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

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Abstract: The asphaltenes prepared from low temperature carbonization coal tar were subjected to hydrolysis to determine the percentage yield of hydrocarbon from this process. Open column chromatography carried out on the asphaltene hydrolysis gave a percentage recovery of 96 %, suggesting that this process is a veritable tool for the release of bound hydrocarbons in asphaltene matrix.

Keywords: Asphaltenes, Hydrocarbons, Hydrolysis

INTRODUCTION

Coal carbonization is the pyrolytic decomposition of coal in the absence of oxygen, and based on the purpose, it can be categorized as either low or high temperature process. When coal is carbonized, char or coke, tar, and oven gas are the major products. Coal tar is formed from the condensation of hot gases produced, giving rise to two distinguishable portions, a light fraction containing aliphatic and aromatic hydrocarbons, and other constituents containing heteroatoms such as sulphur, oxygen and nitrogen, and a heavy fraction containing asphaltene and polar compounds (Novotny, Strand, and Smith,1981). Coal carbonization process has become an operation of research interest for environmental scientists due to the enormous and diverse toxic liquid products and wastes streams generated in this process. Leakages from coke ovens generate high levels of PAHs and other toxic organics calling for environmental and occupational concern. Emissions from coke ovens are often characterized by compositions ranging from volatile monoaromatics (alkyl benzenes) to 5-6 ring PAHs and their substituted derivatives such as O-PAHs, N-PAHs and S-PAHs (Lao, Thomas, and Monkman, (1975); Andeson, Levin, and Nilson, (1983) ; Kirton, Ellis, and Crisp,1991). Four main products are produced by low temperature carbonization: the final semicoke, a tar consisting of a complex mixture of liquid hydrocarbons, fixed gases and aqueous liquor. A variety of low temperature carbonization ovens exist including the Phurnacite process, affixed bed vertical slot oven operated at temperatures of around 850°C; the Rexco process, whereby the ovens are heated internally by the heat from the products of

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combustion of part of the gas yield; and the Parker or Coalite process, a moving bed vertical retort oven with an operating temperature of between 600 and 700°C. However, the Coalite process will be discussed. The Parker retort for the production of domestic smokeless fuel, or Coalite, was an early development in British low temperature carbonization practice (Wilson and Clendenin, 1963). The first installation went into production in 1927 and a further plant was installed at Bolsover, near Chesterfield in 1936, which is in operation today. Carbonisation of the blended small coals takes place in vertically positioned retorts of approximately 300kg capacity assembled in batteries of 40 units. The retorts are manufactured from a specific grade of iron, cast as a single block to include twelve tubes 2.75m in length. Each retort has a cast-iron head fitted to the top to provide space for coals during the charging cycle and is fitted with a branch to transport gaseous products of carbonization to the hydraulic mains, which run along each side of the battery. The head is sealed from the atmosphere by a lid fitting into a water-filled trough cast into the upper periphery of the retort head. The hydraulic mains collect gases from all retorts and pass them to pipes leading to the gas treatment plant where they are cooled and condensed. The liquids are separated by decantation into coal oil and aqueous liquor. Uncondensed gases are fed through electrostatic precipitators, where light fresh oil is extracted before going to gasholder storage prior to recycling as a heat source for the next carbonizing cycle. The yields (wt %) of the four main products of Coalite low temperature carbonization process are; Char (semicoke) 74, tar plus liquid, 6, gas, 15 and water 5 (Van Krevelin, 1993). A number of pyrolysis techniques has been employed in the quantitative and qualitative study of hydrocarbons both in geochemical and environmental research, amongst these is hydro pyrolysis of asphaltenes (Murray, 2001). However, to generate representative hydrocarbon/biomarker profiles, which are more useful for geochemical and environmental correlations, it is expedient that a high proportion of the bound hydrocarbons/biomarkers be assessed under reaction conditions to minimize the extent of secondary product transformations. Asphaltene hydropyrolysis has been found credible in providing reliable data for correlation and environmental studies (Murray, 2001, Ivwurie, Emelife, Snape, and Sun, 2015).

