

Full Length Research Paper

Comparison of low temperature coal tar solvent extractible and bound biomarker distribution for correlation studies

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Solvent extractible and bound biomarker profile for low temperature coal tar were compared using the biomarker ratios obtained from the selective ion resolution for pristane, phytane, n-C₁₇ and hopanes ratios of GC-MS results, with a view to ascertaining whether or not the data for asphaltene-derived biomarker can be used for effective correlation studies, and if serious alterations arising from biodegradation and other environmental factors could affect the use of the solvent extractible ones. The Pristane/phytane, pr/n-C₁₇ ratios and carbon preference index are 4.0, 1.1 and 0.9, respectively for the free aliphatics and 4.2, 1.2 and 1.2 for the bound. These values are quite similar to each other. The hopanes are less mature for the bound than for the free, this is a general trend found for most hydrolysis products.

Key words: Biomarker, coal tar, asphaltene.

INTRODUCTION

Biological markers are organic compounds that have an established biological origin, and exhibit little or no change in chemical structure from their parent precursor compound found in living organisms. Their characteristics include source-specificity, restricted occurrence, molecular stability and suitable concentration for analytical detection. They can be used as signatures of organic matter sources (Rogge et al., 1993; Schauer et al., 1996; Ivwurie, 2011a).

For instance, the 17 α (H), 21 β (H)-hopanes, the extended triterpanes, the steranes and the isoprenoids (pristane and phytane) have been used for this purpose. Pristane and phytane are regular acyclic isoprenoid hydrocarbon biomarkers and are readily present in sedimentary organic rocks, coals and petroleum. For crude oil, transport fuels and vehicular exhaust emissions, Pr/Ph and Pr/n-C₁₇ ratios are often ≤ 2 , typically ~ 1 , with no major variations observed (Schauer

et al., 1996; Sun, 2001).

The stereo-chemical changes which take place at the C₁₇ and C₂₁ chiral positions of hopanes are often used to determine the maturity of geological organic matters, where hopanes with configuration of 17 β (H), 21 β (H) indicates immaturity, 17 β (H), 21 α (H), shows moderate maturity; and 17 α (H), 21 β (H), is an evidence of high maturity. Besides petroleum, however these biomarkers can be found in coal, with their distribution being dependent on coal maturity.

Asphaltenes are of significant interest in geochemical and related studies. Van et al., (1986) investigated biomarker distribution in asphaltenes and kerogens using flash pyrolysis-gas chromatography-mass spectrometry and they observed differences between biomarker distributions of asphaltene and kerogen pyrolysates (Buenrostro-Gonzalez, 2001, Ivwurie et al., 2011b).

This research paper compares the solvent extractible and bound biomarker profile for low temperature coal tar with a view to ascertain whether or not the data used for asphaltene-derived biomarker can be used for effective correlation studies, and if serious alterations, arising from Biodegradation and other environmental factors affect

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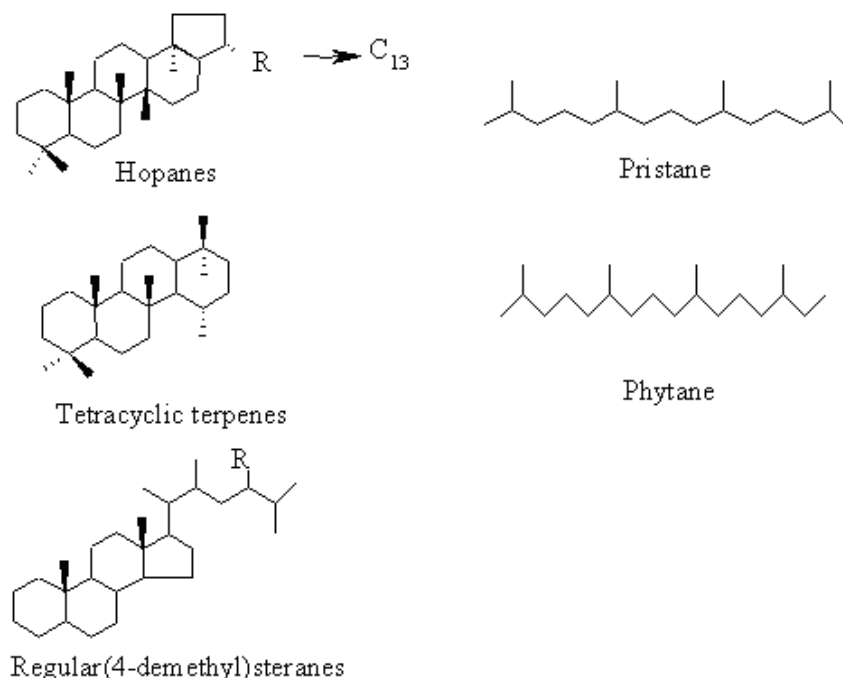


