which stretches from Okitipupa ridge/western edge of Niger delta to as far west of Ijebu-ode in Ogun state (Ekweozor and Nwachukwu, 1989). The Nigerian bitumen belt lies on the onshore areas of Eastern Dahomey (Benin) Basin. The probable reserve of bitumen and heavy oil in the entire Nigerian belt is about of 30 – 40 billion barrels of bitumen. The exploitation and exploration of the Nigerian natural bitumen deposits can best be described to be at the planning stage(Adegoke and Ibe, 1982; Oboh*et al.,* 2006).

Nigerian oil sands are known to flow naturally, to the surface in form of an outcrop during hot season,in lots of places in the oil sand belt, mostly in Ondo and Ogun states. The government of Nigeria is now

working towards the production of synthetic crude from the sands especially now that the price of oil is high and oil sand exploitation is very profitable (Adebayo and Kazim, 2011).

Bitumen contains low concentration of low molecular weight hydrocarbons and abundance of high molecular weight polymeric materials.This makes bitumen distinctive from its conventional oil counterpart (Ritcey and Ashbrook, 1984). The Nigerian bitumen possesses relatively large quantity of the high molecular weight hydrocarbons (naphthenes, aromatics and asphaltenes) that are similar in composition to conventional oil. The chemical composition that is, hydrogen, carbon, and small amount of nitrogen, sulphur, oxygen, and trace metals, of bitumen is similar to that of light crude oil (Akinmosin, Osinowo and Oladunjoye, 2009). This makes the Nigerian bitumen a very useful alternative source of petroleum hydrocarbons and a potential feedstock for petrochemical industries (Adegoke*et al.,* 1991).

Trace metals form a very important part of the non-hydrocarbon component of Bitumen. They are described as metals occurring at 1000mg/kg (or 1000 mg/L) or less in the environmental matrix. Bitumen consist of both the heavy (density > 5g/cm^3) and light (density < 5g/cm^3) trace metals, and these include Cd, Cr, Cu, Fe, Hg, Ni, V, Pb, As, Zn, Co, Mn, Pt, Ag, Au etc. They are introduced into bitumen through many processes such as the biodegradation of natural organometallic plant metabolites; for example, chlorophyll and morphins, and water washing of light crude. Nigerian bitumen is believed to have formed in a similar process. A number of these metals are essential at low concentrations but become deleterious at high concentrations, hence they are of great economic importance (Adebiyi,Thoss,andAkinola, 2014).

The composition of bitumen and other heavy fractions has been the subject of several investigations over the years. According to Oyekunle, 2006, the chemical composition of the various grades of bitumen gives information of their physical properties. The method of production greatly influences its structure and the chemical composition of bitumen