

## ANALYSIS OF HYDROCARBONS RELEASED THROUGH HYDROPYROLYSIS OF ASPHALTENES OBTAINED FROM SOIL SAMPLE IN ERHIEMU, NIGERIA.

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### ABSTRACT

Erhiemu soil sample was collected and extracted, asphaltenes were then precipitated from the extracts. The asphaltenes were subjected to hydropyrolysis to determine the percentage yield of hydrocarbon from asphaltene matrix. Open column chromatography was performed on asphaltene hydropyrolysate which gave a percentage recovery of 71%. This suggests that the process is a veritable tool for the release of bound hydrocarbons in asphaltene matrix.

**Keywords:** Soil, Asphaltenes, Hydrocarbons, Hydropyrolysis

### INTRODUCTION

Hydrocarbons are organic compounds made up of hydrogen and carbon atoms. Hydrocarbons has been categorized in different forms , some of which are saturated hydrocarbons these are single chained carbon atoms C-C ; unsaturated hydrocarbons these are double or triple chained carbon atoms C=C or C≡C; aliphatic hydrocarbons which are straight chained or

cyclic hydrocarbons without the benzene structure in the compounds; aromatic hydrocarbons these are hydrocarbons with the benzene structure, these compounds, particularly polycyclic aromatic hydrocarbons can find their way into the environment through various processes. One of such processes is by biomass combustion. Biomass burning or combustion has been reported to account for 14% of the

worldwide energy supply, 1 to 3% in industrialized countries and as high as 43% in developing countries (Bhatia, Mittal, Mehrotra and Mehrotra, 1989). The major constituents of biomass include cellulose, hemi-cellulose and lignin. Biomass utilization has been employed in various industrial applications such as biomass gasification (Palonen, Lundqvist, and Stahl, 1995), the production of hydrocarbon fuels (Bhatia et al., 1989), and its liquefaction or co-liquefaction with other materials (Lalvani et al., 1991; Akash, Muchmore, and Lalvani, 1994). The quantity of heat emitted from biomass combustion varies between species, climate, dryness of wood, etc. however approximately 20 megajoules of energy is produced per dry kilogram of biomass. Residential wood combustion alone was reported to account for over 30% of anthropogenic PAH emission in Eastern North America (U.S. EPA 1994). Nielson et al., (1992) also noted that PAH emission levels depended on the quality of

wood burned. Domestic burning of scrap wood and wood briquettes caused a much higher emissions than virgin wood burned. This emissions can ultimately find their way in to soil. Hydrocarbons are a widespread class of contaminants in recent environmental studies, this is due to the multiplicity of their sources (McElroy, Farrington and Teal, 1989; Mazeas, Budzinski, and Raymond, 2002). Various pyrolysis techniques have been employed in the quantitative and qualitative study of hydrocarbons both in the geosphere and the environment, amongst these is hydro pyrolysis of asphaltenes (Murray, 2001). To be able to generate representative hydrocarbon/ biomarker profiles, which are more useful for geochemical and environmental correlations, then a high proportion of the bound hydrocarbons/ biomarkers must be assessed under reaction conditions to minimize the extent of secondary product transformations. Asphaltene (molecular substances found in

crude oil, along with resins, aromatic hydrocarbons, and saturates.) hydropyrolysis has been found formidable in providing reliable data for correlation and environmental studies (Murray, 2001; Ivwurie, Emelife, Snape, and Sun, 2015 ).

Pyrolysis, at high hydrogen pressures (ie. above 10 mPa) has been developed as an analytical pyrolysis technique that possesses the exclusive ability to release high yields of bound hydrocarbons/ biomarkers from petroleum source rocks (Love, McAulay, Snape and Bishop, 1997; Love, Snape, Carr and Houghton, 1995). Hydropyrolysis of asphaltenes isolated from severely biodegraded oil seeps have shown that the sequestered biomarker/hydrocarbon structures are exceptionally well preserved against microbial alteration and their interpretable hydrocarbon/ biomarker profiles can be generated (Murray, Snape, Love and Bailey, 1999; Ivwurie et al., 2015).