Figure 1. Chemical structures for title molecules/biomarkers.

Table 1. Pristane/phytane, pristane/ $n\text{-C}_{17}$ ratios and CPI for low temperature coal tar.

Sample name	Pristane / Phytane	Pristane / $n\text{-C}_{17}$	CPI
Low temp coal tar Free aliphatics	4.0	1.1	0.9
Low temp coal tar Hypy aliphatics	4.2	1.2	1.2

the use of the solvent extractible ones.

METHODS

Low temperature coal tar (coal tar processed at a temperature range of 500 to 850°C) sample supplied from the coalite smokeless fuel plant near Chesterfield, United Kingdom, was fractionated using open column chromatography to obtain aliphatic fraction from which different biomarkers were investigated. Asphaltenes were obtained from low temperature coal tar by precipitation with 40-fold excess of n -heptane (Jones et al., 1988). The asphaltenes were mixed with silica in the range of 10 to 50 mg of asphaltene to 1 g of silica. The mixture is 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. The sample is then dried in a vacuum oven at 60 to 70°C after which it is placed in a reactor tube. When attached to the hydrolysis set-up, it is resistively heated from 50 to 250°C at 300°C min^{-1} , then to 500°C at 8°C min^{-1} maintaining a hydrogen pressure of 15 mPa and a flow rate of 10 $\text{dm}^3\text{min}^{-1}$. The liquid product is then

collected in a trap cooled with dry ice and recovered with dichloromethane (2 to 5 ml) for subsequent separation (Love et al., 1997, 1998; Murray, 2001; Meredith et al., 2004).

The biomarker distribution for the solvent extractible (free) and hydrolysis products (bound) were compared using GC-MS on a Fisons instruments 8000 gas chromatograph interfaced to a MD 800 mass spectrometer with a quadrupole mass analyzer (ionizing energy 70 eV, 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 μm , stationary phase is polyphenylmethylsiloxane.

RESULTS

Chemical structures for title molecules/biomarkers are shown in Figure 1. The pristane/ $n\text{-C}_{17}$ (Pr/ $n\text{-C}_{17}$), pristane/phytane (Pr/Ph) ratios and carbon preference index (CPI) are calculated and listed in the Table 1. Pristane/phytane, pr/ $n\text{-C}_{17}$ ratios and carbon preference index are 4.0, 1.1 and 0.9, respectively for the free aliphatics and 4.2, 1.2 and 1.2 for the bound.

Figure 2 shows total ion chromatograms for aliphatic hydrocarbons of both free and bound low temperature coal tar. The hopane and sterane maturity parameters for

