
Polycyclic Aromatic Hydrocarbons in Free and Asphaltene Derived High Temperature Coal Tar

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ABSTRACT

Free and asphaltene derived samples of high temperature coal tar (HTCT 1 and 2 respectively) from the Kopper plant in Scunthorpe, North Lincolnshire were analyzed for polycyclic Aromatic Hydrocarbons using gas chromatographic-mass spectrometry (GC-MS). The concentrations of the individual PAHs ranged from 1.2 mg/g-98 mg/g with a mean concentration of 390.7 mg/g \pm 23.05 mg/g. The study showed a higher concentration of the high 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.

Keywords: Polycyclic Aromatic and Asphaltene

INTRODUCTION

Hydrocarbons are a widespread class of contaminants in recent environments due to the multiplicity of their sources [9, 10]. These hydrocarbons can be synthesized by living organisms (biogenic origin), produced during the degradation of the organic matter (diagenic origin), formed during incomplete organic matter combustion (pyrolytic origin) and introduced in the modern environment via natural and anthropogenic release of fossil fuel combustibles (petrogenic origin) [9].

Amongst the organic species that find their way into the environment as a result of diverse industrial and domestic operations are the polycyclic aromatic hydrocarbons (PAHs). These originate from the incomplete combustion of organic materials or directly from fossils fuels, as well as from direct biogenic precursors [1]. The fate of PAHs in the environment has drawn attention from various researchers. This is because PAHs come from different sources, coupled with the diverse pathways that they follow when they are discharged into

the environment. Samples of tar and pitch from the Kopper plant at Scunthorpe were investigated. The temperature of this process is 900-1050°C giving rise to the production of metallurgical coke. The tar produced during this carbonization process is a complex mixture of aromatic condensed ring compounds, phenolic and heterocyclic compounds and their alkyl derivatives. Up to 5 % non-aromatic hydrocarbons are also present. Substituent groups (hydroxyl or alkyl) have been largely removed in the process resulting in a tar acid content below 5 % and there is a predominance of unsubstituted aromatic hydrocarbons over their alkyl derivatives [2]. The degree of condensation of the molecules increases as the boiling range is ascended with single ring compounds (benzene, toluene, xylene, phenols, cresols, xylenols, pyridine, and methyl pyridines) accounting for about 3 % of the tar. These are followed by fused six and five- membered ring systems (indene, coumarone and indole), which make up a further 2-3 %. This is followed by systems containing two six-membered rings, two six-membered and one five-membered ring, and three six-membered rings. This range accounts for 30-35 % of the tar; naphthalene and phenanthrene are the major components with other unsubstituted

aromatics (acenaphthene, fluorene and anthracene) also prominent.

Heterocyclic compounds, with the oxygen atom in a 5-membered ring, are the most common heterocyclic compounds, followed by bases with the nitrogen as =N- in a 6-membered ring or as -NH- in a 5-membered ring; ring compounds with a sulphur atom in 5-membered rings are also present [2]. Typical properties of the coke generated in this process (ultimate analysis) are 96.5 % for carbon, 0.5 % for hydrogen and 2.0 for oxygen. Moisture content is 2.0% and a net calorific value (air dried basis) of 29.8 MJ/Kg [10]. It is therefore the objectives of this work to determine the concentrations and the distributions of the PAHs in free and asphaltene derived high temperature coal tar from the Kopper plant in North Lincolnshire.

DESCRIPTION OF STUDY AREA

The study area is the Kopper plant which is in Scunthorpe. Scunthorpe is a town in North Lincolnshire 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 N_2 . The asphaltene derived was obtained through asphaltene hydrolysis, followed by column chromatographic separation of the asphaltene product.

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 $30^\circ C$ for DCM solutions and $45^\circ C$ for DCM/methanol mixtures. The extract was concentrated and dried using a stream of N_2 . Open column chromatographic separation was then carried out on each extract obtained and the neutral aromatics containing the PAHs together with the aliphatics were kept for analysis.

PAH Analysis

The aromatic fraction was analyzed for Naphthalene, Acenaphthalene, Acenaphthene, Fluorene, Methylfluorene, Phen/Anthr, Fluoranthene, Pyrene, Benz (a) Anthr/Chrysene, Benz (b)/(k) fluoranthene, Benz (a) pyrene, Dibenz (a, h) anthr/Inden (1,2,3-cd) py and Benzo (ghi) perylene 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 $280^\circ C$). The gas chromatograph capillary column is 50 m long; i.d. is 0.32 mm and a film thickness of $0.25\mu m$, 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 1.2 mg/g to 98 mg/g dry weight (Table 1.) with a mean concentration of $390.7\text{ mg/g} \pm 23.05\text{ mg/g}$. This range is by far, higher than the range ($1-10\ \mu g g^{-1}$) reported in Zhang *et al.*, 2006, associated with endogenous soils resulting from plant synthesis and natural fires. The PAH concentration was highest in the HTCT 2 (98 mg/g) which is the asphaltene derived sample. The samples generally showed a greater concentration of the 4-6 membered rings. This implies that the

area has been contaminated by the plant emissions and as such, the soil has a great tendency to be toxic and carcinogenic. Generally, the 2-3 ring PAHs constituted 30% of the total PAH concentration and the 4-6 ring PAHs constituted the remaining 75%. As reported by Chadwick *et al.* (1987) and Homann *et al.* (1994); 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.

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

Ind PAHs	HTCT1	HTCT2
Naphthalene	1.2	3
Acenaphthylene	4.4	5
Acenaphthene	9.8	11
Fluorene	17	20
Phen/Anthr	75	77
Fluoranthene	36	40
Pyrene	29	34
Benz (a) Anthr/Chrysene	18	20
Benz (b)/(k) Fluoranthene	96	98
Benzo (a) Pyrene	41	44
Dibenz (a,h)Anthr/Inden(1,2,3-cd) Py	29	33
Benzo (ghi) Perylene	18	22

Note: Concentration determined using 2-ethyl anthracene as the internal standard.

Key: Concentration listed in Table 1 is for PAHs and/or aromatics co-eluting at the same retention time.

HTCT 1= Free high temperature coal tar

HTCT 2= Asphaltene derived high 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 [4, 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 [3]. 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 isomer ratio (Flu/ (Flu+Py)) for this study was found to be >0.5 , confirming equal contributions from coal combustion sources.

CONCLUSION

The PAH concentrations of the study sample ranged from 1.2-98 mgg^{-1} . There was a predominance of the high molecular weight PAHs and the PAH diagnostic ratio showed an equal input from coal combustion.

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