This study is aimed at testing hydropyrolysis of asphaltenes, to ascertain the yield of hydrocarbon from asphaltene hydropyrolysis of soil sample collected from Erhiemu in Delta State, Nigeria.

### **MATERIALS AND METHODS**

The soil sample was collected from Erhiemu in Delta State, Nigeria. The soil was dried at a temperature of 105°C for 3 to 4 hours and then ground to pass through a 60-mesh sieve.

The sample was extracted by soxhlet extraction and refluxing techniques using redistilled dichloromethane (DCM) and dichloromethane-methanol (93:7) mixture. The weight of soil sample extracted was altered to obtain sufficient amounts for hydrocarbon analysis. 100 g of soil to 250 ml of solvent mixture was used for each extraction. When refluxing and Soxhlet extraction were completed, the slurries were filtered to obtain the extract solution. The extract of each sample was concentrated using rotary evaporator at 30°C for

DCM solutions and 45 °C for DCM/methanol mixtures. The extract was concentrated and dried using a stream of N<sub>2</sub>. Asphaltenes were prepared from this extract and dissolved in a minimum volume of dichloromethane. A 40-fold excess of n-heptane was added and the suspension stirred for 20-30 minutes. The suspension was transferred to a centrifuge tube and spun for 5 minutes at 2500 rpm. The n-heptane supernatant (containing dissolved maltene) was removed with a pipette. The asphaltenes were redissolved in a minimum volume of dichloromethane and the precipitation process repeated three more times (making four precipitations in total). The asphaltenes, being the precipitate remaining in the centrifuge tube was dissolved in DCM and kept in a clean vial. The combined n-heptane washings were rotary evaporated to remove solvent and yield maltenes. This process is carried out at the lowest temperature possible to avoid volatile losses (Jones, Douglas, and Connan, 1988).

This procedure has been used widely in the laboratory.

The asphaltenes were mixed with silica in the ratio of 50 mg of asphaltene to 1 g of silica. The mixture was then impregnated with an aqueous methanol solution (20 %v/v) of ammonium

dioxydithiomolybdate catalyst to give a nominal solution of 3-wt %. The catalyst was prepared by slow addition of ammonium heptamolybdate to ammonium sulphide solution. The heptamolybdate salt was then dissolved using a magnetic stirrer and solution stirred until a precipitate of ammonium dioxydithiomolybdate is formed. The precipitate was collected with the aid of a Buchner funnel and dried in a vacuum oven. A schematic diagram of the hydropyrolysis rig is given in figure 1. The sample was then dried in a vacuum oven at 60-70°C after which it was placed in a reactor tube. When attached to the hydropyrolysis set-up, it was resistively heated from ambient temperature (50 °C) to 250°C at 300°C min<sup>-1</sup>, then to 500°C at 8° min<sup>-1</sup> maintaining a

hydrogen pressure of 15 mPa and a flow rate of 10 dm<sup>3</sup>min<sup>-1</sup>. The liquid product was then collected in a trap cooled with dry ice and recovered with dichloromethane (2-5 ml) for subsequent separation (Murray, 2001; Meredith et al., 2004, Ivwurie et al., 2015).

The hydropyrolysate was separated by open column chromatography. About 15-20 g of the activated silica gel was packed into an open column (about 0.5 cm i.d.) with a glass-wool plug at the bottom. The hydropyrolysate was then

carefully transferred onto the top of the column and compacted. Elution of each fraction was performed using 50ml of n-hexane to elute the aliphatics, 30ml of Hexane: 30ml dichloromethane(1:1v/v) for the aromatics, and 30ml dichloromethane:30ml methanol(1:1v/v) for the polar fraction respectively(Sun, 2001,Ivwurie et al, 2015). All solutions obtained were then evaporated to dryness using a stream of nitrogen at temperatures below 30°C to give the different fractions.

