ANALYSIS OF HYDROCARBONS RELEASED THROUGH HYDROPYROLYSIS OF ASPHALTENES OBTAINED FROM COAL TAR PITCH.

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ABSTRACT

Soil samples collected in South Wales was extracted and asphaltenes were precipitated from the extract. The asphaltenes were then subjected to hydropyrolysis to determine the percentage yield of hydrocarbon from asphaltene matrix. Open column chromatography was performed on asphaltenehydropyrolysate gave a percentage recovery of 92 %, suggesting that this process is a veritable tool for the release of bound hydrocarbons in asphaltene matrix. The mass balance for hydrocarbon distribution is consistent with literature

Keywords: Soil, Asphaltenes, Hydrocarbons, Hydropyrolysis

INTRODUCTION

There are a large number of hydrocarbons, and amongst these, some are more environmentally and biologically significant than others. Of utmost significance are the polycyclic aromatic hydrocarbons(PAHs). The U.S. Environmental Protection Agency (U.S.EPA 1994) has outlined 16 parent PAHs as a frame of reference, based on their significance. In terms of physical properties, PAHs exhibit characteristics governed by their□π-electron systems via fused benzene rings, giving rise to a significant level of chemical stability (Lee *et al.*, 1981). PAHs have boiling points higher than those of n-alkanes or alkenes, with the same carbon number. Most PAHs are solids at ambient temperature and have very low volatility. In addition, PAHs are highly characterized by low hydrophilicity and high lipophilicity. As a result of these features, when they are released into the environment, they exist as aerosols in the atmosphere, or in combined form with other particulate matter in sedimentary environments (Chadwick *et al.*, 1987, Homann, 1994, Sun, 2001). On the other hand, the chemical properties of PAHs are related to their molecular structure. The atmospheric stability of different PAH varies significantly depending on their molecular structure, light intensity, the nature of particles that they are associated with, and the presence of other pollutants such as

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SOx, O_3 and NOx. Another interesting observation about PAHs was reported by Howsam *et al* (2001) in studying the dynamics of PAH depositions, cycling and storage in a mixed deciduous (Quercus-Fraxinus) woodland ecosystem. They observed that the relative importance of storage and loss processes was closely related to the physico-chemical properties of the PAHs. Different pyrolytic techniques has been employed in the quantitative and qualitative study of hydrocarbons both in the geosphere and the environment, one of these is hydropyrolysis of asphaltenes (Murray, 2001). To release representative hydrocarbon/ biomarker profiles, which are more useful for geochemical and environmental studies, it is important that a high proportion of the bound hydrocarbons/ biomarkers must be assessed under reaction conditions to minimize changes in the chemistry of products formed. Asphaltene hydropyrolysis has been found reliable in providing credible data for correlation and environmental studies (Murray, 2001, Ivwurie, Emelife, Snape, and Sun, 2015). Pyrolysis, at high hydrogen pressures (>10 mPa) has been put up as an analytical pyrolysis technique that show cases 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 obtained (Murray et al., 1999, Ivwurie et al., 2015). In this research paper, hydropyrolysis of asphaltenes has been employed, to ascertain the yield of hydrocarbon from asphaltene hydropyrolysis of coal tar pitch.

MATERIALS AND METHODS

The asphaltenes prepared from coal tar pitch 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-1, then to 500°C at 8° min-1 maintaining a hydrogen pressure of 15 mPa and a flow rate of 10 dm^3min-1. 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 product from hydropyrolysis 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 30oC to give the different fractions.

RESULTS AND DISCUSSION

Mass balances are summarized in Table 1 for the coal tar pitch sample.

Table 1: Mass balances for the analysis of coal tar pitch

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
Coal tar pitch	0.2000	3.3	0.0129	0.0608	0.1103	92

From table 1, 3.3% of asphaltenes were precipitated from coal tar pitch sample.

0.2000g of the asphaltenes precipitated was then subjected to hydropyrolysis, followed by Open column chromatographic separation of the hydropyrolysis product. The separation gave 0.0129g of aliphatics, 0.0608g of aromatics and 0.1103g of polar fractions released from asphaltene matrix respectively. The percentage recovery of hydrocarbons from asphaltene hydropyrolysis was found to be 92%.

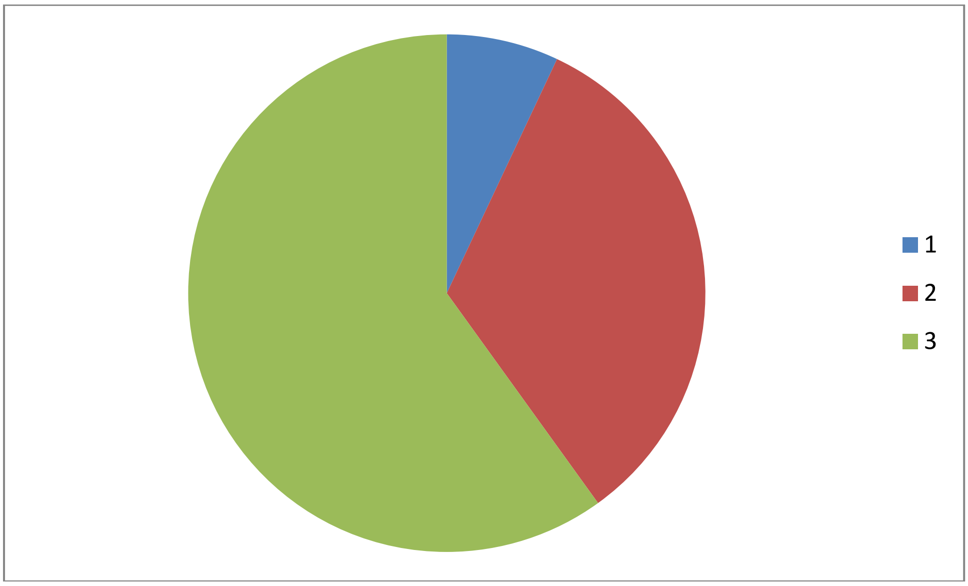

Figure 1: **Pie Chat Presentation of weight of Aliphatics (1); Aromatics (2); and Polar (3) from coal tar pitch**

From the pie chat in figure 1, it implies that the sample contains more aromatic and polar compounds than aliphatic This is consistent with literature given that the sample is a product of coal carbonization (Sun, 2001).

This high percentage recovery indicates that hydropyrolysis of asphaltene is a reliable tool for the release of hydrocarbons which were bound in asphaltene matrix of the coal tar pitch. (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 coal tar pitch was found to be 92 %, 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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