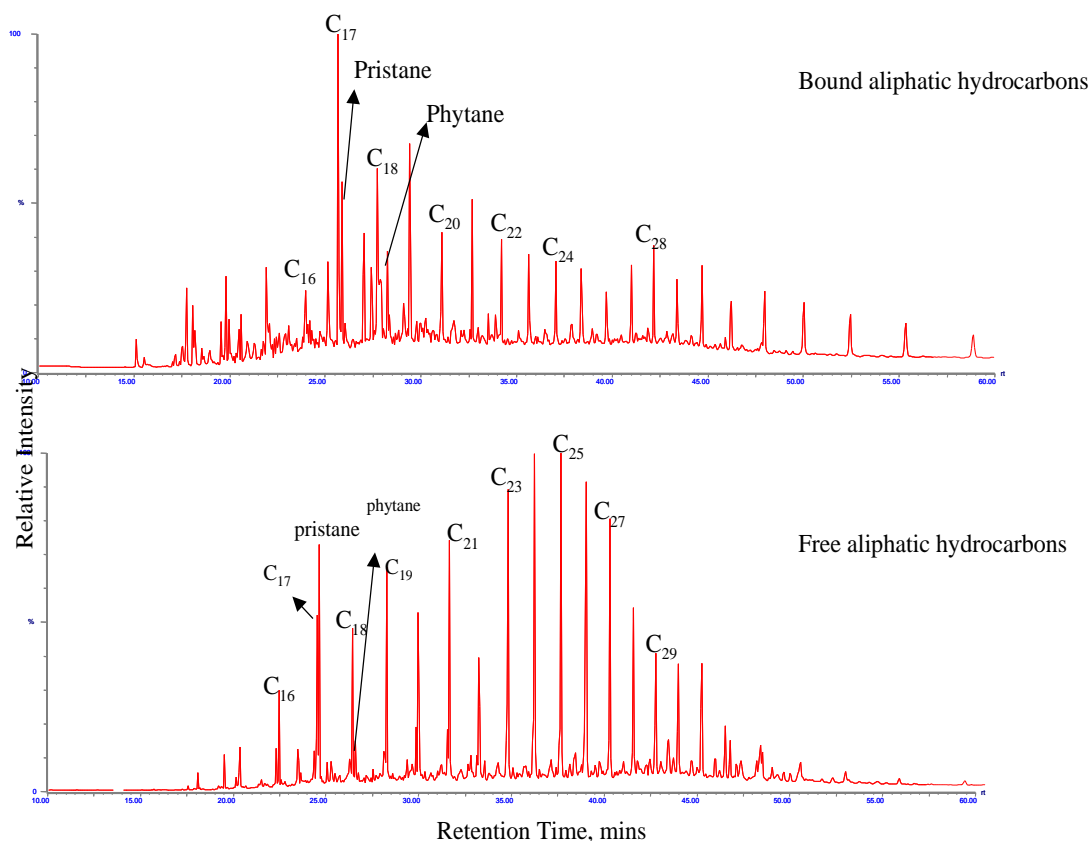


Figure 2. Total ion chromatograms for free and asphaltene-derived aliphatics from low temperature coal tar.

Table 2. Hopane and sterane maturity parameter ratios for free and bound biomarkers for low temperature coal tar.

Biomarker	Low temp. coal tar free biomarker ratio	Low temperature coal tar asphaltene-derived biomarker ratio
29 β α / α β Hopane	0.24	0.28
30 β α / α β Hopane	0.32	0.50
31 α β S/S+R Hopanes	0.55	0.52
29 α α S/S+R Sterane	0.53	0.54

Key: ratios were computed using peak areas of m/z 191 and 217 SICs of the biomarkers listed above.

the free and bound aliphatics have been compared in Table 2 as well as in Figures 3 and 4.

DISCUSSION

This study was conducted to be able to generate representative biomarker profiles, in cases of severe biodegradation and environmental alteration that are useful for source apportionment studies, after which a high proportion of the bound biomarkers must be assessed under reaction conditions to minimize the extent of product secondary transformations. Asphaltene hydrolysis was used in providing reliable data for

correlation studies (Murray, 2001). Low temperature coal tar, a primary source was investigated for this correlation studies to aid source apportionment.

The use of biomarker parameters like pristane/phytane ratios, pristane/ nC_{17} , and the maturity of hopanes for correlation studies is well established (Murray, 2001; Meredith et al., 2004).