## RESULTS AND DISCUSSION

Mass balances are summarized in Table 1 for the Erhiemu Soil sample .

**Table 1: Mass Balances for the Analysis of Erhiemu Soil Sample**

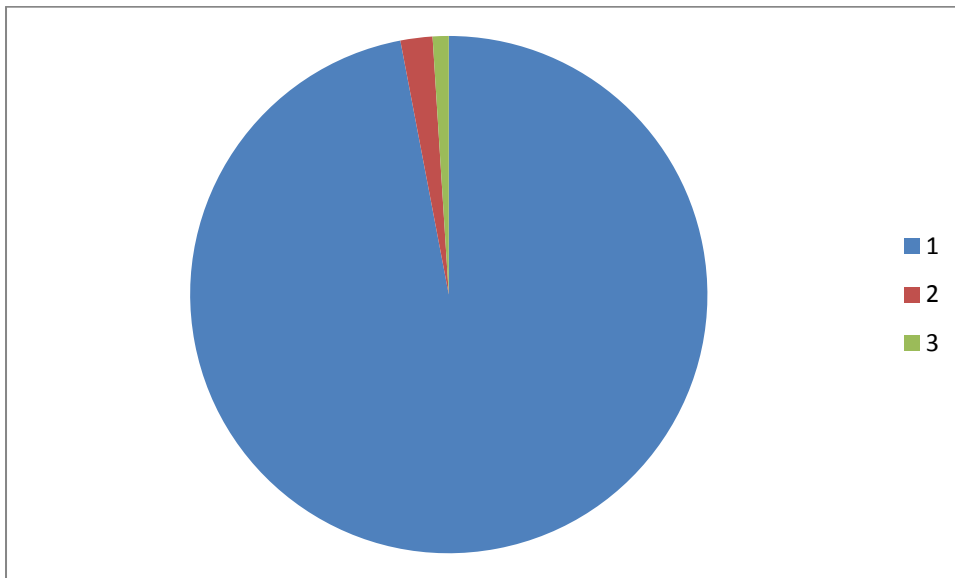
Name of sample	Weight of Asphaltenepyrolysed (g)	% Asphaltene content	Weight of Aliphatics (g)	Weight of Aromatics (g)	Weight of Polar	% Recovery for hypy of asphaltenes
Erhiemu Soil sample	0.0140	2.0	0.0097	0.0002	0.0001	71

From table 1, 2.0% of asphaltenes were precipitated from the Erhiemu soil sample investigated.

0.0140g of the asphaltenes precipitated was then subjected to hydropyrolysis, followed by Open column chromatographic separation of

the hydropyrolysis product. The separation gave 0.0097g of aliphatics, 0.0002g of aromatics and 0.0001g of polar fractions released from

asphaltene matrix respectively. The percentage recovery of hydrocarbons from asphaltene hydropyrolysis was found to be 71%.



**Figure 1: Pie Chart Presentation of Weight of Aliphatics (1); Aromatics (2); and Polar (3)**

The Pie Chart presentation in Figure 1 indicates that the quantity yield of Aliphatics is higher than the Aromatics and the Polar. This could be due to the effect of crude oil pollution in the soil which is aliphatic based. (Ivwurie et al., 2015)

This high percentage recovery indicates that hydropyrolysis of asphaltene is a veritable tool for the release of hydrocarbons which were bound in asphaltene matrix of soil extract. (Love et al., 1995, 1997, Meredith, 2004, Ivwurie et al., 2015)

### CONCLUSION

In conclusion, percentage recovery of hydrocarbons

released through hydropyrolysis of asphaltenes precipitated from Erhiemu soil

was found to be 71 %, this high percentage recovery indicates that this pyrolysis tool is

credible in the recovery of hydrocarbons that are bound in asphaltene matrix.

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