

## ANALYSIS OF HYDROCARBONS RELEASED THROUGH HYDROLYSIS OF ASPHALTENES OBTAINED FROM SOUTH WALES SOIL SAMPLE

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### ABSTRACT

Soil samples collected in South Wales was extracted and asphaltene were precipitated from the extract. The asphaltene were then subjected to hydrolysis to determine the percentage yield of hydrocarbon from asphaltene matrix. Open column chromatography was performed on asphaltenehydrolysisate gave a percentage recovery of 91 %, 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, Asphaltene, Hydrocarbon, Hydrolysis

### INTRODUCTION

Hydrocarbon, particularly polycyclic aromatic hydrocarbon 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 et al., 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 et al., 1995), the production of hydrocarbon fuels (Bhatia et al., 1989), and its liquefaction or co-liquefaction with other materials (Lalvani et al., 1991; Akash et al., 1994). Residential wood combustion alone was reported to account for >30% of anthropogenic PAH

emission in Eastern North America (U.S. EPA 1994). To further elucidate this point, Nielson et al., (1992) 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 environments due to the multiplicity of their sources (McElroy et al., 1989; Mazeas et al., 2002). Various pyrolysis techniques has 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 hydropyrolysis has been found formidable in providing reliable data for correlation and environmental studies (Murray, 2001, Ivwurie et al, 2015).

Pyrolysis, at high hydrogen pressures ( $>10$  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 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 South Wales.

## MATERIALS AND METHODS

The soil sample was collected from a location near a high temperature carbonization process plant in South Wales. 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 mins 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 is carried out at as low a temperature as possible to avoid volatile losses (Jones et al, 1988). This procedure has been used widely within 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 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<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 10dm<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). 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 South Wales soil sample.

**Table 1. Mass balances for the analysis of South Wales soil**

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
South Wales soil sample	0.0300	1.8	0.0012	0.0152	0.0109	91

From table 1, 1.8% of asphaltenes were precipitated from the south Wales soil sample investigated. 0.0300g of the asphaltenes precipitated was then subjected to hydrolysis, followed by Open column chromatographic separation of the hydrolysis product. The separation gave 0.0012g of aliphatics, 0.0152g of aromatics and 0.0109g of polar fractions released from asphaltene matrix respectively. The percentage recovery of hydrocarbons from asphaltene hydrolysis was found to be 91%.

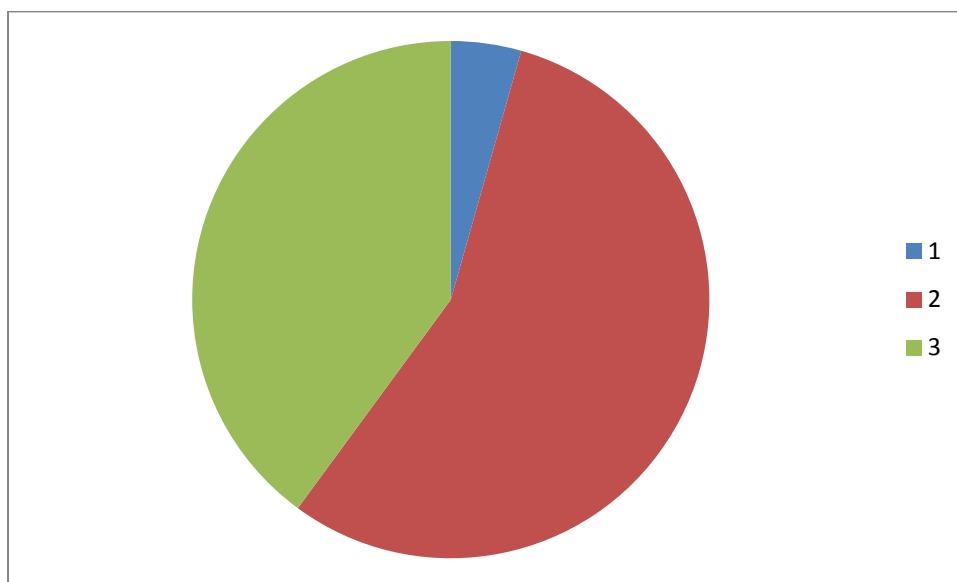


Figure 1: Pie Chart Presentation of weight of Aliphatics (1); Aromatics (2); and Polar (3) from hydrolysis of asphaltenes obtained from South Wales soil

The pie chart in figure 1 shows that the sample investigated is dominated by aromatic and polar organic hydrocarbon and heterocyclic compounds.

