

ANALYSIS OF HYDROCARBONS RELEASED THROUGH HYDROPYROLYSIS OF ASPHALTENES OBTAINED FROM HIGH TEMPERATURE COAL TAR

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ABSTRACT

The asphaltenes prepared from high temperature coal tar were subjected to hydrolysis to determine the percentage yield of hydrocarbon from asphaltene matrix. Open column chromatography performed on asphaltene hydrolysis gave a percentage recovery of 90 %, suggesting that this process is an effective tool for the release of bound hydrocarbons in asphaltene matrix.

Keywords: Asphaltenes, coal tar, Hydrolysis

INTRODUCTION

The high concentration of hydrocarbons, particularly polycyclic aromatic hydrocarbons (PAHs) in the environment suggests the extent of anthropogenic contribution (Ohkouchi, Kawamura, and Kawahata, 1999). The enhanced distribution of anthropogenic PAHs due to various terrestrial and atmospheric pathways, has been reported even in such most remote areas as the Arctic and Antarctic, deep sea beds in central Pacific and high altitude mountains and lakes (Novotny, Strand, and Smith, 1981; Fernandez, Vilanova, and Grimalt, 1999). It is difficult to estimate the amount of PAHs and the yearly input on a global basis. However, on the basis of annual consumption of fossil fuels, an approximate quantification has been made that the annual global release of PAHs to the atmosphere is approximately an order of 10^5 tonnes, including 10^3 tonnes of benzo (a) pyrene, and that the annual input of crude and processed oil containing 1-3% PAHs to the oceans of the world is 1.1×10^6 tonnes (Kirton, Ellis, and Crisp, 1991). For example, in the UK,

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it was reported that over 53,000 tonnes of some 12 of the 16 PAHs listed by the U.S. EPA are estimated to be present in the contemporary environment, with soil being the major repository (Kirton, *et al.* 1991). PAH emissions into the U.K. atmosphere from primary combustion sources are estimated to be greater than 1000 tonnes per annum, approx. 210 tonnes of which finds its way to terrestrial surfaces through atmospheric dry or wet deposition. The United States Environmental Protection Agency as well as the European Community has regarded polycyclic aromatic hydrocarbons as priority pollutants. For example, the UK government's Expert Panel on Air quality Standards (EPAQS), proposed a U.K. air quality standards for benzo(a)pyrene of 0.25 ng/m³, air limit being extremely stringent given the diverse sources of PAH emissions (Dimashki, Lee, Harrison, and Harrad (2001). The widespread distribution of these compounds could also be associated with common volatility properties, pointing to atmospheric transport as the main distribution pathway in the environment (McVeety and Hites, 1988). In the mid-latitude of the northern hemisphere, PAHs are mainly derived from fossil fuel combustion in various industrial and domestic facilities, power generation, wood burning and petrol and diesel exhausts. In contrast, PAHs from biomass burning occur predominantly in the lower latitudes. Another source of PAHs is coal carbonization (Sun, 2001)).

Diverse techniques have been employed to study the fate of hydrocarbons in the environment. Amongst them is the pyrolysis techniques. Although various pyrolysis techniques exist, hydropyrolysis has been found to be very reliable in the studies of hydrocarbons. (Murray, 2001, Ivwurie, Emelife, Snape, and Sun, 2015). This is because, to be able to generate representative hydrocarbon/ biomarker profiles, which are more useful for geochemical and environmental correlations, it is important that 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 in this regard (Murray, 2001, Ivwurie et al., 2015). It is pyrolysis, at high hydrogen pressures (>10 mPa) that possesses 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 high temperature coal tar.

MATERIALS AND METHODS

The asphaltenes precipitated from coal tar obtained through high temperature carbonization process 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 dm³min⁻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

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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 high temperature carbonization coal tar.

Table 1: Mass balances for the analysis of hydrocarbon from hydropyrolysis of High temperature coal tar

Name of sample	Weight of Asphaltene pyrolysed (g)	% Asphaltene content	Weight of Aliphatics (g)	Weight of Aromatics (g)	Weight of Polar	% Recovery for hypy of asphaltenes
High temperature coal tar	0.1310	3.8	0.0121	0.0107	0.0943	90

From table 1, 3.8% of asphaltenes were precipitated from high temperature coal tar.

0.1310g of the asphaltenes precipitated was then subjected to hydropyrolysis, followed by Open column chromatographic separation of the hydropyrolysis product. The separation gave 0.0121g of aliphatics, 0.0107g of aromatics and 0.0943g of polar fractions released from asphaltene matrix respectively. The percentage recovery of hydrocarbons from asphaltene hydropyrolysis was found to be 90%.

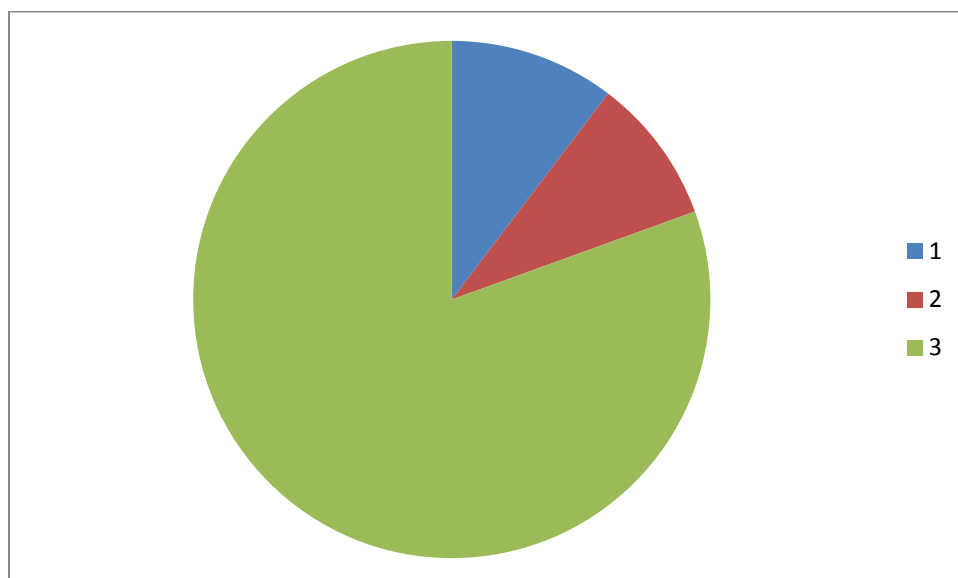


Figure 1: Pie Chart Presentation of weight of Aliphatics (1); Aromatics (2); and Polar (3) from hydropyrolysis of high temperature coal tar

The pie chart in figure 1 shows that the sample contains more of aromatic and Polar compounds than aliphatics. This is generally the trend for coal derived products (Sun, 2001). This high percentage recovery indicates that hydropyrolysis of asphaltene is a credible instrument for the release of hydrocarbons which were bound in asphaltene matrix. (Love, McAulay, Snape and Bishop, 1997; Love, Snape, Carr and Houghton, 1995; Meredith, 2000; Ivwurie et al., 2015)

CONCLUSION

In conclusion, percentage recovery of hydrocarbons released through hydropyrolysis of asphaltenes precipitated from high temperature carbonization coal tar sample was found to be 90 %, 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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