The pristane/phytane, pristane/ nC_{17} values for both free and bound coal tar are quite similar to each other, indicating that source information revealed by the bound constituents are representative of the source as the free constituents (Fu et al., 1992; Hughes et al., 1995; Sun, 2001). Similarly, n -alkanes up to C_{32} and similar values for carbon preference index are visible in both free and

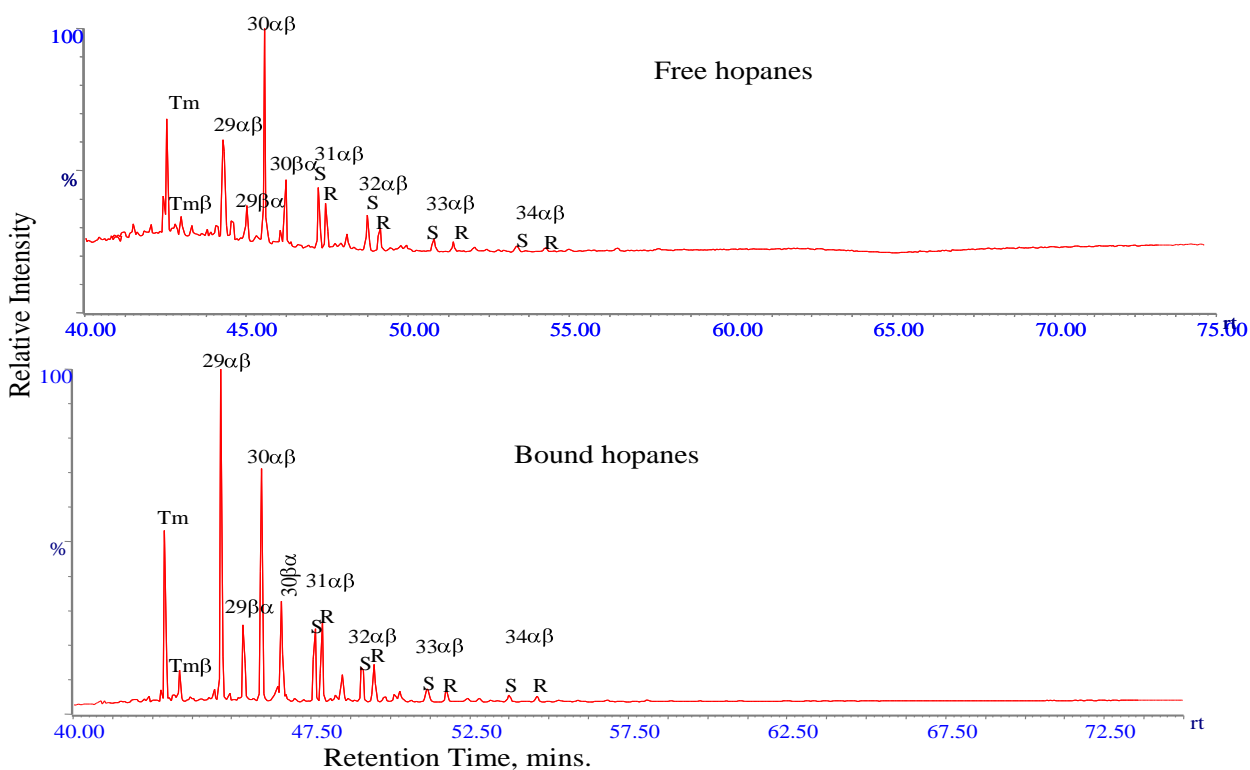


Figure 3. m/z 191 (hopane) fragmentograms for low temperature coal tar free and bound species.