This high percentage recovery indicates that hydrolysis 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 hydrolysis of asphaltenes precipitated from South Wales soil 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.

## REFERENCES

- Akash, B.A., Muchmore, C.B., and Lalvani, S.B. (1994) Coliquefaction of coal and newsprint-derived lignin. *Fuel Processing Technology*. 37, 203–210.
- Bhatia, V.K., Mittal, K.G., Mehrotra, R.P. and Mehrotra, M. (1989) Hydrocarbon fuels from biomass. *Fuel*. 68, 475–479.
- Ivwurie, W., Emelife S.C., Snape, C.E. and Sun, C. (2015) Polycyclic aromatic hydrocarbons in free and asphaltene derived low temperature coal tar from the coalite plant near Chesterfield. *Journal of Medical and Applied Biosciences*, 7(2), 54–59.
- Jones, D.M., Douglas, A.G., and Connan, J. (1988) Hydrous pyrolysis of asphaltenes and polar fractions of biodegraded oils. In L. Matavelli and L. Novelli (eds). *Advances in Organic Geochemistry*. Pergamon Press, Oxford.
- Lalvani, S.B., Muchmore, C.B., Koropchak, J., Akash, B., Chivate, P. and Chavez, C. (1991) Lignin-augmented coal depolymerization under mild reaction conditions. *Energy and Fuels*. 5, 347–352.
- Love, G.D., Snape, C.E., Carr, A.D. and Houghton, R.C. (1995) Release of Covalently- bound alkane biomarkers in high yields from Kerogen via catalytic hydropyrolysis. *Organic Geochemistry*. 23, 981–986.
- Love, G.D., McAulay, A., Snape, C.E. and Bishop, A.N. (1997) Effects of Process variables in catalytic hydropyrolysis on the release of covalently bound aliphatics hydrocarbons from sedimentary organic matter. *Energy and Fuels*. 11, 522–531.

- Mazeas, L., Budzinski, H. and Raymond, N. (2002). Absence of stable carbon isotope fractionation of saturated and polycyclic aromatic hydrocarbons during aerobic bacterial biodegradation. *Organic Geochemistry*. 33, 1259-1272.
- McElroy, A. E., Farrington, J.W. and Teal, J. M., (1989) Bioavailability of PAH in the aquatic environment. In: Varanasi, U. (Ed.) *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*. CRC Press, Boca Raton, USA. pp 41-68.
- Meredith, W.; Russell, C.A., Cooper, M., Snape, C.E., Love, G.D., Fabbri, D. and Vane, C.H. (2004) Trapping hydropyrolysates on silica and their subsequent thermal desorption to facilitate rapid fingerprinting by GC-MS. *Organic Geochemistry*. 35, 73-89.
- Murray, I.P., Snape, C.E., Love, G.D. and Bailey, N.J.L (1999) Hydropyrolysis of Heavy Oils For Source Correlation Studies, Abst. For 19th Int. Meeting on Organic Geochemistry, Istanbul, 6-10 September 1999, Part 1, No. PB10. 341-342.
- Murray, I.P. (2001) Release of covalently bound biological marker molecules from sedimentary organic matter via catalytic hydropyrolysis. Unpublished PhD thesis, University of Strathclyde.
- Nielson, P.A., Grove, A. and Olsen, H. (1992) The emission of PAH and mutagenic activity from small wood stoves is greatly influenced by the quality of the wood. *Chemosphere*. 24, 1317-1330.
- Palonen, J., Lundqvist, R.G., and Stahl, K. (1995) IGCC technology and demonstration. In *Proceedings of Power Generation from Biomass II*. VTT, Espoo, Finland. pp 10-12.
- Sun, Cheng-gong. (2001) Sourcing PAH in the environment. Unpublished PhD thesis. University of Strathclyde.

U.S. EPA (1994) Deposition of Air Pollutants to the Great Lakes; 1st Report to Congress; EPA 453/R93-055.

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