
ANALYSIS OF HYDROCARBONS RELEASED THROUGH HYDROLYSIS OF ASPHALTENES OBTAINED FROM NORTH SEA CRUDE OIL.

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***Abstract:** Asphaltenes precipitated from the North Sea crude oil were subjected to hydrolysis to determine the percentage yield of hydrocarbon from asphaltene matrix. Open column chromatography which was performed on asphaltene hydrolysate gave a percentage recovery of 70 %, suggesting that this process is a veritable tool for the release of hydrocarbons trapped in asphaltene matrix.*

Keywords: Asphaltenes, Hydrocarbons, Hydrolysis

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INTRODUCTION

Hydrocarbons are generally found in the environment due to the multiplicity of their sources (McElroy, Farrington and Teal, 1989; Mazeas, Budzinski, and Raymond, 2002). These hydrocarbons can be biogenic by origin (that is synthesized by living organisms), diagenic, (that is produced during the degradation of the organic matter), pyrolytic (that is formed during incomplete organic matter combustion) and are

introduced in the modern environment via natural and anthropogenic release of fossil fuel combustibles (petrogenic origin) (Mazeas *et al.*, 2002). The combustion of coal, petroleum, wood by various industries in their routine operations has been reported to be the predominant stationary contributor of PAH emissions, while transportation, gives rise to mobile sources of PAHs. When hydrocarbons, particularly polycyclic aromatic hydrocarbons

come in contact with biological entities in particular and the environment in general, it carries negative consequences, given that they are genotoxic (have harmful effect on genes), and they could find their way into the atmosphere as aerosols or other forms in soil, water, or come directly in contact with man, other animals as well as plants. Jones, Douglas, and Connan (1988) reported a steady increase in the polycyclic aromatic hydrocarbon content of an agricultural soil over the last century. In their study in which all the soil analyzed were collected from the plough layer (0–23 cm) of an experimental plot for which atmospheric deposition will have been the only source of PAH input, the total PAH burden of the plough layer has increased approximately 4-fold since the 1880/1890s, with some compounds notably benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(e)pyrene, pyrene, benzo(a)anthracene, and indeno(1,2,3-cd)pyrene showing substantial greater increases. In

order to effectively characterise hydrocarbons, different pyrolysis techniques has been employed in the quantitative and qualitative study, both in the geosphere and the environment, amongst these is hydropyrolysis of asphaltenes (Murray, 2001). To be able to obtain representative hydrocarbon/biomarker profiles, which are more useful for geochemical and environmental correlations studies, then a high proportion of the bound hydrocarbons/ biomarkers must be assessed under reaction conditions to minimize the extent of secondary product transformations. Asphaltene 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 (>10 mPa) has been developed as an analytical pyrolysis technique that carries the exclusive ability to release high yields of bound hydrocarbons/ biomarkers from petroleum source rocks (Love et al., 1995,1997). 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 et al., 1999, Ivwurie et al., 2015). In this research paper, hydropyrolysis of asphaltenes is being tested, to ascertain the yield of hydrocarbon from asphaltene hydropyrolysis of soil sample collected from North Sea crude Oil.

MATERIALS AND METHODS

The asphaltenes prepared from the North Sea crude oil 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 dioxodithiomolybdate 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 dioxodithiomolybdate 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 10dm³min⁻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 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). 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 North Sea crude oil.

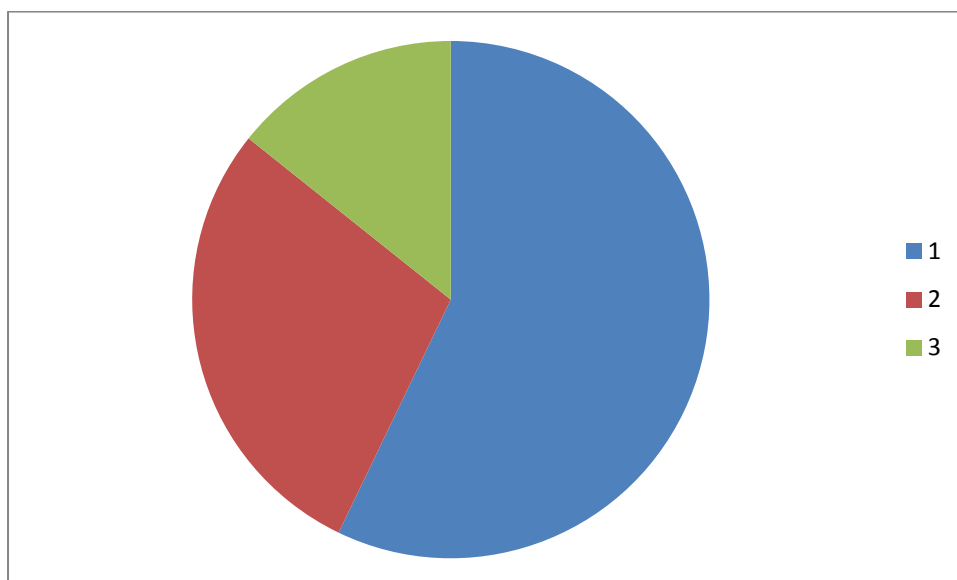
Table 1: Mass balances for the analysis of North Sea crude oil.

Name of sample	Weight of Asphaltene pyrolysed (g)	% Asphaltene content	Weight of Aliphatics (g)	Weight of Aromatics (g)	Weight of Polar	% Recovery for huppy of asphaltenes
North Sea crude oil sample	0.0100	1.0	0.0040	0.0020	0.0010	70

From table 1, 1.0% of asphaltenes were precipitated from the North Sea Crude oil sample investigated.

0.0100g of the asphaltenes precipitated was then subjected to hydropyrolysis, followed by Open column chromatographic separation of the hydropyrolysis

product. The separation gave 0.0040g of aliphatics, 0.0020g of aromatics and 0.0010g of polar fractions released from asphaltene matrix respectively. The percentage recovery of hydrocarbons from asphaltene hydropyrolysis was found to be 70%.



Pie Chart Presentation of weight of Aliphatics (1); Aromatics (2); and Polar (3)

The above pie chart shows that sample contains more of Aliphatics than Aromatics and Polars, indicating that the North Sea crude oil is aliphatic based.

This high percentage recovery indicates that hydrolysis of asphaltene is a veritable tool for the release of hydrocarbons which were bound in asphaltene matrix. (Love, McAulay, Snape and Bishop, 1997; Love, Snape, Carr and Houghton, 1995, Meredith et al., 2004; Ivwurie et al., 2015).

CONCLUSION

In conclusion, percentage recovery of hydrocarbons released through hydrolysis of asphaltenes

precipitated from North Sea crude oil was found to be 70 %, 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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