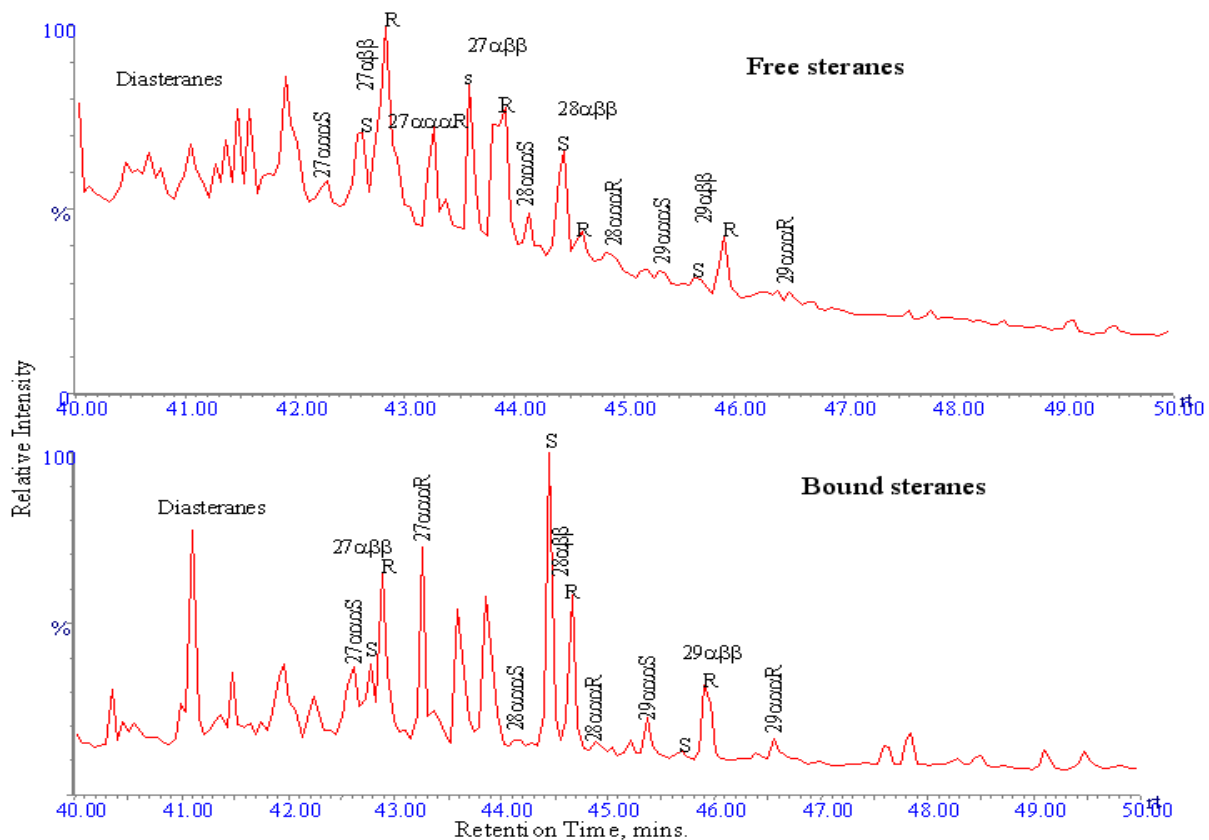


Figure 4. m/z 217 fragmentogram (steranes) for low temperature coal tar free and bound species.

bound aliphatic fractions as shown in Figure 2.

The hopanes are less mature for the bound than for the free, this is a general trend found for most hydropyrolysis products (Figure 3) (Love et al., 1997, 1998; Meredith, 2004). There is also no extended sidechain survival in both. Alkyl- S/S + R ratio is close to thermodynamic equilibrium.

The virtual absence of n-C₂₉ sterane suggests that cracking reactions were induced during the carbonization process of the coal tar (Figure 4). Generally, the compositions of alkane fractions are similar to those of the free and bound constituents (Ivwurie et al., 2009).

Conclusion

This paper compared the biomarker (pristane, phytane, hopane and sterane) distribution of free and bound low temperature coal tar as a basis for future source apportionment studies from secondary sources such as pollution sites (example, contaminated soil, sediments and water).

Aliphatics hydrocarbon distribution for both free and bound coal tar shows similar carbon preference index; while pristane/phytane and pristane/C₁₇ ratios were within the range reported in previous studies on similar samples (Fu et al., 1992; Hughes et al., 1995; Love et al., 1997, 1998; Sun, 2001). The results obtained, clearly demonstrates that both aliphatic and biomarkers released from asphaltenes via hydropyrolysis could provide useful information such as history of coal formation, environmental influence and processing conditions for source apportionment. This is because molecular profiles of biomarkers for both free and bound coal tar aliphatics show similar profiles, except in the hopane distribution where the free hopanes are more matured than the bound.

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