

Polycyclic Aromatic Hydrocarbons in Free and Asphaltene Derived Low Temperature Coal Tar from the Coalite Plant Near Chesterfield

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ABSTRACT

Free and asphaltene derived samples of low temperature coal tar from the coalite plant near Chesterfield, England were analyzed for polycyclic aromatic hydrocarbons using GC-MS. The individual PAH concentrations ranged from 1mg/g-14 mg/g with a mean concentration of 78.35± 14.64 mg/g. The study showed a predominance of the low molecular weight PAHs for both free and asphaltene derived low temperature coal tar implying that the asphaltene derived can be used for correlation and source apportionment studies where the free has been altered.

INTRODUCTION

To compare extractable free hydrocarbons and bound hydrocarbons released from asphaltenes via hydrolysis, coal emission sources were investigated. The sample was supplied from the Coalite smokeless fuel plant near Chesterfield. The temperature range for the processing of this coal is 500-850 °C; the coal from this process generates smokeless fuels or semicoke due to the incomplete nature of carbonization. Crude low temperature coal tar is an extremely complex mixture of hydrocarbons, phenols, heterocyclic nitrogen, oxygen and sulphur compounds ranging from

simple substances of low molecular mass and boiling point, like alkyl benzenes and alkyl phenols, to highly complex materials with molecular masses in the thousands [1]. Within this mixture of organic compounds there is approximately 3-5 % water and a small amount of solid particulate matter. Low temperature coal tar is much less viscous than tar made from the same coal at higher temperatures. Its specific gravity is 1.02- 1.07, and owing to the low temperature at which it is formed, it is mainly paraffinic in character, whereas high temperature tar is almost wholly aromatic. Some of the use of the coal tar distillation products includes as fuel oil (used for

generating steam and heat, 20 % of tar, phenols and cresylics and high boiling tar acids (sold to manufacturers of phenol, formaldehyde resins, plasticisers, pharmaceuticals, wetting agents, inhibitors, disinfectants, antiseptics, insecticides), catechol and homologues, resorcinol and homologues (sold to manufacturers of antioxidants, inhibitors, photographic developers, azo-dyestuffs, tanning agents, pharmaceuticals, synthetic glues and adhesives), various pitch fractions(used as a binder), creosote (containing 30 % tar acids, used in large quantities for the preservation of timber), flotation oils (consisting of selected neutral oil and acid and base containing oils, used in coal cleaning plants to separate coal from mineral impurities), rubber solvent(a selected gasoline fraction boiling from 90-150°C, containing 50 % alkenes, used as a particularly effective synthetic rubber solvent, due to the high alkene content, which is a special characteristics of low temperature tar distillates [8]. Ultimate analysis (percentage by mass) and calorific value of the dry tar include carbon, 82-84 %, 8-8.5 % for hydrogen, 0.5 to 0.7 % for nitrogen, sulphur 0.7 to 0.9 %, ash is negligible, oxygen 7.0 to 9.0 % and a gross calorific value of 38.4 to 39.1 MJ/kg [10,11,12].

DESCRIPTION OF STUDY AREA

The study area is the coalite plant near Chesterfield in England.

SAMPLE ISOLATION AND PURIFICATION

Low temperature coal tar sample was separated using open column chromatography into aliphatic, aromatic and polar fractions. N-hexane was used to elute the aliphatic fraction while hexane/DCM mixture was used to elute the aromatic fraction and concentrated using a stream of N₂. The asphaltene derived was obtained through asphaltenehydropyrolysis, followed by column chromatographic separation of the asphaltene product.

PAH Analysis

The aromatic fraction was analyzed for Naphthalene, 2,4-dimethylnaphthalene, 1,2,4-trimethylnaphthalene, Fluorene, methylfluorene, Phen/Anthr, Fluoranthene, Pyrene, methylpyrene, Benz (a) Anthr/Chrysene, Benz (b)/(k) fluoranthene, Benz (a) pyrene, Dibenz (a, h) anthr/Inden (1,2,3-cd) py, Benzo (ghi) perylene, Ethylchrysene and using GC-MS at the School of Chemical, Environmental and Mining Engineering, University of Nottingham. The GC-MS analysis was performed on a Fisons instruments 8000 gas chromatograph interfaced

to a MD 800 mass spectrometer with a quadrupole mass analyzer (ionizing energy 70eV, source temperature 280° C). The gas chromatograph capillary column is 50 m long; i.d. is 0.32 mm and a film thickness of 0.25 μ m, stationary phase is polyphenylmethylsiloxane. Lab base software written by VG was used for data acquisition and Mass lynx for interpretation. The determinations were at selected ion monitoring (SIM) mode. Concentrations of the various PAHs were determined using internal standard injection. Identification of the various PAHs was achieved by comparison with authentic standards.