This is pyrolysis, at high hydrogen pressures (>10 mPa), developed as an analytical pyrolysis technique that possesses the unique capacity to release high yields of bound hydrocarbons/biomarkers from petroleum source rocks and even environmental samples (Love, McAulay, Snape and Bishop, 1997; Love, Snape, Carr and Houghton, 1995; Ivwurie et al., 2015). 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, hydroxyrolysis of asphaltenes is being tested, to ascertain the yield of hydrocarbon from asphaltene hydroxyrolysis of coal tar derived from high temperature carbonization process.

MATERIALS AND METHODS

The asphaltenes prepared from coal tar obtained by low 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 dioxidythiomolybdate 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 dioxidythiomolybdate is formed. The precipitate was collected with the aid of a Buchner funnel and dried in a vacuum oven. A schematic diagram of the hydroxyrolysis 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 hydroxyrolysis 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).

The hydroxyrolystate 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 hydroxyrolystate 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 low 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 huppy of asphaltenes
LTCT2	0.1961	1.5	0.0598	0.0474	0.0800	96

Table 1: Mass Balances for the Analysis of Hydrocarbons from Hydroxyrolysis of Low Temperature Coal Tar

From table 1, 1.5% of asphaltenes were precipitated from the low temperature coal tar.

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0.01961g of the asphaltenes precipitated was then subjected to hydropyrolysis, followed by Open column chromatographic separation of the hydropyrolysis product. The separation gave 0.0598g of aliphatics, 0.0474g of aromatics and 0.0800g of polar fractions released from asphaltene matrix respectively. The percentage recovery of hydrocarbons from asphaltene hydropyrolysis was found to be 96%.

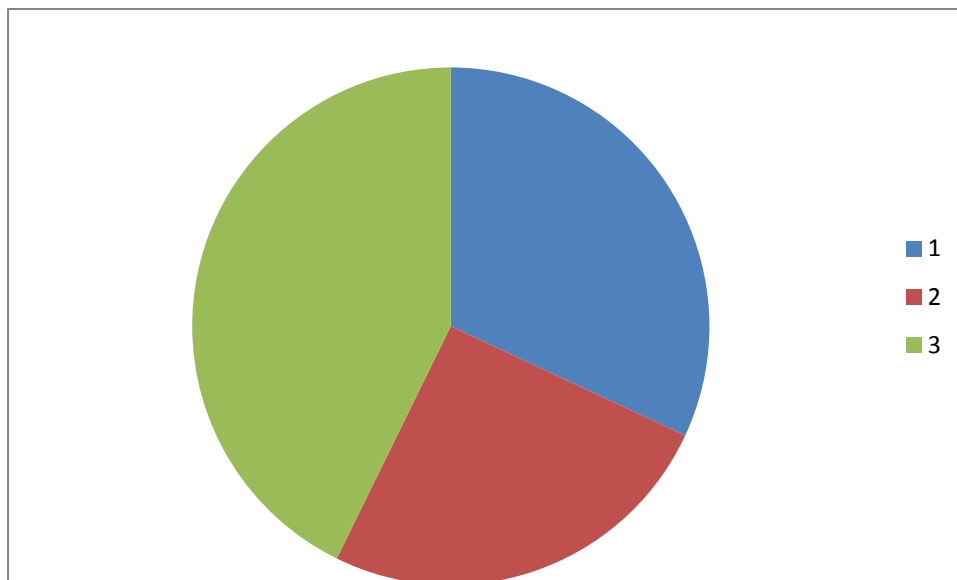


Figure 1: Pie Chart Presentation of weight of Aliphatics (1); Aromatics (2); and Polar (3) obtained from hydropyrolysis of low temperature coal tar

The Polar compounds were slightly higher than Aliphatics and Aromatics compounds. This could be due to the temperature of the carbonization process or other reactions arising from the process (Sun, 2001)

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

CONCLUSION

In conclusion, percentage recovery of hydrocarbons released through hydropyrolysis of asphaltenes precipitated from low temperature coal tar was found to be 96 %, 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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