RESULTS AND DISCUSSION

The PAH concentrations of the samples ranged from 1 mg/g to 14 mg/g with a mean concentration of 78.35 mg/g \pm 14.64 mg/g. This range is by far, higher than the range (1-10 μ g g^{-1}) reported in Zhang *et al.*, 2006, associated with endogenous soils resulting from plant synthesis and natural fires. The PAH concentration was highest in the LT 2 (14 mg/g) which is the asphaltene derived sample. The samples generally showed a greater concentration of the 2-3 membered rings. Generally, the 2-3 ring PAHs constituted 64% of the total PAH concentration and the 4-6 ring PAHs constituted the remaining

36%.Molecular structure of PAH dictates their level of carcinogenicity, mutagenicity and toxicity. Low molecular weight PAH (≤ 3 rings), often display acute toxicity and low carcinogenicity, while high molecular weight PAH (> 3 rings), show low toxicity, but outstanding carcinogenicity and or mutagenicity [5, 7].

Table 1: Summary of Concentrations of Individual PAHs in Free and Asphaltene Derived Low Temperature Coal Tar (mg/g)

Ind PAHs	LT1	LT2
Naphthalene	7*	8.2
2,4-dimethylnaphthalene	10	12*
1,2,3-trimethylnaphthalene	12	13
Fluorene		
Methylfluorene	10	14*
Phen/Anthr	6	8
Fluoranthene	4	5*
Pyrene	5*	7
Methylpyrene	6	9*
Benz (a) Anthr/Chrysene	5*	7
Benz (b)/(k) Fluoranthene		
Benzo (a) Pyrene	1	3*
Dibenz (a,h)Anthr/Inden(1,2,3-cd)Py		
Benzo (ghi) Perylene		
Ethylchrysene	2*	2.5*
Trimethylphenanthrene		

Key: * **Note:** Concentration determined using 2-ethyl anthracene as the internal standard. Concentrations listed in Table 1 are for

PAHs and/or aromatics co-eluting at the same retention time due to complex molecular profiles.

LT 1 = free Low temperature coal tar
LT 2 = asphaltene derived low temperature coal tar

Sources of PAHs

To evaluate the risks of PAHs to the environment, it is very important to find out their origin and sources. A number of studies have demonstrated the usefulness of PAH isomer ratios in source apportionment [3, 9, 15]. One of the frequently used isomer ratios is the Ant/ (Ant + Phe) ratio. According to this isomer ratio, the ratio < 0.1 indicates petroleum input and the ratio > 0.1 indicates pyrogenic input [2]. However, there are limitations to the use of this isomer ratio as demonstrated by Fraser *et al.* (1998). They demonstrated that Anthracene undergoes more rapid photochemical reaction in the atmosphere than Phenanthrene. The implication is that during atmospheric transport, the original composition information will not be preserved. Therefore, in order to carry out an accurate PAH source apportionment in soils, isomer ratios where the isomer pairs degrade photolytically at comparable rates have to be adopted. From CCME (2008), the isomer ratio

Flu/ (Flu + Py) is a more accurate ratio as it meets with the condition. The Flu and Py isomer pair degrades photolytically at comparable rates. The ratio < 0.4 indicates petroleum input; ratio between 0.4-0.5 indicates liquid fossil fuel (vehicle and crude oil) combustion input and ratio > 0.5 indicates grass, wood or coal combustion input [13].

The diagnostic ratio (Flu/ (Flu+Py)) for this study was found to be within the range 0.4-0.5 confirming equal contributions from liquid fossil fuels combustion.

CONCLUSION

The PAH concentration of the samples ranged from 1 mg/g to 14 mg/g. the study showed a predominance of low molecular weight PAHs and the diagnostic ratio suggested contributions from liquid fossil fuels.

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Reference to this paper should be made as follows: Ivwurie W.; et al. (2015), Polycyclic Aromatic Hydrocarbons in Free and Asphaltene Derived Low Temperature Coal Tar from the Coalite Plant Near Chesterfield. *J. of Medical and Applied Biosciences*, Vol. 7, No. 2, Pp. 54 - 59.
